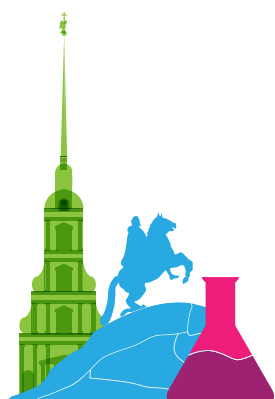




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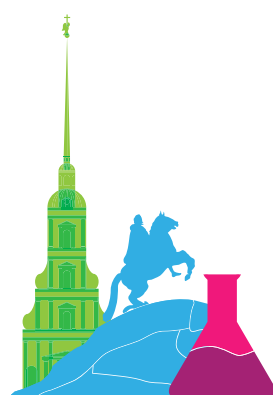
International Sol-Gel Conference

Next Generation

St Petersburg, Russia
August 25-30, 2019

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ISBN 978-5-600-02520-2

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WELCOME TO SOL-GEL 2019!

Dear participant of the International Sol-Gel Conference, St Petersburg,
August 25-30, 2019,

We are glad you are taking part in this **20th conference anniversary**, the first
in Russia in this series of conferences.

For this conference we have launched several novelties:

- To keep a high level and broad scope of all lectures they are all either invited or plenary lectures, given by group leaders or broad-scope researchers.
- Selecting the invited speakers: We have asked the whole community of the members of the International Sol-Gel Society for recommendations on whom to invite. In that way we gave the community an active role in deciding on the nature and content of the conference.
The response to our invitations for plenary and invited lectures was overwhelmingly positive, and the resulting oral program is rich and diverse with all of the frontier topics in sol-gel science and technology.
- The more specific topics, which characterize usually the work of PhD students, post-docs and early career researchers, will be presented in high quality posters.
At our focus in this conference are these young scientists – therefore the theme of the conference is, **“The Next Generation”**.
- Plenty of special activities are devoted to **the Next Generation**, including 10 minutes slam presentations, a panel discussing their future career, various awards, participation of the younger generation in all social activities including the banquet, and substantial financial support and low or zero registration fees.
- Last but not least in the novel aspects, the local organizing committee was international, bringing in that way local expertise with long-term experience of previous conferences.

Finally, we thank the International Sol-Gel Society and particularly the Chairman Prof. Masahide Takahashi for the full support he gave us in organizing these conference with its special features.

We did our best – Please, enjoy the meeting!

The local organizing committee

Vladimir Vinogradov, Vadim Kessler and David Avnir

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ORGANIZERS

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TIMETABLE

	Sunday 25th August	Monday 26th August	Tuesday 27th August	Wednesday 28th August	Thursday 29th August	Friday 30th August
8:00						
8:30		Registration* 8:00-18:00	Registration 8:30-18:00	Registration 8:30-18:00	Registration 8:30-18:00	
9:00	Registration 9:00-18:30		Poster mounting	Poster mounting		
9:30		Opening ceremony at BDT theatre				Markus Niederberger
10:00		Mari-Ann Einarsrud at BDT theatre	Andrey Rogach Kazuki Nakanishi	Aziz Muzafarov Mario Pagliaro	Life Achievement Award.	Session: Non-hydrolytic sol-gel materials
10:30		Coffee break at BDT theatre. Move to ITMO University	Coffee break. Poster mounting	Coffee break. Poster mounting	Ulrich Award.	Coffee break
11:00			Parallel sessions: 1. Photonic sol-gel materials 2. Hybrid materials	Joanna Aizenberg Bicasa presentation	ISGS Fellow Ceremony	
11:30		Peter Fratzl		Parallel sessions: 1. Silica and Silsesquioxanes 2. Fundamental aspects of sol-gel chemistry	Coffee break	Frank Caruso
12:00			Buffet lunch + Poster Session I 13:00 - 15:00		Parallel sessions: 1. Optically active sol-gel 2. Biomaterials	
12:30		Buffet lunch		Parallel sessions: 1. Silica and Silsesquioxanes 2. Fundamental aspects of sol-gel chemistry	Buffet lunch 13:30 - 15:30	Closing session
13:00	Aerogel Workshop		ISGS Meeting			
13:30		Nicola Huesing	Eugenia Kumacheva Merck presentation	Buffet lunch + Poster Session II	Meeting of ISGS and the JSST board	
14:00		Break	Parallel sessions: 1. Coating and Films 2. Biosafety and Bioapplication		Science communication lecture	
14:30			Parallel sessions: 1. Processing of sol-gel materials 2. Membranes		Parallel sessions: 1. Electrochromism, electrocatalysis and electrospinning 2. Sol-gel coatings	
15:00		Coffee break	Coffee break	Guided city bus tour		
15:30		Parallel sessions: 1. Applied sol-gel materials 2. Silica and sesquioxanes	Panel discussion: How to build a successful career?			
16:00						
16:30						
17:00						
17:30						
18:00	Welcome Reception					
18:30		Russian Evening	Evening on own/ "Like a local" program		Closing Reception and Science Slam	
19:00						
19:30						
20:00						
20:30						
21:00						

* 08:00 - 18:00 at ITMO University
08:00 - 11:00 at BDT theatre



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SPONSORS

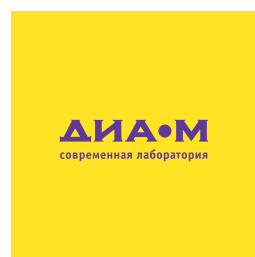
Platinum



Gold



Silver



ABSTRACTS OF PLENARY SPEAKERS



Aqueous and Nonaqueous Sol-Gel Chemistry: Similarities and Differences

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Abstract: Aqueous and nonaqueous sol-gel routes represent powerful tools to synthesize a broad range of metal oxides and oxide-based hybrid materials. Although both methods have a comparably long history of over 100 years, it took much longer for the nonaqueous sol-gel method to find wider resonance. However, meanwhile it is widely used by the scientific community, offering a promising alternative to aqueous methods.

The high reactivity of metal oxide precursors and the double role of water as ligand and solvent makes aqueous sol-gel chemistry rather complex, which turned out to be a particularly serious issue when it comes to the synthesis of nanoparticles with precise size and shape control. Nonaqueous sol-gel chemistry, on the other hand, is dominated by the moderate reactivity of the C-O bonds present in the organic solvents typically applied in such synthesis routes. The chemistry of the C-O bond is well established in organic chemistry, which helps to systematically study and categorize the underlying nanoparticle formation mechanisms.

The lecture will start with a short historical overview of aqueous and nonaqueous sol-gel chemistry, followed by introducing the fundamental chemical reactions in both approaches. Based on selected examples for the synthesis of metal oxide nanoparticles, similarities and differences as well as advantages and limitations of the two processes will be discussed. A fascinating aspect of sol-gel chemistry is the possibility to obtain aerogels [1]. The talk will present strategies for the production of compositionally and morphologically complex aerogel monoliths from preformed metal oxide nanoparticles (Figure 1) as building blocks and how these aerogels can be applied in gas phase photocatalysis [2].



Figure 1. Photograph of an aerogel monolith composed of titania nanocrystals.

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2. M. Schreck, M. Niederberger, *Photocatalytic Gas Phase Reactions*, Chem. Mater. 2019, 31, 597.

Solution Processable Light-Emitting Colloidal Nanostructures

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Abstract: I will provide an overview on various kinds of light-emitting colloidal nanostructures synthesized by wet chemistry methods in our labs, which include carbon dots [1] and perovskite nanocrystals [2]. Each of these light-emitting systems have their merits and some drawbacks, as will be highlighted in this talk. Applications of those nanostructures are plenty, in particular in light emitting devices and displays, which can also be fabricated by solution based processing [3].

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Aqueous chemical deposition of thin oxide films

Mari-Ann Einarsrud, Kristine Bakken, Anders Bank Blichfeld, Evgeniya Khomyakova, Nikolai H. Gaukås, Trygve Ræder, Julia Glaum, Tor Grande⁽¹⁾

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Abstract: Chemical solution deposition (CSD) is the preferred manufacturing process of thin functional oxide films due to simplicity, versatility and the possibility to upscale the method. The principles of the CSD are illustrated in Fig. 1a where a solution containing the precursors is deposited onto a substrate, followed by drying, annealing to decompose the precursors, and finally crystallisation and densification. The properties of the final film depend strongly on the processing parameters. Hence, we have developed a unique in situ characterization unit (Fig. 1 b) to reveal information of the decomposition, nucleation and crystallization mechanisms of the as-deposited films to be able to design thin films with desired properties. Further, we have developed an environmental-friendly aqueous chemical solution deposition method for the preparation of thin films of selected lead-free ferroelectric oxide materials e.g. BaTiO_3 , $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ (KNN) $\text{Ba}_{1-x}\text{Ca}_x\text{Zr}_{1-y}\text{Ti}_y\text{O}_3$ (BCZT) and $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ (SBN). The aqueous solutions were used for depositing thin-films on various substrates ($\text{MgO}(100)$, $\text{SrTiO}_3[(100),(110),(111)]$ and platinized Si). The crystallization of the amorphous as-deposited thin-films was studied by X-ray diffraction during annealing up to 1000°C and with a heating rate up to 20°C s^{-1} . The crystallization of the deposited thin-films was also related to the evolution of the structure of the precursor powder studied by infrared spectroscopy as well as in situ total scattering and analyzed with pair-distribution-function (PDF). Detailed understanding of the decomposition of precursors, formation of any intermediate phases, nucleation and crystallization mechanisms was revealed for the formation of the oxide thin-films depending on type of substrate, solution concentration, composition and heating rate.

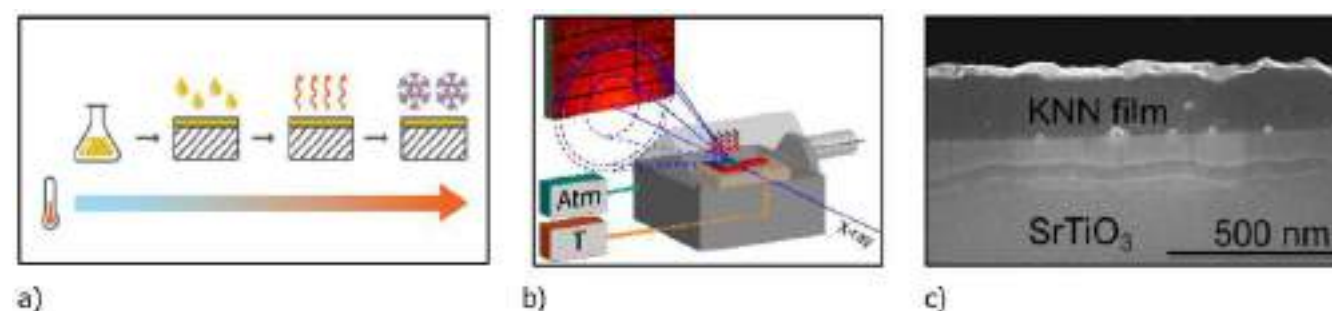


Figure 1. a) Principles of the chemical solution deposition, b) schematics of in situ set up for X-ray diffraction during annealing of films and c) epitaxial $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ thin film on SrTiO_3 prepared by CSD [1].

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Financial support from NTNU Norwegian University of Science and Technology and The Research Council of Norway under the Toppforsk program to the project (No 250403) "From Aqueous Solutions to oxide Thin films and hierarchical Structures" is gratefully acknowledged.

Bridging the Gap between Molecules and Nanoparticles

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Abstract: For more than a hundred years, colloidal particles have been used to model the behavior of atoms or molecules. Recently, this approach has been reversed: chemical reactions between molecules are now being used to model self-assembly of nanoparticles. Owing to the well-defined number and controllable spatial distribution of attractive surface regions, "patchy" particles exhibit directional interactions and assemble in clusters mimicking the symmetry of molecular structures.

In particular, polymer science offers unique strategies to address the challenges in nanoparticle assembly. By using lessons of polymer physics and chemistry, we develop new paradigms for nanoparticle surface patterning and nanoparticles self-organization. To generate "colloidal molecules", we utilized thermodynamically driven formation of surface-pinned micelles [1-3]. A striking resemblance between block copolymers and nanoparticles enabled nanoparticle assembly in nanostructures with varying morphologies, all mapped by state diagrams [4]. A marked similarity between step-growth polymerization and nanoparticle self-assembly enabled nanoparticle assembly with quantitative prediction of the architecture of linear, branched, and cyclic nanostructures, their aggregation number and size distribution, as well as the formation of isomers [5]. Building on this similarity, we proposed the concept of colloidal chain stoppers [6], as well as random and block copolymers [7].

This work has far-reaching implications for the molecular world (by offering simple, easy to visualize nanoscale models for polymerization reactions), and for the nano-world (by providing a polymer approach to nanostructures with structure-dependent electronic, optical, and magnetic properties).

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Sol-Gel Catalysts for Synthetic Organic Chemistry: Milestones in 30 Years of Successful Innovation

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Abstract: From metal nanoparticle to organometallic catalysis, from biocatalysis through organo-, electro- and photocatalysis, all domains of catalysis have been affected by the introduction of sol-gel entrapped catalysts more than twenty five years ago.¹ Far from remaining a field of academic interest only, several sol-gel catalysts were successfully commercialized.² For example, providing a method to make silicone precursors of high purity at low cost using a green reaction process, a new stable (Fig.1) and highly active catalyst in spherical morphology enables to carry out the hydrosilylation of olefins under solvent-free and mild reaction conditions.³ What are the main advantages of these materials? Do they only stem from the possibility to heterogenize homogeneous catalysts and streamline processes? Is the application potential of these materials fully realized? What are the obstacles to their widespread uptake in the fine and specialty chemical industry? Besides proving right, the theses of nanochemistry pioneers calling for the obsolescence of the single discipline “silos” approach to the practice of research in chemistry,⁴ the historical development of sol-gel catalysis has numerous lessons to teach to scholars engaged in reshaping chemistry education to foster creativity.⁵

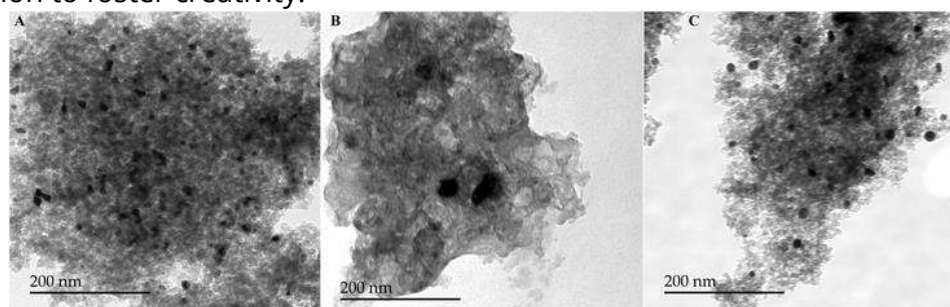


Figure 1. TEM images after the reusability test of: (A) spherical Pt/MeSiO_{1.5} (O/W emulsion synthesis), (B) Pt/MeSiO_{1.5} and (C) Pt/SiO_{1.5}-Al₂O₃ in irregular shape, in the hydrosilylation of 1-octadecene with chlorodimethylsilane [Reproduced from Ref.4, with kind permission].

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I am indebted to Rosaria Ciriminna, CNR, Valerica Pandarus and François Béland, SiliCycle, Laura M. Ilharco, Alexandra Fidalgo, Instituto Superior Técnico, David Avnir, Hebrew University of Jerusalem, Sandro Campestri, University of Padova, Serge Kaliaguine, Université Laval, Massimo Carraro, now at the University of Sassari, Giovanni Palmisano, now at Khalifa University of Science and Technology, Francesco Parrino, now at University of Trento, Babak Karimi and Mina Ghahremani, Institute of Advanced and Basic Studies, Yi-Jun Xu, Fuzhou University, Leonardo Palmisano, University of Palermo. My debt to these eminent scholars goes beyond co-authorship of numerous scientific articles in sol-gel catalysis.

Water-mediated forces in biological materials

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Abstract: Biological extracellular tissues are based on proteins, polysaccharides and, in certain cases, minerals. Their complex multiscale structure confers them a wide range of properties in accordance with the tissues' functions [1]. While active functionality are usually attributed to cells, there are also examples of materials synthesized by living organisms, such as plant seeds, which fulfil an active function without living cells and work as mechanosensors and actuators [2]. Water is an important component of all such extracellular tissues. While it is well known that the level of hydration determines the mechanical properties of many biological materials, it is less appreciated that water also plays an active role in generating forces within the materials. In particular water absorption and desorption provides actuation in a variety of plant seeds, including wild wheat [3], stone plant [4] and banksia seed capsules [5]. The shape change upon water uptake that provides the actuation is controlled by specific cellulose fibre architectures. In this way, well-controlled movements, such as bending, twisting or curling are programmed in these materials by structure of the underlying cellulose microarchitecture [6]. The required deformation energy is provided by the absorption of water from the environment [7]. Finally, the absorption of water to specific molecules and the resulting osmotic pressure is also providing internal stresses which control, for example, the mechanical behaviour of collagen in tendon [8], bone [9] and dentin [10]. The lecture will review general concepts for the roles of water in biological materials, both in the context of biology and of bioinspired engineering.

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Advanced Materials via Supramolecular Gelation

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Abstract: Advanced materials with bulk network structures prepared via supramolecular gelation are of widespread interest. In particular, the growing interest in supramolecular gels driven by metal-ligand coordination interactions (known as metallogels) stems from the opportunity to blend various properties (e.g., redox, optoelectronic, mechanical) into a gel matrix and utilize the dynamic nature of coordination bonding to design advanced systems with tailored properties. Our recent exploration in this field has revealed the direction gelation behavior of naturally abundant polyphenols with transition metals via supramolecular assembly — an unprecedented phenomenon that has largely remained unexplored. This metallogel system is formed by simple mixing at ambient conditions and displays a range of properties including optical transparency, self-healing, shape persistence, injectability, adhesiveness, and tunable mechanical properties. One of the salient features of this system is its robust and adaptive nature that leverages in situ cogelation of diverse additives and crystallization of metal-organic frameworks in the gel matrix. We are currently using these gel systems as a medium for controlled crystallization of drugs, which remains a critical issue in processing different formulations in pharmaceutical industries. We are also exploring their potential for catalysis, metal sequestration, and environmental remediation. It is envisioned that the inherent advantages of these types of systems, including the use of cost-effective and abundant components and their facile preparation, can provide a general platform to explore advanced composites for targeted applications.

Hyperbranched polyethoxysiloxanes and molecular nanogels based on them

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Abstract: Sol-gel method has long become a separate field of chemical technology, which plays an important role in obtaining materials with unique properties. Among the most prominent representatives of this class of materials are silica aerogels and ceramic materials based on aluminum, zirconium and hafnium oxides. Widespread are polymer composites, filled with the sol-gel method.

Sol-gel technology implies the inevitable transformation of the intermediate sol into a macroscopic gel with varying degrees of control over this transition. The black box approach is mainly used for studying and optimizing such processes.

The approach¹⁻⁴ that our group develops in this area has two fundamental differences. The first is that at the beginning we obtain an acyclic hyperbranched structure (hyperbranched polyethoxysiloxane), which further undergoes chemical transformation into molecular silicasol. The second difference is that unlike a conventional sol the molecular silicasol is stable being solved in organic solvents, and therefore can be also molecularly solved in various polymer matrices.

Molecular silicasols are nanogels by their structural organization – polycyclic macromolecules with a three-dimensional architecture, all three dimensions of which do not exceed 100 nm. Moreover, these formations can be further stabilized via blocking and fractionated to investigate their properties in detail and thereby to open up the lid of the “black box”.

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Highly Porous Materials by Non-Conventional Sol-Gel Precursors and Processes

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Abstract: Highly porous materials are of interest for a variety of applications, e.g. heat insulation, or separation science to name just two very prominent examples. A deliberate control over the pore architecture including pore sizes, pore connectivity and tortuosity as well as pore shape is in many cases a prerequisite for their applicability, however often difficult to achieve in a laboratory.¹ Simple and general methods to prepare (functional and/or monolithic) materials with well-controlled pore architectures, composition and surface functionality are therefore highly desired.

In this presentation, sol-gel processing towards highly porous monoliths by using non-conventional sol-gel precursors will be presented. This includes the application of glycolated precursors, such as tetrakis(2-hydroxyethyl)orthosilicate and the corresponding organoglycoxysilanes, as well as a discussion of the advantages but also challenges resulting from substitution of the alkoxy groups by glycoxy moieties.² We will also discuss whether this concept is transferable to (transition) metals, e.g. glycolated titanium or aluminum precursors. In addition, the synthesis of organic porous monoliths by applying wood-derived precursor molecules, such as mimosa tannins, as a non-conventional precursor molecule will be presented.

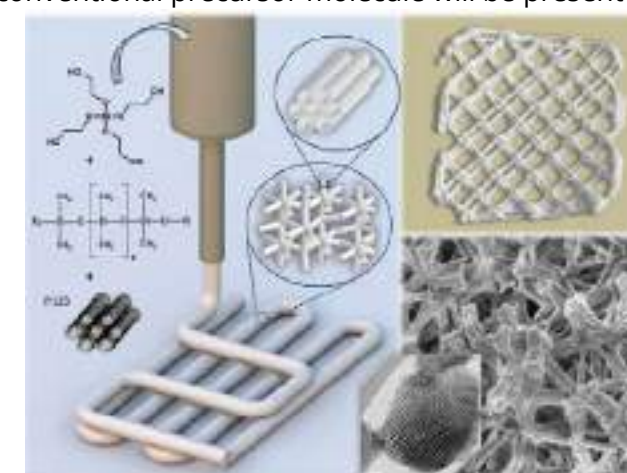


Figure 1. Schematic illustration of the synthesis route towards 3D printed hierarchically structured silica using a glycolated silanes.

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Porous Inorganic Monoliths: Challenges in extending chemical compositions for broader applications

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Abstract: Utilizing the sol-gel process accompanied by phase separation, monolithic materials with controlled macropores have been synthesized in a variety of chemical compositions. In some cases, multiple precursors, such as alkoxide and corresponding metal salt, can be conveniently used for identical final inorganic compositions. Representative precursors and applicable compositions are listed below.

Alkoxides

Silica, titania and zirconia are prepared relatively easily from their corresponding alkoxides. Silica and silsesquioxanes are easiest and most versatile composition with highly controlled pore structures and materials shapes/dimensions [1]. Reactivity of Ti and Zr can be controlled by additions of chelating agents and electrolytes [2]. Post gelation process for mesopore formation usually require hydrothermal conditions.

Metal Salts with Polymers

Starting from pure alumina system, various aluminates and ferrates including spinels, garnets and LDHs are synthesized from simple metal salts such as chlorides and nitrates according to Gash method [3]. Appreciable solubilities of most salts in aqueous system make it possible to extend the chemical compositions, including complex oxides, greatly. Titanates and zirconates are also obtained which is rather difficult from alkoxides. Most oxy/hydroxides of transition and rare earth metals can be synthesized using strongly hydrogen-bonding polymers such as poly(acrylic acid) and poly(acrylamide) as structure-supporting components [4]. Phosphates of various metals can be obtained similarly requiring sophisticated combination of additive polymers [5]. The problem of low oxide content of resultant gel network (large shrinkage and collapse of macropore structures) can be circumvented using aprotic polar compounds as major component in the solvent phase with the use of weakly hydrogen-bonding polymers.

Metal Salts with Coordination Ligands

Physical aggregation of colloidal particles, gelation of water glass on neutralization, as well as purely organic polymerization, have been known to be applied to the macropore formation process by phase separation with well-defined structures. Recent developments include reactions between coordinating ligands and metal ions. Aggregation and gelation by multi-valent carboxylic acids, often used as structural components of metal-organic frameworks (MOFs), can also combined with phase separation to give well-defined macroporous monoliths [6]. Well-defined trimodal pore distribution is obtained by combining macro/mesopores and highly-ordered microporous arrays of crystalline MOFs [7].

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Sol-gel-derived inverse-opal structures for photonic, catalytic and sensing applications

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Abstract: This lecture will introduce a sol-gel co-assembly approach that results in large-scale, highly ordered materials with embedded, uniformly distributed, and accessible nanoparticles (Fig. 1 left). The unique coloration of these inverse opal films combines iridescence with plasmonic effects. The composition and optical properties of these films are demonstrated to be locally tunable using selective functionalization of the doped opals. The latter exhibit a sharply defined threshold wettability for infiltration. This liquid-specific wetting behavior naturally couples to macroscopic color changes (Fig. 1A-F). We are exploiting this effect in the development of simple and low-cost colorimetric indicators for liquid detection and encryption, in catalysis, or as a tag for low-cost monitoring of tampering or material aging.

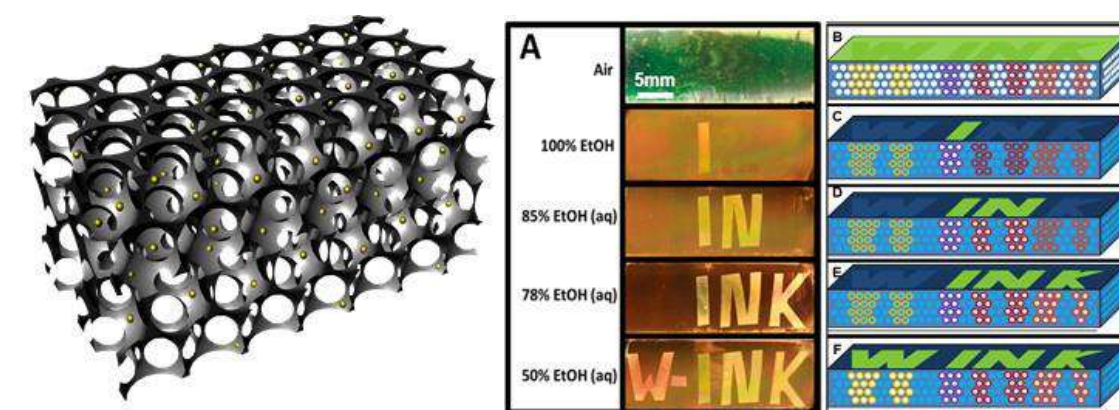


Figure 1. Sol-gel derived inverse opal films.

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ABSTRACTS OF AWARD SPEAKERS

Forty years of research in the field of sol-gel: a bit of history, personal experiences and ideas for the future

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Abstract: In this lecture, given for the ISGS Life Achievement Award, I will correlate my research experience on sol-gel during the last forty years, with the development of the Sol-Gel Science and Technology. Starting from the first researches on the structure and thermal evolution of gels toward the glassy state, to those on nanocomposite systems, I will give few examples of the research in my lab related to the development of some important topics in Sol-Gel, showing how this method is strongly correlated to what is now named nanotechnology. The Sol-Gel method is still far from expressing all its potentiality, both from the scientific and the application point of view, and the future is bright for those young researchers who are starting now their scientific adventure.

Mesoporous silica and sol gel science

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Abstract: Sol gel science has played a major role in materials science, including a wide range of researches on porous materials. Ordered mesoporous silica is a typical example of structural ordering of silica-based materials by mainly using templates. In this paper I will present personal accounts of mesoporous silica and relevant materials including microporous silica synthesized using well defined alkoxylated oligosiloxane.

Porous silica with ordered mesopores can be prepared from various silica sources and a wide variety of templates. Initially we reported the formation of mesoporous silica from layered silicate kanemite and alkyltrimethylammonium ions in 1988 to 1990. MCM-41 type ordered mesoporous silica was reported in 1992 by Mobil. Co. Presently thousands of papers, including “mesoporous” as keyword, are published every year.

Tetraalkoxysilanes are useful starting materials for preparing mesoporous silica. In particular, morphologies of mesoporous silica, such as films, nanoparticles, fibers, etc. can be controlled in various ways. Particle and mesopore sizes can be controlled by synthetic conditions including the kind of tetraalkoxysilanes.

Organoalkoxysilanes are also important for functionalization of mesoporous silica. So called “periodic mesoporous organosilica (PMO)” has been developed in these 20 years. Reagents possessing both alkoxy groups and various organic fractions have been used to synthesize PMOs with advanced functionalities. Organotrialkoxysilanes themselves are also useful to create mesostructured and mesoporous materials. On the basis of materials design, cyclic and cage siloxanes containing alkoxy groups are very useful for building block approaches of well-ordered silica-based porous materials.

Sol gel science is essential in the development of molecular-level design of ordered porous materials. Various building blocks can be alkoxysilylated and the resultant precursors can be used to prepare advanced functional materials. Great development of sol gel science and technology is yet to come.

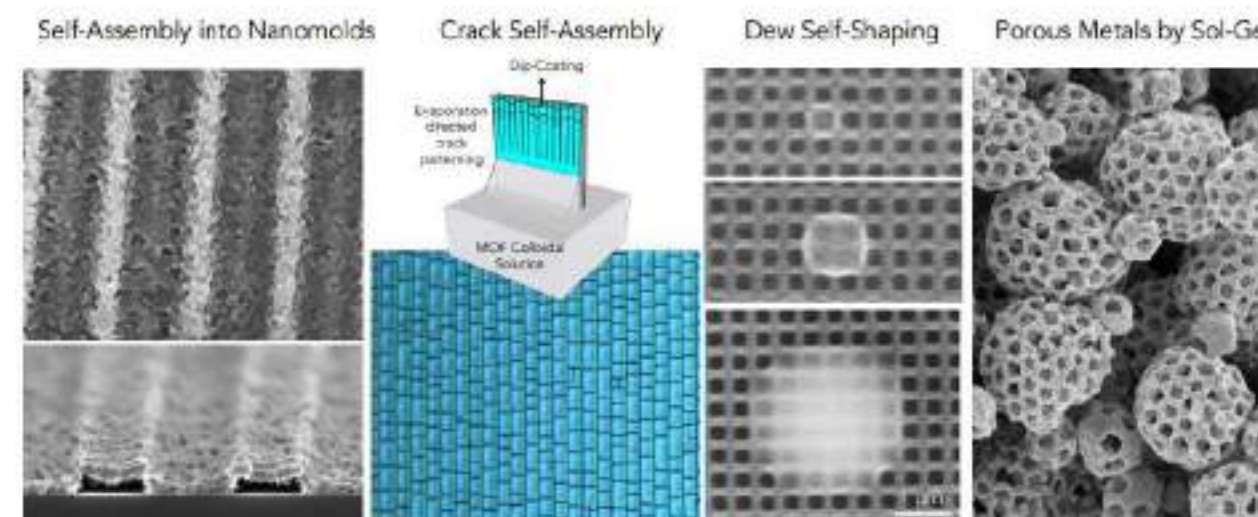
I greatly acknowledge the board members of the International Sol Gel Society for nominating me as a recipient of Life Achievement Award. I very much thank the contributions of the graduates and post-docs collaborated with me for long time. I very much appreciate collaborations and friendship with international and domestic friends of mine.

Emerging self-assembly and self-shaping processes of Nanomaterials for sensing, dew engineering and electrocatalysis

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Abstract: In this talk, I will describe our initiative in shaping inorganic and hybrid nanomaterials (inorganic and hybrid colloids, gels and Metal-Organic Frameworks) at multiple scales [1] by « emerging » bottom-up approaches. The goal is to rationally combine the original properties of the functional nanomaterials (composition, confinement, high porosity, sorption selectivity, capillary condensation...)[2] and of the periodic structures (light and liquid confinement, guiding...) to achieve new multifunctional platforms for fundamental studies and applications in electrocatalysis, dew engineering and sensing. Several original strategies will be described: (i) confined colloidal self-assembly into nanomolds, [3] (ii) crack self-assembly of colloidal gels [4] and (iii) dew self-shaping and manipulation on hybrid surfaces [5]. Examples of application of these systems will be presented. Sensing platforms (1D, 2D photonic crystals, graded materials, diffraction gratings) based on several nanoporous materials were developed for the easy-detection of toxic compounds by using a simple and accessible tool such as the camera of a smart phone [3,4,6]. Unusual wetting at the nanoscale and self-shaping of femtoliter dew droplets on sol-gel hybrid surfaces will be also described [5]. At last, an « unexplored » solgel chemistry of noble metals (e.g. Iridium based materials) is proposed to fabricate hollow and ultraporous catalytic films for Oxygen Evolution Reactions in PEM electrolyzers [7].



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ABSTRACTS OF INVITED SPEAKERS



Perovskite-based photocatalysts: sol-gel synthesis, properties and doping for application in visible light

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Abstract: The development of sustainable and reliable technologies for environmental remediation is nowadays of key importance to assure the well-being of living organisms. In the last decades, a research interest in obtaining and studying of nanoscale porous monoliths on the basis of titanium dioxide has been significantly increased. Among the advanced oxidation processes heterogeneous photocatalysis is considered as first hand option for environmental remediation. We have been working on the development of visible light active nanostructured perovskite-based photocatalytic materials. Different synthetic strategies have been implemented in order to control the composition, morphology, band gap and size distribution of the materials [1,2]. A facile synthetic pathway of novel porous titania based nanomaterials and perspective ways of their modification (Figure 1): development of the versatile way for the fabrication of perovskite monoliths $ATiO_3$ containing alkaline-earths ($A = Mg, Ca, Sr$ and Ba) with hierarchical pore structures, to control the formation of porous alkaline-earth metal titanates with narrow pore size distributions; fabrication of nitrogen-doped TiO_2 and its heterostructured monoliths with well-defined macroporous structure in the range of 1.3–1.7 μm and bicrystalline framework using sol-gel reaction accompanied by a phase separation followed annealing under a modest flow of ammonia gas. Along with simple perovskite (ABO_3) structures, development of doped heterostructured perovskites that induce mid-gap states in the band gap allowing visible light absorption will also be presented. It was observed that the photoinduced charges caught by defects of crystal structure and recombined/migrated to the surface of doped perovskites and initiated photooxidation process with adsorbed organic pollutants. Various strategies employed for enhancing the photocatalytic performance will be discussed, emphasizing the specific advantages and challenges offered by perovskite-based monolithic photocatalysts.

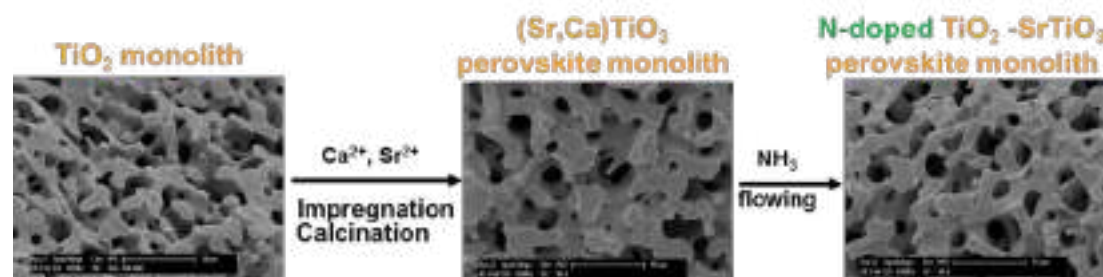


Figure 1. General scheme for the facile formation of porous TiO_2 based perovskite materials.

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Transparent glass-ceramics produced by sol-gel: a suitable alternative for photonic materials

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Abstract: Phosphor materials emit light under exposition of an external stimulation, such as electron beam, light at different wavelength or voltage or electric field. These materials are widely applied in light emitting diodes, solar cells, sensing, catalysis, integration in photovoltaic devices, and more recently in biosensing, bioimaging or medical diagnosis. Oxyfluoride nano-glass-ceramics are very attractive as host materials, because they combine the very low phonon energy of fluoride nanocrystals with the high chemical and mechanical stability of silicate glass matrix. These nanomaterials present a high transparency, result of the nanoscale size of the precipitated nanocrystals, always lower than 40 nm. The usual method to prepare these materials is the traditional glass melting process but the high evaporation of chemical components at high temperature, in particular the fluorine, results in uncontrollable compositions respecting to F and Ln.

Sol-gel is a promising alternative process to obtain nano-crystalline oxyfluorides embedded in matrices such as silica or silica-alumina. Sol-gel process allows controlling the composition, the crystal size, usually below 10 nm, and the doping amount. It is also possible to significantly increase the concentration of fluoride crystal fraction perfectly dispersed. Additionally, this method provides appropriated control of active Ln^{3+} species, respecting to dispersion, homogeneity and concentration.

The first work published about sol-gel oxyfluoride glass ceramics appeared in 1999 by S. Fujihara et al., reporting the preparation of transparent ($SiO_2-PbF_2-ErF_3$) materials. Most of further publications are focused on the SiO_2-LaF_3 system, including other alkaline earth fluorides, and containing a wide range of lanthanides as dopants. Many of these publications are focused on producing powdered materials; furthermore, the maximum amount of fluorides incorporated in these glass-ceramics materials is always lower than 10% molar.

In our research group GlaSS we have prepared by sol-gel transparent oxyfluoride glass-ceramic materials in the system SiO_2-LnF_3 ($Ln = La, Gd$), deposited as coatings and treated between 500-700°C. The processing parameters have been optimised to obtain coatings up to 2-3 μm with concentrations of nano-fluoride crystals up to 30-40% wt. Self-supported layers have been also obtained. Nd^{3+} , Er^{3+} , Pr^{3+} , Yb^{3+} were included as dopants or co-dopants to obtain up-conversion and down-conversion properties. The structural features were characterized by XRD, XANES and GXRD with Synchrotron radiation and HR-TEM; DTA and dilatometry were used to study the thermal behaviour and to identify the crystallisation mechanisms ruling this process. Optical characterisation was carried out through UV-Vis absorption spectra together with excitation and emission luminescence spectra. Finally, the relationship between processing-structure-optical properties of these materials is discussed.

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Fluorolytic sol-gel route and electrochemical properties of AFeF₃ (A=Na,K,NH₄) perovskite nanoparticles and polyanionic transition metal phosphate fluorides

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Abstract: Li-ion batteries (LIBs) are omnipresent in consumer electronics and are seen as the most promising technology for electric vehicles. Na-ion batteries (NIBs) have emerged as viable and cheaper alternatives for stationary applications where Li-ion batteries are too expensive. However, the larger size of sodium ion compared to lithium makes traditional positive materials for LIBs not always suitable for the reversible insertion of sodium ions.

3d-transition metal fluorides, such as FeF₃, have drawn attention as NIBs and LIBs positive electrode material due to their ability to deliver high potential thanks to the high polarity of the metal-fluorine bond. However, the insulating character of these highly ionic materials in practice leads to high polarisation and slow insertion kinetics [1-3]. Moreover, since the positive electrode in current LIBs and NIBs is the reservoir of alkali ions, metal fluorides are not applicable in alkali-ion technology against a carbonaceous anode without pre-lithiation/sodiation [1].

Therefore, in order to solve these problems, here we introduce a fluorolytic non- hydrolytic solution synthesis of AFeF₃ (A=Na,K,NH₄) perovskite nanoparticles. The perovskite AFeF₃ materials show a reversible electrochemical activity of 1Na or 1Li per iron with low polarisation and excellent capacity retention. The unexpected reversible insertion of both sodium and lithium ions, studied through ex-situ and operando X-ray diffraction measurements, is attributed to a kinetic stabilization of corner-shared cubic (Li,Na)xFeF₃ frameworks along the cycles involving low volume change without high thermodynamic cost as supported by a polymorphism theoretical analysis [4].

In this report, it will also be shown how the fluorolytic non-hydrolytic synthesis route can be extended to fluorine-containing polyanionic compounds with the general formula A_aM_bX_cO₄F_d (A= Li, Na...; M= Ti, V, Mn, Fe, Co, Ni...; X = P or S). In particular a novel non- hydrolytic fluorolytic sol-gel chemistry to tavorite-type LiFePO₄F and Li₂CoPO₄F materials and their electrochemical characterization will be discussed [5]. It will be proven that the versatility of the original reported route allows to produce a variety of fluorine-containing polyanionic compounds, which are of great interest for energy storage applications.

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Hyperbranched polyethoxysiloxane – a unique silica precursor polymer for preparation of silica-based nanostructured materials

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Abstract: Monomeric tetraethoxysilane is the best-known silica precursor in a sol-gel process. Here we report a unique silica precursor polymer, hyperbranched polyethoxysiloxane (PEOS), which is a highly hydrophobic liquid and exhibits interfacial-activity in an oil/water system due to amphiphilicity induced by hydrolysis of ethoxy-groups at the oil/water interface (Figure 1). PEOS can stabilize different kinds of emulsions such as oil-in-water [1], water-in-oil, water-in-oil-in-water [2] and even high-internal-phase emulsions [3] without any additional surfactants. After conversion of PEOS to silica, the internal phase can be encapsulated in silica. When a monomer is used as the oil phase [1b, 2], the synergy of polymerization and PEOS conversion can lead to the formation of polymer@SiO₂ core-shell particles, nanocapsules, nanorattles or Janus-like particles as the result of a delicate interplay between PEOS hydrolysis and condensation rate, polymerization kinetics, emulsion stability, and phase separation in the emulsion droplets.

In another approach, PEOS becomes amphiphilic via substitution with hydrophilic poly(ethylene glycol) monomethyl ether (Figure 1). The amphiphilic PEOS derivatives can self-assemble in water and the resulting soft assemblies are subsequently converted to mesoporous aerogel particles with very low density, hollow nanoparticles or ultrasmall solid particles under basic conditions depending on the degree of substitution [4]. It is shown that enzyme can be encapsulated in silica hollow nanoparticles with a high efficiency by dispersing the suitable amphiphilic silica precursor polymer in the aqueous solution of the enzyme. The microencapsulated enzyme exhibits significantly enhanced stability against the change of environmental conditions and can be repeatedly regenerated without a significant activity loss [5].

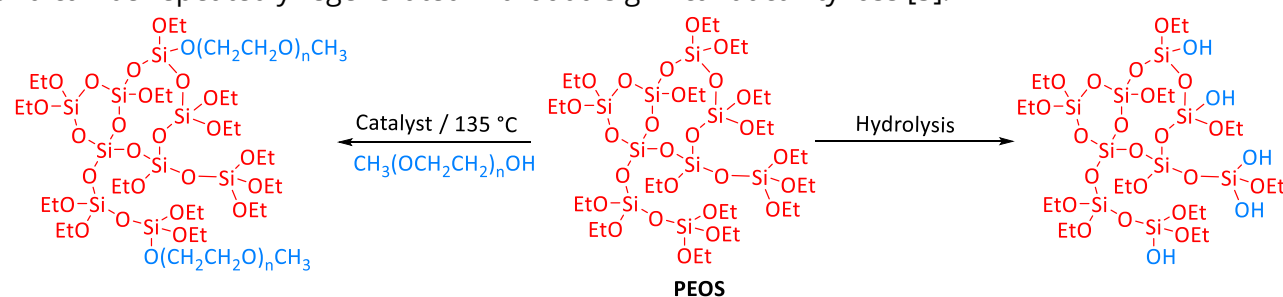


Figure 1. Chemical structure of polyethoxysiloxane (PEOS) and its amphiphilicity induced by hydrolysis or substitution with hydrophilic poly(ethylene glycol).

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Spectroelectrochemistry of sol-gel protective coatings for AA 2024

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Abstract: Protective coatings against corrosion can be designed from organic-inorganic hybrids on a molecular level¹. Different precursors can be applied, for example various trialkoxysilanes, as well sol-gel functionalized polyhedral oligomeric silsesquioxanes or cyclic siloxanes. The possible variations in precursors' structures, and/or addition of appropriate modifying molecules can contribute to increased hydrophobicity or other desired functionality.

In this study various precursors were used to produce protective coatings on aluminum alloy AA 2024. The coatings were dip-coated from sols and then characterized by standard techniques like SEM and AFM microscopy, contact angles, IR and Raman spectroscopy. Electrochemical techniques were used to get insight into the protective effectivity of the coatings. While the potentiodynamic polarization is quick technique for comparison of various coatings, impedance spectroscopy can offer more profound view on processes that occur inside of the coating during its exposure to the action of the electrolyte. Combination of electrochemical tests with vibrational spectroscopy, on the other side, in addition to information on current density in the electrochemical cell offer also IR or Raman spectra. Thorough examination of these vibrational spectra obtained during forced polarization of the coating towards more anodic potentials can give us important information on the identification of the changes in the coatings. It is possible to identify the bonds that are the most prone to cleavage, detect hydration during the exposure of the coating to the electrolyte, in some cases even to identify the breaking of Al-O-Si bonds between the protective coating and the alloy. Combined spectroelectrochemical measurements can be performed ex situ or in situ. The disadvantage of the ex situ approach is the exposure of the coating to the atmosphere during the transfer from the electrochemical cell to the sample compartment of the spectrometer. In situ approach, however, often demands cells' geometries that are not the most optimal regarding the electrochemical considerations.² Accordingly, we have combined IR reflection-absorption (IR RA) and Raman spectroscopy with electrochemical techniques and investigated the behavior of various sol-gel protective coatings.

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Multifunctional nanosurfaces for water purification and biocatalysis

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Abstract: Production of hybrid materials combining mineral nanoparticles as inorganic constituents with organic or biomolecular functions grafted on them has already become a highly addressed and utterly promising research field [1]. Functional organic molecules attached to either porous or magnetically retractable nanomaterials have been proved to offer efficient and selective tools in removal of hazardous metal cations from wastewaters and drinking water [2]. Nano formulation of biocatalysts (enzymes) has been proved to enhance their thermal and chemical stability and improve their chemical activity especially for hydrolases, e.g. urease [3], perspective in medical applications, such as blood dialysis.

In our recent studies we turned the attention to creation of multifunctional surfaces of nanomaterials combining organic ligand and enzymatic functionality, at the same time broadening the biocatalyst library to involve especially oxidase and peroxidase enzymes [4]. Possible application area lies in the domains of complex water purification and biotechnology. The addressed challenges are in getting understanding of the mutual effects of different functions on each other's performance, especially in how adsorption of hazardous transition and heavy main group metals by organic ligand functions influences the bioactivity. A separate and important challenge is achieving a successful grafting of different functions and thermal and chemical stability of the multifunctional materials. The approaches to immobilization of biocatalysts are strongly dependent on their chemical composition and configuration of the molecules, guiding the choice between covalent grafting, entrapment, or multiple hydrogen bonding. Stability of organic functions can in their turn also be compromised by the activity of biocatalysts, influencing the type of grafting that can be utilized.

This contribution will present several examples of multifunctional materials, produced exploiting the obtained insights for tailoring highly efficient and stable adsorbents for removal of diverse hazardous products of human activity, especially the antibiotic and painkiller medicines from the waste- and drinking waters.

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Sol-Gel Derived Siloxanes for (Opto)Electronic Applications

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Abstract: Silicon-based sol-gel materials offer significant advantages in optoelectronic applications compared to other materials because of their tailorable chemical composition, high purity, extraordinary processing possibilities, and high stability. We studied the formation of siloxanes by the polycondensation reactions of dialkoxy- and trialkoxysilanes as well as functionalized polysiloxanes. The resulting polymers still contain cross-linkable alkoxy-silane groups, which can be used for a thermal cross-linking and the formation of elastic and transparent siloxane resins. We tailored the refractive index and hardness of these materials by changing the chemical composition of the alkoxy-silane monomers. Contrary to commercially available polysiloxanes applied in optical applications, which are two component systems cured by platinum catalyzed hydrosilylation reactions, our materials are one component materials with a long shelf-life and catalyst free thermal curing. The tailorable composition of the matrix allows the incorporation of organic fluorescent dyes, which show extraordinary stabilities in high power LED applications.

Furthermore, we applied similar polymeric materials for the continuous production of polysilsesquioxane beads in a microjet reactor. The beads were converted in a pyrolytic reaction into silicon oxycarbide materials with conserved morphology. A further etching step allowed the removal of the silicon backbone and the production of porous carbon. The thus obtained silicon oxycarbide and carbon spheres reveal properties, which are influenced by the substitution pattern of the silicon atoms in the original polysilsesquioxane beads. Both materials were tested for applications as energy storage materials in supercaps and batteries.

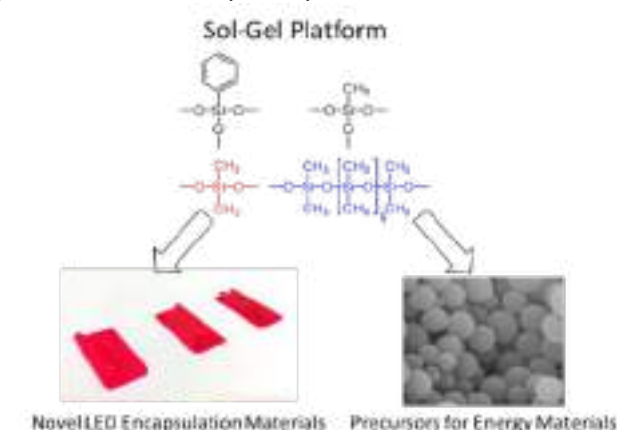


Figure 1.

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Hydrogen peroxide sol gel processing: fundamentals and applications

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Abstract: The speciation of p-block element oxide precursors in aqueous hydrogen peroxide solutions are different from aqueous solutions which distinguish sol gel processing and its products. Some general features of the competition between hydrogen peroxide/hydroperoxo(peroxo) and aquao/hydroxo(oxo) ligation are discussed. Hydrogen peroxide interacts with boron, germanium, tin, antimony and other p-block elements only under basic conditions and then peroxo- or hydroperoxo complexes are formed [1-4]. Additionally, since hydrogen peroxide is acidic, it induces polycondensation and sol formation by ololation, oxolation and to a limited extent also by peroxo bridging mechanisms. In addition, hydrogen peroxide acts also as a capping agent and the hydroperoxo coordination prevents gelation and stabilizes the sol state, which can be used to form thin films on particulates [5-7]. Finally, hydrogen bonding of peroxo-capped colloids to oxygen rich surfaces is discussed [8-10].

For practical applications, sols of peroxogermanate, peroxostannate and other p-block element peroxocomplexes are used as precursors to coat clays, graphene oxide and other oxygen containing particulates and then can be transformed to corresponding oxide and chalcogenide thin films [10-16]. The benefits of using hydrogen peroxide capping are discussed.

Some demonstrating energy storage application based on hydrogen peroxide sol gel processing of p-block elements are briefly demonstrated [10-17].

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Molecular and Nanoparticle Imprinting by Electrochemically Deposited Sol-Gel Thin Films

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Abstract: Sol-gel technology provides a very versatile and convenient approach for the formation of tailor-made films and coatings. Combining electrochemistry and sol-gel is even more powerful as electrochemistry provides the tools for controlling very precisely the thickness of the sol-gel film. This contribution will focus on a few examples where electrochemistry and sol-gel were used in imprinting. The latter is a known approach for assembling matrices with high selectivity. Molecularly imprinting polymers have been widely used as a means of imprinting molecular species for primarily sensing and separation.

We will show how electrochemistry is used to electrochemically deposit thin sol-gel films for imprinting molecular species and more recently nanoparticles. One system¹ deals with imprinting a thiolated stable protein (SP1) in a sol-gel matrix on a gold surface. We studied the electrochemistry of numerous redox couple at the Au/SP1/sol-gel interface and found that the nanochannel array shows charge and structural selectivity, which is based on the interactions between the redox species and the functionalities of SP¹.

Nanoparticle imprinted matrices (NAIMs) is a new approach, in which nanoparticles (NPs) are imprinted in a matrix followed by their removal to form highly selective voids that can recognize the original NPs. We examined the effect of a sol-gel matrix on the imprinting and reuptake of gold nanoparticles². Specifically, indium tin oxide films were modified with a positively charged polymer on which the negatively charged AuNPs stabilized with citrate were adsorbed. This was followed by the electrochemical deposition of sol-gel matrices with different thickness and functional groups. Electrochemical oxidation dissolved the gold nanoparticles and formed cavities in the sol-gel films, which fit both the size and shape of the AuNPs-cit. Furthermore, the thickness of the sol-gel layers as well as the type of the silanes that were deposited, play an important role on the recognition ability of the NAIM.

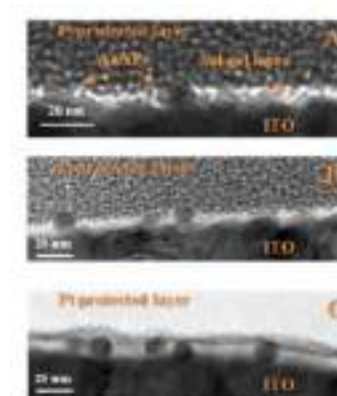


Figure 1. TEM images of a sol-gel film cross-section where Au nanoparticles were imprinted.

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Enabling Martian habitability with silica aerogel via the solid-state greenhouse effect

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The low temperatures and high ultraviolet (UV) radiation levels on Mars today currently preclude the survival of surface life. All previous ideas for making the martian surface more habitable involve massive environmental modification that will be well beyond human capability for the foreseeable future. Here we present a new approach to this problem, where we show that widespread regions of the surface of Mars could be made habitable to photosynthetic life in the future via a solid-state analogue to Earth's atmospheric greenhouse effect. Specifically, we demonstrate via experiments and modeling that under martian environmental conditions, a 2 to 3-cm thick layer of silica aerogel will simultaneously transmit sufficient visible light for photosynthesis, block hazardous ultraviolet radiation, and raise temperatures underneath permanently to above the melting point of water, without the need for any internal heat source. Placing silica aerogel shields over sufficiently ice-rich regions of the martian surface could therefore allow photosynthetic life to survive there with minimal subsequent intervention. This regional approach to making Mars habitable is much more achievable than global atmospheric modification and can be further tested in extreme environments on Earth today. In this remote presentation, I will give a summary of our research on this topic, discuss remaining challenges, and finally highlight the need for future materials science research into planetary and space applications in general.

Clay particles assembly through sol-gel: a new route to clay-based nanoarchitected materials

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Abstract: In recent years, fibrous clays (i.e., sepiolite and palygorskite) are attracting growing interest as promising nanoplateforms for the immobilization of many diverse nanoparticles (NP), giving rise to nanostructured materials for numerous advanced applications such as adsorbents and catalysts for environmental remediation, photoactive materials, electrochemical devices and controlled drug delivery, amongst others (1). Methodologies for assembling NP to these silicates include the use of sol-gel approaches for *in situ* generation of silica and metal oxide NP from their corresponding alkoxides. In fact, the sol-gel method has proved particularly advantages for the preparation of porous clay derivatives by using the organophilic interphase of the so-called organoclays to accommodate the alkoxide molecules, that after controlled hydrolysis/polycondensation processes produced nanoarchitected materials in which the generated oxide NP remain assembled to the clay particles (2). This methodology was firstly applied to produce silica-clay nanocomposites as the polysiloxane network generated from silicon alkoxides previously intercalated in the interlayer region of layered clays, for instance montmorillonite, resembled to typical polymer-clay nanocomposites where the clay nanosheets became delaminated within the silica matrix (3). In the case of fibrous clays the use of organoclays favors that the *in situ* formed oxide NP remain bonded to the external surface of the silicate through its structural silanol groups (4). In this communication we will show how sol-gel based methodologies in combination to organoclays can be used to produce nanoarchitected materials by direct co-assembly of layered and fibrous clays (Figure 1). The resulting solids show high porosity and specific surface area as well as cation exchange properties. This study constitutes a first step towards the production of more sophisticated heteroclays-nanoarchitected materials as the methodology can be extended to use other metal alkoxides (e.g., Ti, Al,...) of interest for instance in catalysis.

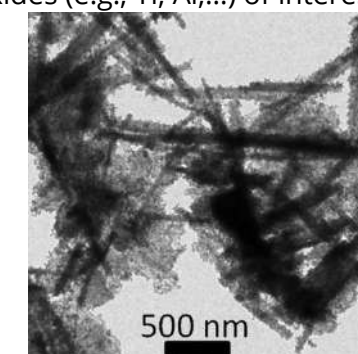


Figure 1. Montmorillonite-sepiolite/SiO₂ nanoarchitected material.

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Sol-gel-synthesis of inorganic nanofiltration membranes

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Abstract: Ceramic NF membranes with a cut-off of 450 Da have been already developed 20 years ago [Ref. 1]. Basis of the preparation was a polymeric sol-gel-technique starting from titania-isopropoxide and zirconium-n-propoxide. The membranes had a pore size of 0.9 nm and a thickness of 50 nm. These membranes have been commercialized by the company inopor GmbH [Ref. 2].

In a second development phase, the pore size was slightly reduced. The hydrolysis of the alkoxides was controlled either by the amount of water and/or the addition of protective groups. The coating of tubes was performed in a cleanroom (class 100) under controlled humidity. Final thermal treatment was performed at a temperature between 300°C and 500°C in air as well as under inert atmosphere. High quality membranes were obtained on high quality substrates with a final intermediate layer of zirconia with a pore size of only 3 nm (Figure 2). On monochannel tubes with an O.D./I.D.=10 mm/ 7 mm a molecular weight cut-off (MWCO) in aqueous solution of polyethylene glycols of 200 Da was achieved with a specific flux of 9 l/(m²hbar) at a transmembrane pressure of 30 bar [Ref. 3].

Current development is focused on a scale-up of the sol-gel coating from 0.25 m²-elements (Figure 1) to 10 m²-elements to meet requirements of large scale applications > 1000 m² [Ref. 4].



Figure 1. Membrane elements with different channel design.

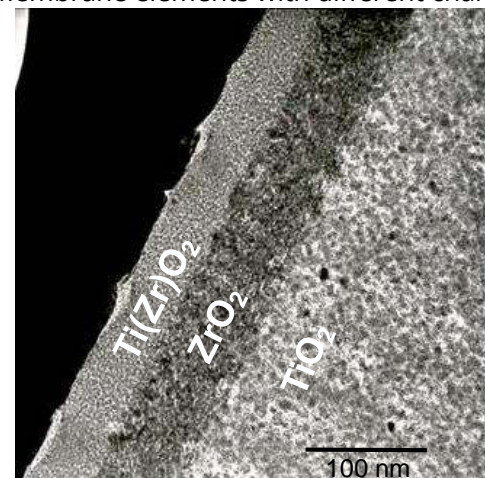


Figure 2. Cross section of a 200 Da NF membrane.

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Stimuli-responsive porous polysilsesquioxanes

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Abstract: Commonly, synthetic materials are static in form and function. However, the demand for dynamic materials in which selected properties can be “switched on” and “off” is significantly growing. Especially, since they are of high interest for a broad application area ranging from optical memory devices, holographic gratings or optical sensors. A prerequisite for their design is the attachment of the responsive entity into a matrix that does not restrict its conformational freedom. Spiropyranes (SPs) for example are one of the most prominent stimuli-responsive molecules. They comprise an indoline and a chromene moiety positioned perpendicular on either side of the spiro C-O bond. As long as both parts are in conjugation, the isomers mainly absorb light in the UV region and the materials appear colorless. However, various external stimuli, e.g., irradiation with UV or visible light, pH changes, heat, etc., can cause a 6- π electrocyclic ring opening reaction of the SPs resulting in fully conjugated merocyanine (MC) forms and highly colored materials. The color of the MC forms can thereby be varied from blue over green to red, depending on the chosen substituents on the aromatic ring system. In this talk, the opportunity to incorporate a spiropyran derivative as a stimuli responsive molecule into a methyltrimethoxysilane (MTMS) based porous framework is presented (Figure 1).

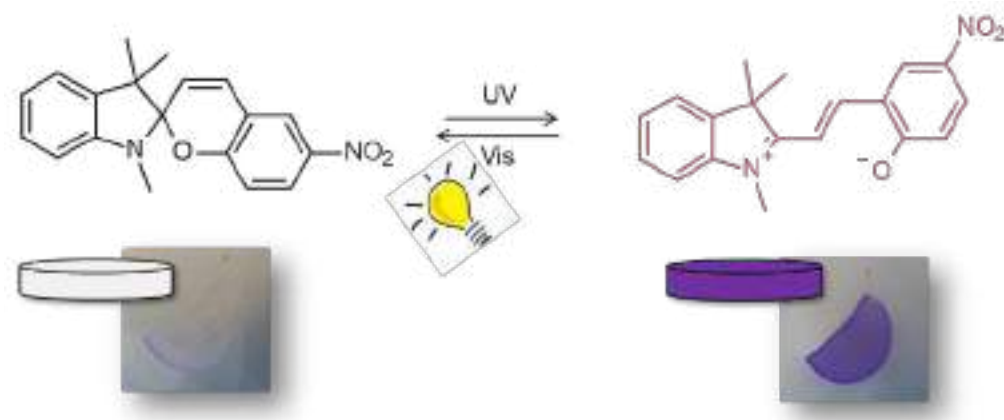


Figure 1. Conversion of a colorless, closed ring spiropyran (SP) isomer into its colored, fully conjugated merocyanine (MC) form, both of which are embedded within porous a methyltrimethoxysilane based framework.

Special attention is given to the covalent attachment of the SP derivative to the MTMS matrix since this (i) guarantees its permanent attachment and therefore minimizes the risk of leaching and (ii) it suppresses intermolecular interactions and the aggregation of the molecules in the macromolecular carrier. The thus obtained materials can repeatedly be converted into the colored MC or the colorless SP form by irradiation with UV or visible light. The influence of this back and forth conversion on the network build-up, the mechanical properties, porosities and surface areas of the SP-modified polysilsesquioxanes will be discussed in detail.

Mechanical stress in sol-gel-derived coatings

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Abstract: Sol-gel ceramic or glass thin films deposited on substrates have in-plane stress, which goes up to several hundred MPa or more. Then what do we know about it? How do the sol-gel chemistry and the deposition conditions affect the stress evolution? Stress data have been obtained by measuring the substrate curvature and accumulated in our group. Based on the data, what we know on these issues will be addressed in the talk.

It is important to distinguish the intrinsic stress from the residual stress. The former is measured in situ during film deposition, heating and cooling, and the latter is measured at room temperature after cooling. In general, they are different in value, and should not be confused. The intrinsic stress during gel film heating causes macroscopic cracking, and hence important. Such stress is tensile in in-plane direction, and is generated basically as a result of the film shrinkage on heating, which occurs via solvent evaporation and condensation reactions in films. The factors that affect the intrinsic stress measured during gel film heating will be addressed, including the amount of water and the catalysts for alkoxide hydrolysis, the chelating agents for alkoxides, the addition of organic polymers, the heating rate, and so on [1,2]. At high temperatures where crystallization occurs, such stress starts to decrease due to the activated atomic diffusion [1,3].

The residual stress is the stress that remains in the film after cooling and measured at room temperature. Such stress is important because the films are used at room temperature in many cases, and it can affect the performance of the films. The residual stress is generated as a result of the stress generation during heating and cooling [1,3]. Since the stress generated during cooling is the thermal stress of the fired, rigid ceramic (or glass) film, it can be either tensile or compressive depending on the difference in thermal expansion coefficient of the film and the substrate. Therefore, the residual in-plane stress can also be either tensile or compressive. How the residual stress is generated, and how the firing temperature affects the residual stress will be addressed in the talk.

Finally, possible relaxation of the residual stress at room temperature will be introduced. The substrate is spontaneously bent and gains curvature when the film has in-plane stress. It results from the strain in the film. Recently we have found that such substrate bending decreases with time when the fired film on the substrate is kept standing at room temperature. This implies the possible relaxation of stress in such fired films at room temperature (Fig. 1). The question is whether or not it is really the stress relaxation, and how it occurs. These issues will be discussed in the talk.

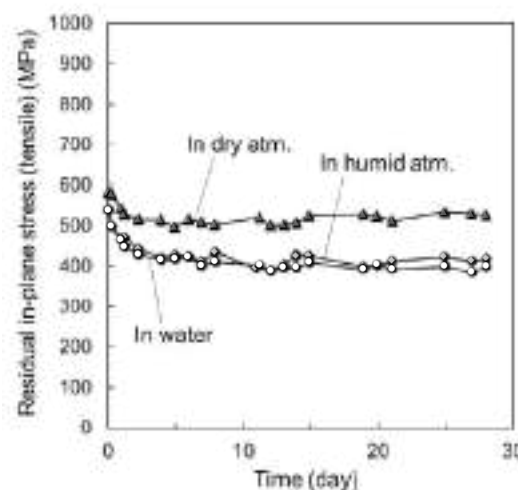


Figure 1. Stress-time relation for a sol-gel-derived titania thin film deposited on an Si(100) wafer and fired at 1000°C. The film was kept standing at room temperature in dry and humid atmosphere and in water.

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Directing pores in framework compounds via sol-gel approach

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Framework compounds such as metal-organic frameworks (MOF) and covalent organic frameworks (COF) are characterized by their uniform micropores which offer a huge accessible surface for applications in gas storage, catalyst and others. Additional functionalities for electronics, photonics and magnetics applications can be attained by an accommodation of functional guests (molecules, ions, or nano objects) into such pores. For example, an electronic or semi-conductive MOF has been achieved by incorporating p-type conductive molecules into the pore of Cu-based MOF¹. An achievement of device scale MOF/COF thin films with controlled crystallographic orientations has been required to enhance these sophisticated functionalities for practical applications. Recently, the authors have reported the heteroepitaxial growth of MOF via solution processing of the precursor metal hydroxide oriented films². The resultant MOF film exhibited crystallographic orientation along all three axes where pores are aligned to the specific directions in the macroscopic scales. The orientation essentially depends on the crystallographic plane of the seed metal hydroxide layer because of the approach based on liquid phase epitaxy. In this presentation, recent advances on the fabrication and application of the oriented MOF/COF films will be reviewed. Topics include (see Figure 1)²⁻⁶ the fabrication of oriented MOF/COF films via solution processing, versatility of the epitaxial growth approach, impregnation of functional molecules and nano particles, and others.

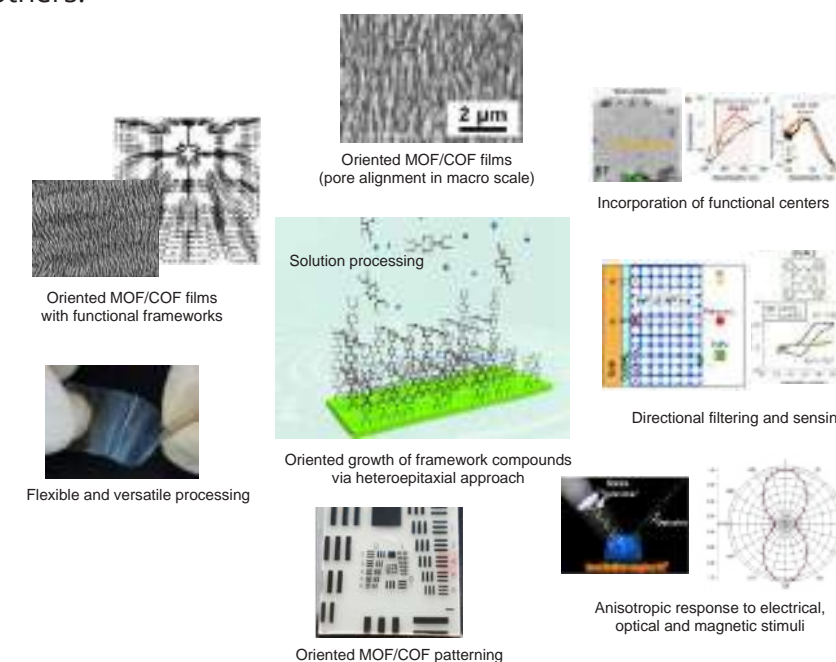


Figure 1. Fabrication of oriented framework compounds and their applications.

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One-Dimensional Silica Nanomaterials: from Synthesis, Functionalization to Applications

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Abstract: Here, we report the synthesis of one-dimensional silica nanomaterials with various architectures (e.g., nanowires (NWs), nanobottles (NBs), and nanotubes (NTs)) via an anisotropic sol-gel growth method in water/n-pentanol emulsions.^{1,2} Detailed studies on using such silica NBs, NWs, NWs and their 3D assemblies as substrates or sacrificial templates for preparing various multifunctional materials for nanocatalysis, nanosensing, and biomedical applications will be discussed.³⁻⁵ Our recent progress on the template-free synthesis of silica NTs, with tunable shell thickness (1–5 nm) and homogeneous diameter (~25 nm), and featuring chemically asymmetric surfaces (i.e., a negatively-charged (–Si–OH) interior surface and a silane-capped outer surface) will also be introduced. Owing to the chemically asymmetric properties of the NTs, various positively charged molecules can be selectively loaded with high content inside the NTs via a simple electrostatic interaction. With the mediation of polyamidoamine (PAMAM) dendrimers pre-infiltrated inside the silica NTs, various noble metal nanoparticles (e.g., Au NPs, Pt NPs, Pd NPs) can be selectively deposited in the NTs with uniform size and high density. Owing to their elongated pore structure (with lengths up to several micrometers) and high specific surface area (618 m² g^{–1}, BET method), the silica NTs exhibit very high loading capacity and prolonged release profiles for positively charged therapeutics (e.g., anticancer drug doxorubicin). The sustained release period could be tuned to last for several months provided the drug-loaded NTs are assembled into a membrane structure.

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Tailoring mesopores in metal organic framework (MOF) and the structural fabrications

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Abstract: Metal-organic frameworks (MOFs) are porous crystalline materials consisting of metal clusters or ions, which act as connecting nodes and rigid organic bridging ligands. The porous and flexible nature has made them attractive for gas storage, separation, and catalytic reaction. A challenge exists, however, on how to introduce larger pores juxtaposed with the inherent micropores in MOFs for various structural forms of MOF, which would open up high level of functions and new applications. Herein, we demonstrate a tailoring hierarchical micro-, meso-, and macro-pores within MOF particles, patterns, and membranes, using a discriminate etching chemistry, called silver catalyzed decarboxylation, under mild conditions. The heterogeneous pore structures were evolved without altering the original appearance, which is extensively applied to various MOFs with high structural stability. A decarboxylated MOF membrane grown on anodic aluminum oxide support is shown to have an exceptional pH-responsive switchable selectivity for the flow-assisted separation of similarly sized proteins. We envision that our facile and unique decarboxylation method allows cooperative utilization of heterogeneous pores for massive transfer and separation of complex and large organic, inorganic, and biological molecules, and that the capability developed here for patterning and positioning meso- and macro-porous MOF films on diverse substrates bodes well for various energy and electronic device applications.

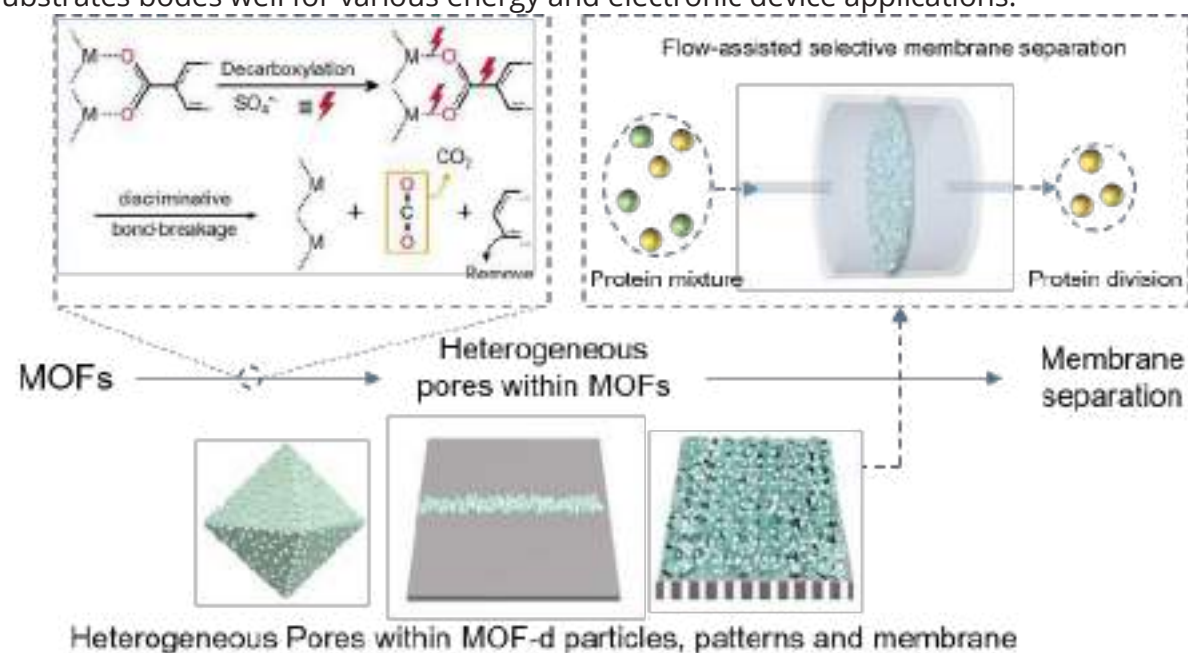


Figure 1.

Pharmacologically active polyolates of biogenic elements and hydrogels based thereof

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Abstract: Sol-gel synthesis is widely used for producing materials with a complex of useful properties, which make them promising materials for biomedical applications. Previously we have proposed a design strategy for the sol-gel synthesis of hydrogels containing biogenic elements. The essence of the strategy is that polyolates of biogenic elements, mainly silicon glycerolates, are used as biocompatible precursors in sol-gel processing, as a rule, in the form of a solution of the corresponding polyol approved for a certain medical application [1,2]. Thus combined polyolates are used to achieve a synergistic pharmacological effect; and bioactive additives or medicines serve as templates and/or as the property modifiers for the formed hydrogel.

Based on the strategy, fairly extensive series of works on sol-gel synthesis was realized, and the study of composition, structure, and physicochemical properties of novel hydrogels based on organic precursors, biogenic elements polyolates (Si, Zn, B, Ti and others), was performed in the Postovsky Institute of Organic Synthesis [1-4]. The influence of various factors (pH, molar ratio of precursor / polyol / water, gel-forming additives) on the process of gel formation was studied. General regularities and features of gelation process were established for various element-containing precursors in comparison with traditional alkoxy precursors. In some cases biologically active compounds, such as chitosan and hydroxyapatite, were used as templates and property modifiers in sol-gel synthesis [5,6].

Pharmacological activity of the synthesized hydrogels was assessed. These hydrogels are non-toxic and possess a broad spectrum of pharmacological activity (reparative, regenerating, transcutaneous, and antimicrobial). They can be used in medical and veterinary practice both as independent medicines for topical application and as bases of pharmaceutical compositions containing active drug additives or biologically active substances for treatment of the skin, soft tissues and mucous membranes diseases of various etiologies.

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Electrospinning and Functionalisation of Silicon Oxide Nanofibres via Sol-Gel Technology

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Abstract: Electrospinning of silica nanofibers without organic polymer addition is regarded as a highly promising methodology for the production of thermal and chemical resistant nanofibrous materials applicable in various advanced applications. The combination of sol-gel technology and the electrospinning process allows for the production of ceramic nanofibrous membranes. By proper control of the sols rheology, addition of an organic polymer can be skipped in the nanofibres preparation procedure. It allows for functionalisation of these nanofibrous membranes with various components that would otherwise not withstand the heat treatment. The influence on viscosity, concentration and degree of cross linking will be described [1,2]. These fibres show a shift from hydrophobic to hydrophilic properties upon time and temperature. This peculiar feature opens room to use them as membranes for separation of heterogeneous azeotropes [3].

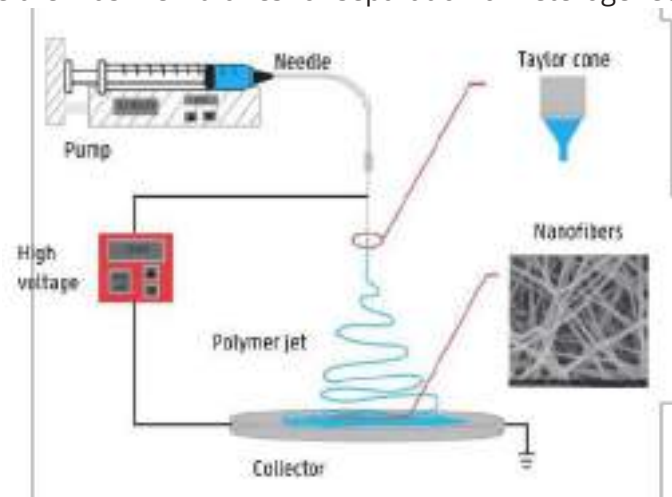


Figure 1. Example of a figure.

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3D Sol-Gel printing for fabrication of Macro- and Micro/Nano-structured photonic devices

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Abstract: 3D-printing has emerged as a fascinating method for fabrication of elements and devices in a wide range of fields. 3D-printing techniques allows fabrication of elements either in the Macro-scale using techniques such as Ink-jet 3D-printing or fabrication of elements in the Micro/Nano-scale using techniques such as Nanoimprint Lithography (NIL) and Direct Laser Writing (DLW). However, for photonics applications the printing material used is a major issue, relating to satisfying specific optical requirements. In photonics applications the requirements from optical elements include optical quality, thermal and environmental stability and, in addition, it is required to be inexpensive and appropriate for mass production. Until now, the common materials used for such 3D-printing techniques are organic polymers and specifically photo-resist materials, which are limited regarding their optical and mechanical properties. In the last decades, the sol-gel process has proven its possibility to be used as a "tool-kit" for production of glassy optical materials which are appropriate for photonic applications¹. Recently, a Fast Sol-Gel (FSG) process² was developed to achieve Sol-Gel hybrid materials which can be applied by either a thermal-curing or UV-curing, and employed for bonding of optical components³. The obtained Sol-Gel material is an inorganic-organic hybrid with less than 30% organic residues and negligible porosity. These hybrids possess high thermal and optical power stability and low optical loss in the visible range. Mechanical and optical properties can be controlled during synthesis and processing. In addition, specific properties can be tailored by adding appropriate additives. In this lecture we will present 3D-printing using Sol-Gel materials and polymers for fabrication of macro-structured & micro/nano-structured photonic devices using either thermal-curing or UV-curing. Using Ink-jet 3D-printing techniques we fabricated Sol-Gel elements in the Micro/Nano-scale with different shapes (Fig. 1). Using nanoimprint lithography (NIL) we fabricated Sol-Gel elements in Micro/Nano-scale elements, specifically optical ring-resonators which can be used as micro-lasers⁴ (Fig. 2). In addition, with direct laser writing (DLW) we demonstrate fabrication of Micro/Nano-scale photonic elements with commercial photo-resist polymers for manipulation of light beams such as; optical phase elements, lens beam shaping elements and mode sorting elements⁵. In conclusion, the use of 3D-printing methods such as nanoimprint lithography (NIL), direct laser writing (DLW) and Ink-jet printing with Sol-Gel materials allows fabrication of a variety of optical devices from the Nano-scale to the macro-scale. We emphasise that the Sol-Gel elements possess high optical quality and environmental stability and can be used for mass-production of photonic elements.



Figure 1. Photo of sol-gel element printed by Ink-jet 3D printer.

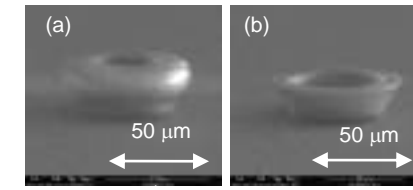


Figure 2. SEM photos of sol-gel ring resonator by NIL (a) toroid resonator, (b) goblet resonator.

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PDMS-based hybrid materials synthesized from CO₂ chemical fixation: a multifunctional platform

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Abstract: Carbon dioxide (CO₂) is a cheap C1 raw chemical and major contributor for Global Warming and many strategies are being studied to fight against its emissions around the Globe. Legislation and socio-education are essential for long-term approaches to minimize these effects. Nevertheless, it is important to propose short to medium-term strategies complementary to long-term actions. The sustainability of CO₂ capture and geological storage (CCS) can be improved by employing the stored CO₂ as raw material for the production of valuable products. Furthermore, a negative emission concept could be applied for already carbon balanced processes such as sugar-ethanol refineries [1]. Therefore, the present studies show some insights on CO₂ insertion into high-tech sol-gel materials. Among, the possible reactions with CO₂, its insertion on epoxides leading to precursor cyclocarbonates (CC) open it up a greener route to urethanes and more recently to versatile hybrid hydroxyurethane. The polydimethylsiloxane (PDMS) diglycidyl ether terminated was converted to the respective PDMS-based bis(cyclic carbonate), denominated CCPDMS. CCPDMS was reacted with different diamines and the chain termination agent 3-aminopropyltriethoxysilane (APTES) [2] leading to the formation of different PDMSUr hybrid materials. Self-supporting films were obtained using isophorene diamine (IPDA) as chain extender and APTES as chain terminator. The film presents good handling properties and were easily modified with Europium polyoxometalates as well as Rhodamine B loaded porous silica nanoparticles[3]. PDMSUr matrix also present potential applications as antimicrobial coatings.

Therefore, the hybrid PDMSUr matrix confirms its utility to be applied in a wide range of industrial and technical fields, including photonics and biomedical areas.

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Optimizing Piezoelectric Ink-Jet Printing of Silica Sols for Biosensor Production

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Abstract: The ink-jet printing of biocompatible silica sols has gained popularity, both for biosensor production and development of holographic devices. However, there still remain significant issues related to premature clogging of ink-jet printheads when printing aqueous silica sols. To better understand the causes of clogging of piezoelectric ink-jet nozzles, printing studies were coupled with studies of colloidal stability along with silica deposition on surfaces, both under normal flow and piezoelectrically-driven oscillating flow through an inkjet cartridge. Our studies show that clogging most likely results from deposition of silica colloids onto the internal surfaces of the printhead, followed by displacement of micron-sized pieces of the deposited material upon piezoelectric deformation of the printhead surface, which then block the nozzles of the printhead. Based on this result, we formulated a low pH sol derived from sodium silicate and evaluated its colloidal stability, binding to silica surfaces and resistance to clogging of inkjet nozzles under normal and voltage driven oscillating flow. We show that silica sols with a relatively acidic pH provide optimal printing behaviour while allowing reproducible printing of spatially controlled silica patterns on paper to produce enzyme-based biosensing devices.

Better (Bio)Ceramics through Chemistry

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Abstract: Human allograft is by far the best solution for repairing and reconstructing human skeleton. Upon trauma or as a consequence of a disease, clinical situations where the surgeon needs bone defect filling materials are very frequent. In many cases neither autograft nor allograft is possible and the surgeon has to use synthetic bone filling materials, either because the volume to be filled is too important or the co-morbidity an issue. Among all potential materials, calcium phosphate bioceramics are the most interesting and commonly used materials due to their osteointegrative and osteoinductive properties.

Beyond these remarkable properties, it is highly desirable to bring multifunctionality to the bioceramic. Chemical doping through ionic substitution is a very efficient and convenient way to do it. In this lecture, we will focus on cationic substitution in hydroxyapatite and tricalcium phosphate. We will try to demonstrate how fine knowledge of crystallo-chemistry taking place in these materials is necessary to fully understand the material behaviour. Using the example of zinc, iron and copper doping in biphasic calcium phosphates [1,2], we will show that unsuspected doping mechanisms can be put forward. In this example, bioceramics with anti-inflammatory property can then be produced with a fine-tuning of the material. Other examples concerning materials with luminescent properties for diagnostic [3], antibacterial activity, anti-osteoporosis property and others will be presented.

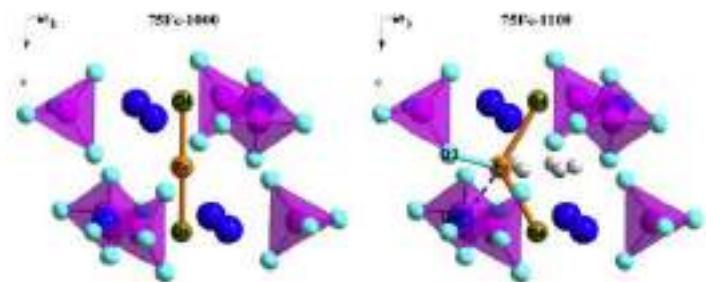


Figure 1. Insertion scheme of Fe³⁺ ion in Hydroxyapatite²

Conclusion

The take home message of this lecture is that upon thorough knowledge of materials chemistry taking place upon doping, it is now possible to reach on demand design of multifunctional biomaterials with improved properties. Sol-Gel chemistry appears to bring a leading advantage to achieve such objectives.

New developments on ammonium-functionalized polyhedral oligomeric silsesquioxane (POSS)

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Abstract: Polyhedral oligomeric silsesquioxanes (POSSs) have attracted much attention in the research field of organic-inorganic hybrid materials. In particular, since reactive ammonium-functionalized POSSs can be applied to various functional hybrid materials, it is expected as useful inorganic materials. So far, we have reported that ammonium-functionalized POSSs can be prepared by hydrolytic condensation of amino-group-containing organotrialkoxysilanes using a superacid as a catalyst in high yield with a short reaction time.¹ In addition, we recently reported a methodology to control the size of ammoniumfunctionalized POSSs.² As new developments on ammonium-functionalized POSSs, in this lecture, temperature-responsive behavior of this POSS in water and preparation of soluble POSS-linking polymer by polycondensation with carboxyl-functionalized POSS are reported.

1. Temperature-responsive behavior of ammonium-functionalized POSS in water

Most of temperature-responsive materials are organic polymers, e.g., poly(N-isopropylacrylamide) (PNIPAM), whereas temperature-responsive oligomers are not common. In particular, to the best of our knowledge, temperature-responsive materials consisting of inorganic oligomers have not been reported. In this study, we found that ammonium-functionalized octamer POSS with triflate counterion (Am-T8-POSS-OTf) in water indicated temperature responsiveness. When aqueous suspension of AmT8-POSS-OTf was heated to 65 °C, it became transparent (Figure 1). Then, when this transparent aqueous solution was cooled, it became turbid (Figure 1). Since these behaviors were reversible and sensitive, we consider that Am-T8-POSS-OTf is regarded as a temperature-responsive material.

2. Preparation of soluble polyamide by condensation of ammonium- and carboxyl-functionalized POSSs

Since POSS is an oligomer, it is difficult to apply it alone as film or bulk materials. Therefore, the preparation of POSS-linking polymers has been actively performed in recent years. However, as POSS generally has multiple functional groups, a polymer obtained by its polymerization usually forms a network structure and is insoluble. In this study, when ammonium-functionalized POSS^{1,2} and carboxyl-functionalized POSS,³ which were previously reported by us, were condensed using condensing agents, we found that soluble POSS-linking polymer were successfully prepared. The resulting polymer was soluble in polar solvents, such as water, DMSO, and methanol. In addition, a self-standing film could form by heating and evaporating aqueous solution of this polymer.



Figure 1. Temperature-responsive behavior of Am-T8-POSS-OTf.

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Multi-functional Sol-Gel Based Coatings

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Abstract: Sol-gel technology provides high versatility for design and chemical formulation of multi-functional coatings in a myriad of industrial applications. In this lecture, several examples of sol-gel based coatings with their functionalities and applications are introduced. For metallic substrates (steel, stainless steel, Al, Mg), decorative, scratch resistant, and corrosion protection are essential. Suitable pre-treatment and sol-gel based multi-functional coatings are excellent solutions. Sol-gel process can also be used to make encapsulations for corrosion inhibitors for smart release properties. Polymers and flexible soft substrates are often used for medical devices, microfluidic chips, printed electronics devices, and 3D printed consumer products. An effective surface modification via plasma assisted surface grafting technique or direct chemical grafting is able to provide the required surface energy, morphology, functional groups, smart selective or switchable surface structures. Sol-gel based easy-clean (hydrophobic or superhydrophilic) coatings are also used on glass and ceramic surfaces for protective and decorative purposes. The fundamental principles and experimental results of the above-mentioned applications will be presented in this lecture. The critical factors for success and future perspectives will be covered as well.

Design of functional hybrid silicas for several application fields

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Abstract: Bridged silsesquioxanes (BS) are known since three decades [1,2] and are obtained by the hydrolysis-condensation of organosilane precursors with bridging units, $(\text{EtO})_3\text{Si-R-Si}(\text{OEt})_3$ (R = organic units). Thanks to the mild sol-gel reaction conditions, the strong covalent Si-C bonds are maintained during the reaction which allows the formation of unique hybrids with a uniform distribution and stoichiometric Si/C ratio of covalently bonded organics to at least two silicon atoms (Figure below).

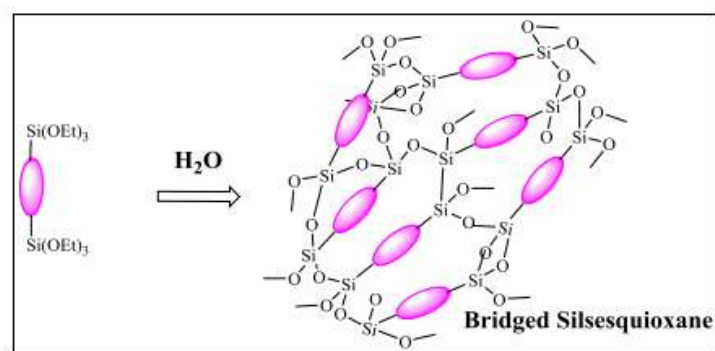


Figure 1. Synthesis of BS from polysilylated precursors.

These hybrid organic-inorganic materials combine the inherent properties of the organic fragments with those of the silica network. With the wide variety of organic units that can be introduced in BS, one can tune the properties of the final materials for targeted applications (e.g. catalysis, optics, magnetic and imaging, etc.). Moreover these hybrids can be structured in mesoporous materials when synthesized with a surfactant. The resulting hybrid is called Periodic Mesoporous Organosilicas (PMO). In this presentation, the design of selected BS precursors will be shown [3]. The role of the organics for the self-directed structuring [4] as well as template-mediated structuring of these hybrids^{5,6} will also be addressed and finally some examples will be given for several fields of application [7,8,9].

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Frequency conversion in lanthanide-doped materials for solar energy and solid state lighting applications

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Abstract: In order to increase the efficiency of photovoltaic solar cells, photon absorption in an extended range of the solar spectrum is necessary, for example by means of up-conversion (UC) of sub-bandgap photons to minimize transparency losses. While lanthanide (Ln)-doped luminescent layers may be deposited on solar cell materials to achieve spectral conversion effects by methods like CVD or PVD, sol-gel (SG) processing is a low-cost technology which may be a good alternative for this purpose. In this work, Ln-doped SG-derived active layers have been deposited by spin-coating onto c-Si substrates for frequency conversion, with particular emphasis on UC, involving host matrices like aluminosilicate glass and titania ceramic doped with the sensitizer/acceptor pairs Tb/Yb and Er/Yb. The different materials have been characterized by XRD, SEM, Ellipsometry, Raman and photoluminescence (PL) spectroscopies. PL lifetimes have been measured in selected cases and the energy transfer efficiencies have been studied.

White light emitting diodes (WLEDs) based on Ln-doped phosphors still have efficiency limitations, namely because the Stokes shift from UV/blue LED excitation to the emitted lower frequency visible light converts some of the pump energy into heat. However, if white light generation (WLG) is achieved through IR-pumped UC instead, the cost of the LED lamp will be reduced, while the energy loss from Stokes shift can be minimized and UV/blue light leaks may be avoided. SG synthesis of Ln-doped oxide phosphors for UC in WLG has been achieved. The SG-derived matrix was either aluminosilicate glass or titania. The active Ln elements were Yb (as a sensitizer for 980 nm pump absorption), Er (red and green emitter), Tb (green emitter) and Tm (blue/red emitter), to obtain the right proportions of the three primary colors, based on the CIE chromaticity diagram coordinates. The color temperature and color rendering index have also been calculated.

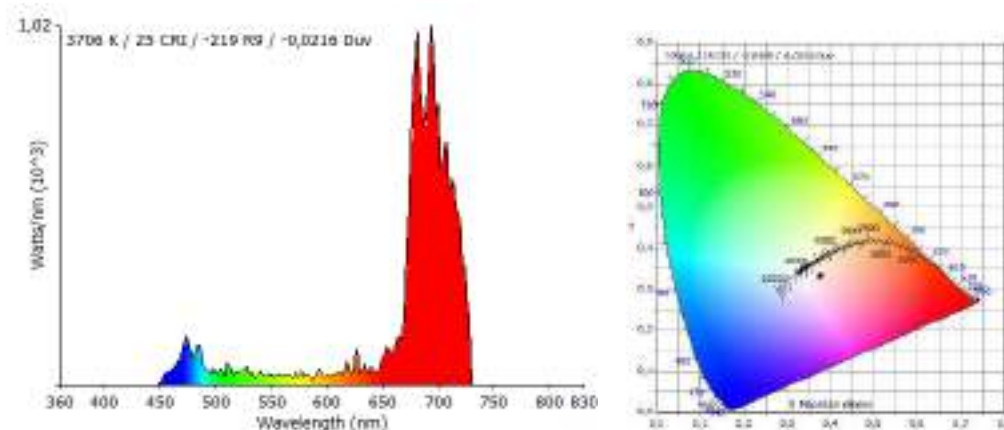


Figure 1. UC spectrum and color diagram for a Tm/Yb-doped aluminosilicate SG glass phosphor.

Lanthanide-Based Ionosilicas for Smart Electrochromic Windows of Nearly-Zero Buildings

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Abstract: Smart electrochromic (EC) windows offer great technological prospects in the present energy scenario. As they allow to adjust in real time the daylight inflow and solar energy to changing weather, to the room conditions or to the occupant's preference, they reduce the building's energy consumption, increase thermal/visual comfort and improve outdoors view. Currently, a major goal of this field is to fabricate windows enabling the fine control of sunlight transmittance (visible radiation) and solar heat gain (near-infrared (NIR) radiation). In addition, the production of dynamic architectural EC glazing featuring different colors is of great interest for aesthetic purposes. The use of electrolytes incorporating mixtures of judiciously chosen lanthanide (Ln³⁺) complexes is an attractive solution, because these compounds exhibit high emission quantum yields covering the visible-to-NIR spectral region depending on the selected Ln³⁺ ion. Here new ionosilicas [1] comprising a pendant imidazolium-terminated alkyl chain and luminescent Ln³⁺-based anionic complexes as counter-ions were synthesized. The new materials were employed as electrolytes in EC devices [2] with enhanced performance.

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sSEBS/SiO₂-P₂O₅-ZrO₂ hybrid membranes with improved methanol crossover and cell performance for DMFCs applications

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Abstract: The body of your abstract begins here. Your abstract has to be maximum 1 template page (from the title to acknowledgements).

Membranes commonly used in direct methanol fuel cell (DMFC) not only are expensive but also show a great permeability to methanol which reduces fuel utilization and leads to mixed potential at the cathode. In this work, sulfonated styrene-ethylene-butylene-styrene (sSEBS) modified membranes with zirconia silica phosphate sol-gel phase are developed and studied in order to evaluate their potential use in DMFC applications. The synthesized hybrid membranes and sSEBS are subjected to an exhaustive physicochemical characterization by liquid swelling, ion exchange capacity, atomic force microscopy, X-ray photoelectron spectroscopy and dynamic mechanical and thermogravimetric analyses. Likewise, the potential use of the prepared membranes in DMFC is evaluated by means of electrochemical characterizations in single cell tests in order to determine the limiting methanol crossover current densities, proton conductivities and DMFC performances. The hybrid membranes show lower water and methanol uptakes, higher stiffness, water retention capability and power density and lower methanol crossover than sSEBS and Nafion (N112). The membrane infiltrated for 40 minutes achieved the best performance showing a maximum power density 37.9% higher than that of sSEBS. The suitable characteristics of the hybrid sSEBS membranes infiltrated by sol-gel method, along with their low cost, make them a realistic option for DMFCs.

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Recent advances in non-hydrolytic sol-gel synthesis of mesoporous materials

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Abstract: Non-hydrolytic sol-gel involves the reaction in non-aqueous media of precursors with organic oxygen donors instead of water^[1]. The reaction of chloride precursors with an ether or an alkoxide at 80-150 °C provides useful alternatives to conventional sol-gel routes for the design of mesoporous oxide and mixed oxide materials, which have been successfully used as heterogeneous catalyst^[2]. In this presentation I will focus on recent results concerning other materials such as metal oxide-carbon nanocomposites^[3] (Figure 1), other non-hydrolytic routes involving for instance ester elimination^[4-5] (Figure 2), or original phosphonate-based organotinorganic hybrid materials^[6] (Figure 3).

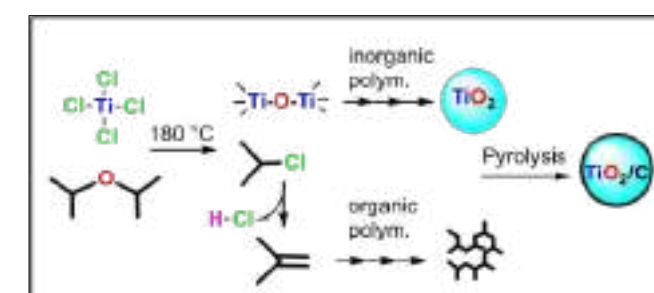


Figure 1: Synthesis of mesoporous TiO₂-carbon nanocomposite using diisopropyl ether as an oxygen donor and a carbon source.

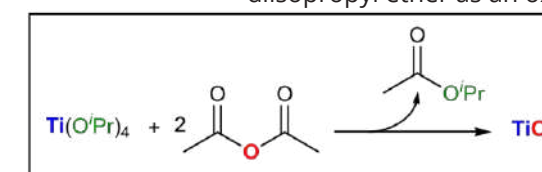


Figure 2: Synthesis of TiO₂ using acetic anhydride as an oxygen donor

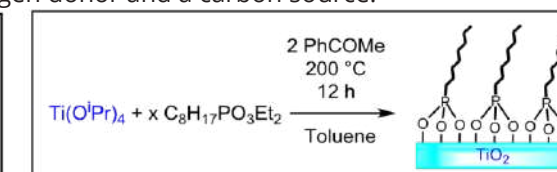


Figure 3: Non-hydrolytic sol-gel synthesis of titanium oxophosphonate hybrid materials

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Nano/micro-structured Si materials for high energy lithium batteries

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Abstract: Silicon anode could deliver exceptional high capacity of 4200 mAh g⁻¹ theoretically and is recognized as a promising alternative of graphite for high energy batteries. However, the drastic volume change during lithiation/delithiation and chemical reaction with electrolyte hinder its practical application. Many efforts have been devoted to handle these problems. Decreasing the Si particle size to less than 150 nm or using the porous structure could avoid cracking and electronic contact loss during lithiation/delithiation [1,2]. Here we propose two simple but effective preparation methods of Nano/micro-structured Si/C composites as anode materials for Li-ion batteries, which demonstrate the excellent electrochemical performances. Porous Si/CNT/C microspheres as shown in Fig. 1a have been prepared by spray drying and the followed carbonization. In the Si/CNT/C composites, silicon particles (about 50–200 nm) are covered by a layer of carbon formed by pyrolysis of phenol-formaldehyde resin (PF), which, in turn, connects with the three-dimensional multiwall carbon nanotubes (MWCNTs) conductive network. Numerous open pores could buffer volume expansion of silicon and improve the electrode kinetics. On the other hand, we adopt electrospinning approach with PAN and Si nano-powder as raw materials and followed high temperature carbonization to prepare free-standing Si/C fibers films for direct anode use (Fig. 1b). Si nanoparticles embedded in carbon fibers can maintain good electronic connection, while the interspace in the film absorbs the volume expansion of Si. Thus, the Si/C film anode possesses excellent cycling stability. The Si/C film anode could be directly lithiated after sandwiching it between Li metal foil and separator and then adding electrolyte when assembling cells. Fig. 1c shows that lithiated Si-S@pPAN cell has better cycling stability than Li-S@pPAN cell. As Li was used as anode, the short circuit occurred after ca. 400 cycles. In contrast, lithiated Si-S@pPAN cell can stably cycle at least for 1000 times.

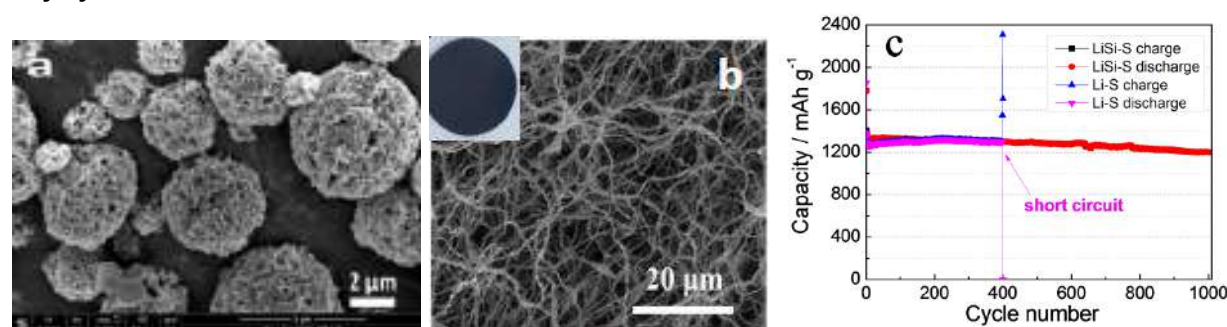


Figure 1. SEM photographs of porous Si/CNT/C spheres (a) and Si/C fibers film (b); Charge and discharge cycle performance of in-situ lithiated Si/C film (or Li)-S@pPAN cell with 1 M LiPF₆-EC-DMC-FEC (45: 45: 10, v/v)

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Sol-gel chemistry for carbon dots, making of fluorescent new generation hybrids

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Abstract: Carbon dots are an emerging class of carbon-based nanostructures produced by low-cost raw materials which exhibit a widely-tunable photoluminescence and a high quantum yield [1]. The potential of these nanomaterials as a substitute of semiconductor quantum dots in optoelectronics and biomedicine is very high, however, they need a customized chemistry to be integrated into host-guest systems [2] or functionalized in core-shell structures [3]. The surface modification, the fine tailoring of the chemical composition and the embedding into a complex nanostructured material are the main targets of combining sol-gel processing with C-dots chemistry. In addition, the synergistic effect of the sol-gel precursor combined with the C-dots contributes to modify the intrinsic chemo-physical properties of the dots, empowering the emission efficiency or enabling the tuning of the photoluminescence over a wide range of the visible spectrum [4]. Some examples of integration and application of carbon-dots into host-guest systems and future challenges of these nanocomposites will be shown.

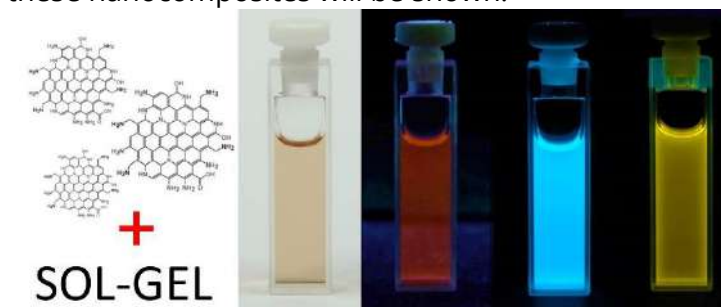


Figure 1.

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Novel sol-gel derived bioinks for 3D bioprinting

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Abstract: Introduction

Combination of bottom-up 'soft-chemistry' sol-gel processing (1) and top-down manufacturing processes (2) have allowed the synthesis of complex structures for biomedical applications. One of the potential barriers to future developments in biofabrication is the limited choice of suitable materials. At present, hydrogels from natural biopolymers are mainly used for 3D biofabrication. These have several limitations, such as batch-to-batch variation, low shape fidelity, limited post-printing strength (3) and uncontrolled degradation. Promising synthetic alternatives are advanced organic-inorganic hybrid materials developed using the sol-gel process. (4,5) This work presents the development of novel sol-gel derived bioinks for the 3D biofabrication of tissue constructs.

Methods

Polyol-modified silanes (PMS) and biopolymers (chitosan and alginate) were reacted to produce organico-inorganic hybrid hydrogels. Briefly, biopolymer dissolved in aqueous media was functionalised with an organosilane coupling agent. To this PMS was added and allowed to react. PMS undergoes hydrolysis and condensation reactions to form organic-inorganic hybrid gels with strong covalent bonding between silica and biopolymer. The structure, chemistry, physical properties as well as the biological properties of the gels were investigated.

Results and Discussion

Homogeneous gels were formed starting from solutions within few minutes to several days depending on factors such as the pH, type of buffer solution used, volume ratio of buffer:PMS and proportions of organic/inorganic. Gel formation was observed to follow the formation of stable colloids which under critical concentration assemble to form stable gels. Gels deform during extrusion printing to produce 3D scaffolds.

Conclusions

This study presents a bottom-up approach to produce bioinks that could be used in biofabrication of tissues and constructs for applications in regenerative medicine. The materials produced promises to be a better alternative to biopolymers which have several drawbacks.

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An hybrid organic-inorganic platform for detection of pesticides in liquid through Raman spectroscopy

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Abstract: We have developed a sensing platform based on a molecularly-imprinted organic-inorganic porous film containing graphene (Figure 1). The platform is capable of enhancing the Raman spectrum of analytes dissolved in water through a combined effect of molecular recognition, due to the imprinted cavities, and graphene-enhanced Raman scattering (GERS), provided by the few-layer graphene embedded in the matrix [1]. A selective platform targeted on paraoxon, a pesticide belonging to the class of highly toxic organic pollutants, has been designed and tested on water samples. A porous hybrid organic-inorganic film, synthesized using tetraethoxysilane, 1,8-bis(triethoxysilyl) octane and cetyltrimethylammonium bromide, has been molecularly imprinted with a structural analog of paraoxon, the diethyl(4-nitrobenzyl) phosphonate, to induce a selective recognition. In addition, exfoliated graphene has been incorporated into the matrix, to provide enhancement of the Raman scattering signal. The Raman sensor has been tested on different concentrations of paraoxon in both ethanol and water/ethanol mixture. The molecular selectivity has been assessed by comparing the Raman spectra of the paraoxon and a similar organophosphate, the bis-(4-nitrophenyl) phosphate. The molecularly imprinted films show a fourfold increase of the paraoxon signal when compared with the corresponding not-imprinted. A further improvement of the sensing technique has been provided by decorating the graphene oxide layers with Ag nanoparticles [3]. These nanocomposites, when incorporated into a molecularly imprinted porous matrix, show a remarkable Raman scattering enhancement and an excellent selectivity towards the targeted analytes with respect to interferents [4]. The material design has allowed coupling the sensitivity of GERS with the selectivity of molecular imprinting into a single, and potentially portable, analytical system.

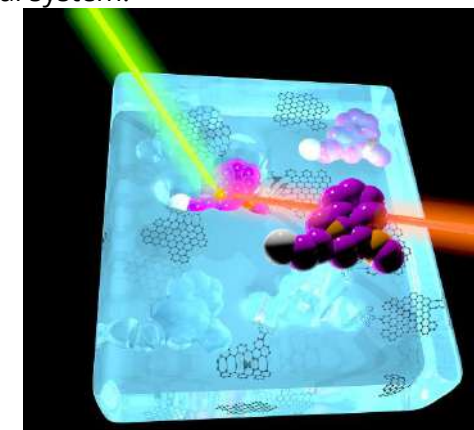


Figure 1. Analyte detection through Molecularly-Imprinted Graphene Enhanced Raman Scattering.

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Sol Gel Nanomaterials and their Applications: Challenges, Opportunities and Risks

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Abstract: Due to the increased specific area - to - volume ratio (S/V), sol-gel nanomaterials may have different and in many cases better chemical and physical characteristics than bulk materials. Many of these properties can be improved by surface modification and functionalization of nanomaterials, which can be done by altering their functionality and characteristics of their surfaces, such as roughness, hydrophilicity/hydrophobicity, surface charge, biocompatibility, and reactivity. Almost all types of materials, including metals, ceramics, polymers, silanes, and composites can be used for coating the surface of nanoparticles, to tune their properties.

In this way, the functionality of nanomaterials can be adapted to the desired application. Due to the extremely fascinating and useful chemical and physical properties, nanomaterials exhibit an interest in many fields of applications such as biomedicine and biotechnology, environmental protection, photonics and sensor technology, production of paints and varnishes, textiles, footwear, packaging, electronics, aerospace and automotive, etc. Until today, nanotechnology has already contributed to the number of innovative products in various engineering disciplines. In the European market, many products containing nanomaterials, e.g., batteries, coatings, antibacterial textiles, cosmetics, food products, are already present.

Although nanomaterials, on the one hand, offer technical and commercial opportunities and challenges, on the other hand, they can pose a risk to the environment and raise concerns about the health and safety of humans and animals, as regulation of nanomaterials is debated and many questions related to the risks of exposure to nanomaterials are still unanswered.

This lecture will introduce some recent examples from our Research Group demonstrating the use and challenges that may be tackled by functional nanomaterials, and some risks will be briefly mentioned:

(a) In the "Environment" for detection and removal of organic pollutants (oils), toxic chemical, and biochemical components.

Recent advances in the design of superparamagnetic iron-oxide adsorbent nanomaterials for the removal of oil-spills and toxic heavy metal ions (e.g., Hg, Pb, Cd, Zn) from water, will be highlighted. Special attention will be focused on the surface functionalization of nanomaterials according to Pearson's acid-base concept and adsorption characteristics (adsorption capacity, adsorption effectiveness, kinetics, thermodynamics, etc). Another topic of focus will be surface functionalized and mesoporous silica (SiO₂) nanomaterials also specifically designed for adsorption applications. [1, 2, 3]

(b) In the "Safety and protection" as an optical chemical sensors for food quality control, detection and protection against UV radiation, and toxic organophosphates.

Optical chemical sensors based on mesoporous silica (SiO₂) and titania (TiO₂) nanomaterial became very widespread in the last decades and rely on the use of "sol-gel" materials, which include e.g. indicators, dyes and other additives.

Our group recently developed a variety of novel "sol-gel" materials in the form of spherical nanoparticles and thin films containing specific dyes which enable more reliable sensing of important parameters such as oxygen, temperature, pH, etc., which will be presented together with the sensing requirements of sensitivity, selectivity, stability, etc. [4, 5]

(c) In the "Health" as an optical chemical sensors for the detection of disease states in-vitro and in-vivo, as well as superparamagnetic hollow spherical nanostructures for drug delivery, as an antimicrobial nanomaterials, etc.

In the last two decades, substantial progress has been made in biomedical applications, in the development and functionalization of superparamagnetic iron-oxide nanoparticles. Due to the simplicity in their use and the ease in their manipulation, functionalized superparamagnetic nanoparticles have been shown as the appropriate in drug and gene delivery, immobilization of biomolecules, cell purification/separation, hyperthermia, etc. Hollow-type nanostructures of superparamagnetic iron-oxide shell containing antitumor therapeutic drug "doxorubicine" (DOX) in the cavity, were prepared by using new modified hard-template method where mesoporous SiO₂ particles served as the templates. This new method of preparing hollow spheres was patent protected granted by the Intellectual Property Office, London. [6]

Furthermore, mesoporous silica (SiO₂) nanoparticles have attracted much attention the last decade in nanomedicine applications due to their biocompatibility, flexible functionalization, tunable pore size and diameter. In addition to the fine control of their size, shape, and pore structures, incorporation of drugs, dyes or indicators is important for their therapeutic applications. Our recent results on the synthesis and functionalization of various types of superparamagnetic nanoparticles ("core-shell") and mesoporous silica nanoparticles having different pore sizes, containing therapeutic agents and dyes, will be presented. We will also briefly present some research done on antimicrobial Ag nanomaterials and their applications.

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Liquid phase fabrication of multiferroic nanocomposite films

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Abstract: Nanocomposite films of ferroelectric BaTiO₃ (BTO) and ferrimagnetic CoFe₂O₄ (CFO) were fabricated using a variety kinds of liquid phase processes, such as sol-gel, anodization, hydrothermal, coprecipitation, and electric-assisted magnetophoretic deposition. Figure 1 shows the scanning electron microscope (SEM) images of an example of the prepared samples. For the fabrication of the nanocomposite film, TiO₂ nanotube arrays (TNTs) were first formed by anodization of a Ti sheet (A, B). Then TNTs were hydrothermally treated in a Ba-containing solution to convert TiO₂ to BTO without collapsing the nanotube array structure (C, D). The obtained BTO nanotube arrays (NTs) were finally spin-coated with a CFO solution (E, F). The microstructure of the nanocomposite film was further analysed using 3-dimensional (3-D) SEM technique, in which a series of cross-sectional images of the sample were taken with a focused ion beam-equipped SEM, followed by reconstruction of the 3-D image. The results revealed that 79, 16, and 5% (in volume fraction) of the nanocomposite were composed of BTO, CFO, and void, respectively. The magneto-electric (ME) effect was evaluated by measuring dielectric property of the nanocomposite in an external magnetic field, and as a result, a relatively large ME effect was confirmed. This is because the nanotube array-based structure suppresses a clamping effect from the substrate and provides a large interface area between BTO and CFO.

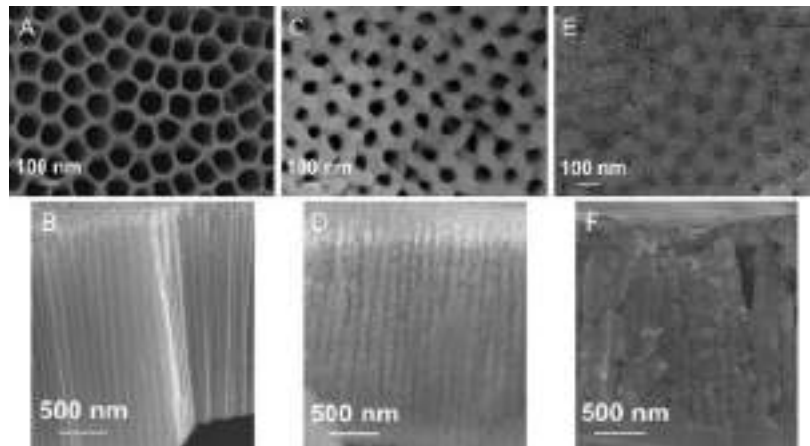


Figure 1. SEM images of TNTs (A, B), BTO NTs (C, D), and BTO-CFO nanocomposite (E, F).

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Coupling pH-regulated multilayers with inorganic surface for bionic devices and infochemistry

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Abstract: We describe how the research moved from light regulated feedback sustainable systems and control biodevices to the current focus on infochemistry in aqueous solution [1]. A major part of the work focuses on the generation and use of localized ion concentration gradient. In situ scanning vibration electrode (SVET) and scanning ion-selective electrode techniques (SIET) are efficient for spatiotemporal evolution of ions on the surface. pH-sensitive polyelectrolytes (PEs) multilayers with different PEs architecture are composed with a feedback loop for bionic devices [2]. We show here that pH-regulated PEs multilayers can change their properties—film thickness and stiffness, permeability, hydrophilicity, and / or fluorescence—in response to light, electrochemical or biological processes instead of the classical acid/base titration. Example of logic operation are shown in Fig. 1a-c. Such operation and feedback processes were regulated on (photo-) electrodes, e.g. as shown in Fig. 1d, and studied by SVET (Fig. 1e). It is attractive to regulate the level of gradient over the surface by using reliable methods for surface nanoengineering, PEs deposition. In Fig. 1f-h it is shown that SVET can easily distinguish pristine Pt surface, Pt covered with polyethylenimine (PEI) and bilayer of PEI and poly(sodium styrene sulfonate) (PSS).

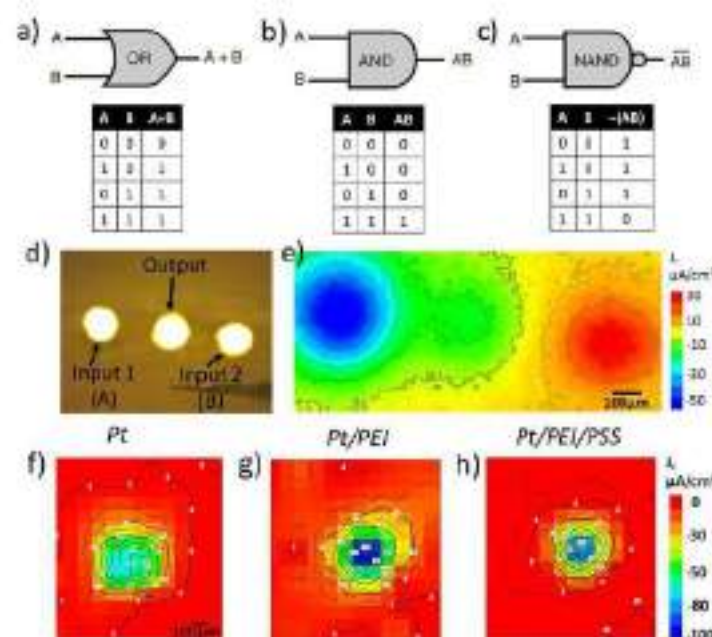


Figure 1. a-c) Basic logic gates and corresponding truth tables: a) OR gate, b) AND gate, c) NAND gate, d) system of three noble metal electrodes embedded in epoxy holder as a prototype of chemical computing iontronic device, e-f) ion currents mapped by SVET in solution: e) ion currents mapped by SVET in solution when positive and negative potentials applied to input electrodes from (d), f-h) ion currents mapped by SVET in solution over electrode under negative potential bias: f) bare Pt electrode, g) Pt/PEI electrode and h) Pt/PEI/PSS electrode. Adapted from [1].

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Acknowledgements

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From Academic Work to a Sol-Gel Company and Innovative Drug Candidates

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Abstract: Sol-Gel Technologies (NASDAQ: SLGL) is a clinical-stage dermatology company focused on identifying, developing and commercializing branded and generic topical drug products for the treatment of skin diseases. Sol-Gel's current product candidate pipeline consists of late-stage branded product candidates that leverage a proprietary, silica-based sol-gel microencapsulation technology platform, and several generic product candidates for multiple indications. I will share my experience in establishing a company around innovative sol-gel chemistry, the invention of sol-gel encapsulated UV filters and the pitfalls in turning this invention into a commercial product ("UV-Pearls"), the decision to switch to dermatology and the implementation of sol-gel chemistry for drug products, our varied business opportunities, clinical trial results of drugs based on sol-gel delivery systems and our future plans and vision.

Titania Gels for Cell Encapsulation

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Abstract: Single-cell nanoencapsulation has recently emerged as a simple but versatile strategy for effectively preserving and protecting living cells from harmful stresses, such as UV irradiation, pH, heat, centrifugation, and enzymatic attack [1]. Although successful in cell protection, most encapsulation methods mask the cell surfaces physically and preclude the juxtacrine interactions, including the antigen-receptor interactions on cell surfaces. To tackle this problem in the cell encapsulation, the formation of titania (TiO_2) gel has been applied to Jurkat cells, as a model for primary immune cells [2]. A durable titania shell increases the cell viability under serum-free conditions and heat, and, more importantly, the CD3 and other antigens on cell surfaces remain accessible to the antibodies after encapsulation. In addition, interleukin-2 secretion is not hampered by the titania shell formation. Other advantages of the titania shell include the breakability under culture conditions, suggesting the potential in cell therapy.

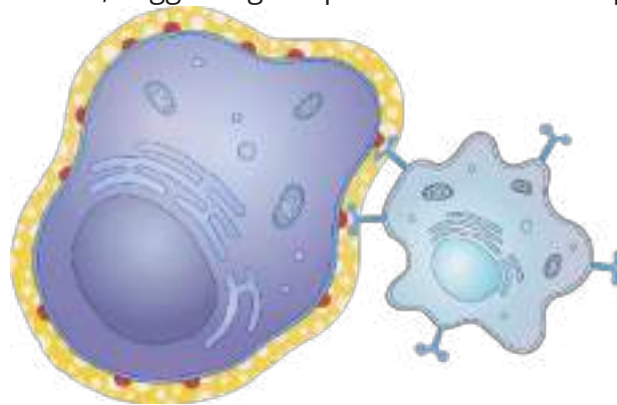


Figure 1. Cytoprotective titania shell with maintenance of juxtacrine interactions.

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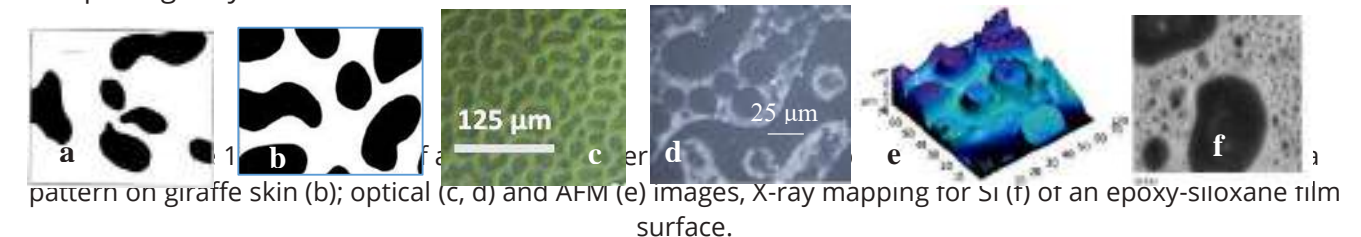
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Fractals, morphogenesis and triply periodic minimal surfaces in sol-gel-derived thin films

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Abstract: Unordered aggregation systems, including sol-gel systems, as a rule have a fractal structure. They are characterized by self-organization and hierarchical structure. The notion about morphogenesis is more often used to describe biological systems. However, the term 'morphogen', invented by A. Turing for biological systems, originally assumed the chemical mechanism of the reactions of the initial components [1]. A. Turing supposed that the shape (morphology) is determined by a certain structure, which is formed due to nonhomogeneous distribution of the concentration of chemicals, which he called 'morphogens'. Precursors of sol-gel synthesis can be called 'morphogens'. In solutions of hydrolyzable compounds (precursors), aggregation structures are formed more and more intensively as they age. These phenomena are also akin to phase separation and microsegregation in glasses. As the sols aging, the pH of the medium and other parameters can change in an oscillatory regime, in which the reaction conditions change periodically, forming a complex space-time structure of the reaction medium. One can talk about the class of chemical reactions of Belousov-Zhabotinsky. The homogeneity in the concentration distribution of the components is disturbed at spin-on coating under the influence of centrifugal force, at dip-coating processes as well as with changes in temperature, humidity, and other factors. This is typically for TEOS-derived sols containing inorganic dopants or organic modifiers [2, 3]. As a result, interpenetrating phases differing in the concentration of the dopant or modifiers are formed in the films. Thus, Turing patterns can be formed not only in emulsions and in biological objects, but also in sol-gel-derived thin films (Fig. 1). The Turing pattern, according to his model [1], patterns on the giraffe's skin [4] and the surface morphology of the sol-gel-derived films [3], are very similar morphologically.



Moreover, the morphology of some thin films suggests a morphological similarity with the structures of triply periodic minimal surfaces. This phenomenon also is extremely important for the production of advanced materials [5].

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ABSTRACTS OF SCIENCE SLAM SPEAKERS

Two-photon microfabrication processes for highresolution 3D printing of hybrids and ceramics

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Abstract: The rapid fabrication of microstructured and nanostructured objects in 3D is in full development and has many interests, especially for the structuring of surfaces. The two-photon microfabrication allows producing high-resolution 3D objects by using the two photon optical process. This method permits a localized control of the photoreactions in the focal point region of the laser. During the last decades, this technique has been used to produce polymer-based structures via photopolymerization. Micro and nanoceramics have been obtained by photopolymerization of resin containing silica precursor (ormocer) followed by removing of the organic part, or by preparing 3D polymer scaffold followed by traditional techniques of mask deposition. To bring new optical properties to the material, transition metals such as zirconium or titanium can be added into these systems.

Recently, the two-photon absorption has been used to control the condensation step of the sol-gel process, allowing thus producing direct silica-based structures [1]. In this new approach, the condensation step is induced via a change of pH possible thanks to a photobase. This molecule rejects a hydroxide when excited, provoking the local condensation and finally the formation of the material. Different systems containing silicium, titanium or zirconium have been considered for this process. This local pH change is also an interesting route to form materials from destabilization of colloids. Indeed, the gelation of colloids is an expanding domain and permits to obtain bulk material from nanoparticles solutions [2-6]. Applying this technique to the two-photon microfabrication allows producing directly high resolution 3D structured ceramics at the nanoscale, without the requirement of pyrolysis.

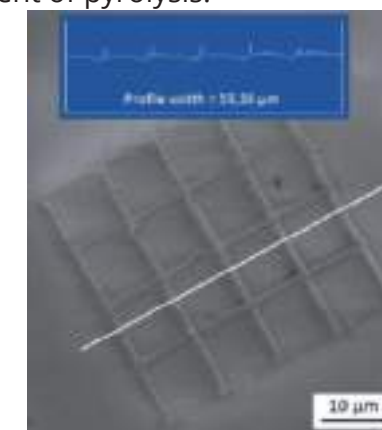


Figure 1. Example of a structure obtained by sol-gel microfabrication.

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Entrapment of Enzymes in Silica Aerogels

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Abstract: Aerogels, the world's lightest solids, possess extraordinary traits. They have immense surface area, high porosity and ultra-low heat conductivity. These traits made aerogels favorable in various fields, from aerospace to building insulation. Nonetheless, the use of pure silica aerogels for the entrapment of enzymes is not known. While enzyme entrapment helps stabilize the enzymes and aids in separation of the catalyst from the reaction pot, the kinetics are usually impaired, as diffusional limitations of the substrate and product arise. When considering aerogels as potential enzyme carriers, their highly porous structure may help facilitate the diffusion of substrates to the embedded enzyme. And yet, reports of enzyme entrapment in aerogels are restricted to lipases only, and even those are in hydrophobically modified silica. The reason for this is probably because of the harsh synthesis procedure of aerogels that only robust enzymes as lipases can withstand. There is a need of a bio-friendly synthesis route for the entrapment of more sensitive enzymes in aerogel. In this work, we present a generalized procedure for the entrapment of enzymes in silica aerogel. All aerogel synthesis steps were modified and optimized, for reducing the risk of enzyme denaturation. The entrapment of three different types of enzymes was demonstrated: glucose oxidase, acid phosphatase and xylanase. All three aerogel-entrapped enzymes showed superior activity over the standard method of sol-gel entrapment in xerogel. Michaelis-Menten kinetics was observed for all three entrapped enzymes, indicating that the enzymes are highly accessible and diffusional limitations are negligible. A key observation is that the Michaelis-Menten constant, K_m , has remained at the same level or even decreased upon entrapment, indicating that enzyme-substrate affinity was not negatively affected. Thermal stabilization was observed in the case of acid phosphatase with the entrapped enzyme reaching peak activity at 70°C. Aerogel enzymes entrapment might be especially attractive for health applications and for catalyzing biotechnological processes, even of large substrate molecules.

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Strong and thermal insulating chitosan-urea aerogels: towards ambient pressure drying of biopolymer aerogels

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Abstract: Biopolymer aerogels are an emerging class of materials with potential applications in drug delivery, thermal insulation, separation and filtration. Chitosan is of particular interest as a sustainable, biocompatible and abundant raw material. Our focus is to produce sustainable chitosan aerogels by supercritical, and if possible, ambient pressure drying. Here we present urea-crosslinked chitosan aerogels with high surface area and excellent thermal and mechanical properties. Chitosan is dissolved in an acidic, aqueous solution of urea and gelation is triggered through the thermal decomposition of urea at 80°C, which induces gelation because of the increase in pH and the formation of urea crosslinks between the chitosan molecules. The gels are dried with both supercritical and ambient pressure techniques to determine the influence of the drying process on the final aerogel properties. The formation mechanism of the gels is monitored by NMR, FTIR, DLS, DSC and SEM, and the aerogels are characterized in terms of shrinkage, density, thermal conductivity, surface area and compression stress. Surprisingly, large monolithic aerogel plates (10x10 cm²) can be produced by ambient pressure drying, albeit at a somewhat higher density. Currently, we are able to produce aerogels with thermal conductivities of <25 and around 36 mW/(m·K) for supercritical and ambient pressure drying, respectively. The urea-crosslinked aerogels display superior mechanical properties compared to traditional biopolymer aerogels: no brittle rupture up to at least 80% strain, and depending on chitosan concentration, they feature relatively high E moduli (1.3 to 9.5 MPa) and final compressive strengths (4.5 to 20 MPa). Our study opens a window for new mesoporous aerogel materials from renewable precursors, with a strong potential for reduced production costs through ambient pressure drying.



Figure 1 Ambient Pressure Dried Sample.

Sol-gel synthesis of multifunctional mesoporous silica nanocontainers with the use of hybrid micellar templates

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Abstract: Mesoporous silica nanocontainers (MSNs) are among the most promising and effective nanocarriers for targeted drug delivery because of their high specific area, ordered porous system and low toxicity. Conventional route of the MSNs' creating implies a sol-gel synthesis with the use of *inert* surfactant micelles as a template. After the synthesis is completed inert template is eliminated from the particles and then obtained MSNs are loaded with targeted drug by its sorption from the solution. However the amount of drug taken up by the MSNs is rather low and the process of drug release is hardly controlled. A new strategy for the synthesis of MSNs based on the using of targeted drug micelles instead of inert ones allows overcoming these drawbacks [1]. Moreover it paves the way for creating multifunctional MSNs loaded with two bioactive compounds. Such opportunity is studied and discussed in the contribution.

To this end water insoluble anti-inflammatory natural substance curcumin is solubilized in the micelles of amphiphilic antimicrobial drugs. The solubilization isotherms are obtained (Fig. 1) and the thermodynamic parameters such as solubilization capacity of the micelles, binding and distribution constants and free solubilization energy are calculated. It is shown that the solubility of curcumin in the micellar solutions is approximately 80 times higher than in water.

For the first time multifunctional MSNs are synthesized using hybrid template comprising of antimicrobial drug micelles with solubilized curcumin. The obtained MSNs are of ellipsoidal shape and hexagonally ordered porous system (Fig. 2). They are characterized by the high amount of the both encapsulated drugs and are pH-sensitive. The kinetics of the curcumin and amphiphilic drug release from the MSNs into the aqueous medium with different pH-values is investigated.

In our opinion such MSNs could be applied as new effective medicinal forms of curcumin providing its high bioavailability, targeted delivery and controlled release.

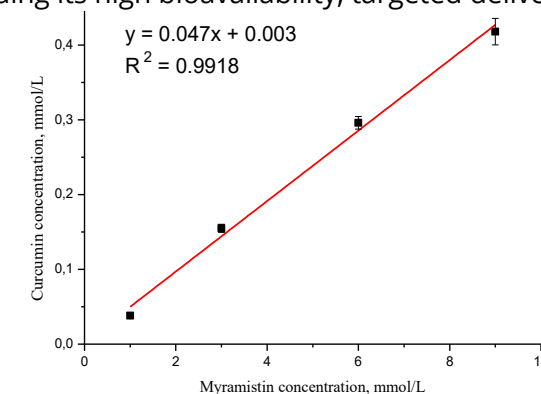


Figure 1. Isotherm of curcumin solubilization in the micelles of amphiphilic drug myramistin.

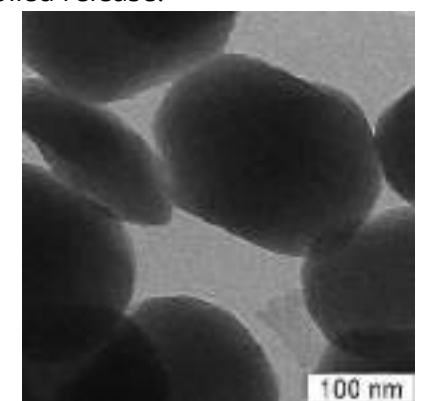


Figure 2. Micrograph of the MSNs.

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Silica-organic composite aerogels and their pyrolyzed carbon-silica counterparts

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Abstract: The aim of composites is to combine two material systems in a synergistic way. Ideally, positive properties of each material are potentiated so that the result combines the best of both worlds. With this in mind silica-organic aerogels and their pyrolyzed silicacarbon counterparts were investigated with the goal of improving thermal transport and sorption properties. Two of the key foreseeable applications are high performance insulation and adsorption heat pumps driven by low-grade waste heat. Pure silica aerogels[1] are amongst the best insulating materials under ambient conditions, however they are lacking the ability to block radiative heat transfer which is essential for higher temperature operation. Graphitic or amorphous carbon, on the other hand, is an excellent IR absorber and thus blocks radiative heat transfer effectively. A silica / carbonaceous composite is therefore expected to perform very well as an insulator at intermediate temperatures (200-400 °C). On the other side of the spectrum, monolithic nitrogen-doped carbon xerogels with embedded hydrophilic silica domains are known to display a unique water sorption behavior, while at the same time keeping a reasonably high thermal conductivity and mass transport properties. This makes them interesting candidates for thermally driven water sorption heat pumps[2]. Here, we will present an experimental study of silica/resin and silica /carbon composite materials based on the co-gelation of a resorcinol-melamine-formaldehyde resin[3] with a pre-hydrolyzed TEOS sol. The tailorability and final properties of the resulting materials will be discussed, focusing on the most promising candidates for the different aforementioned target applications.

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Osteoconductive 45S5 Bioglass coatings based on novel and nitrate-free sol-gel system for applications as bone prosthetics

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Abstract: Bioactive glasses, and in particular Bioglass® 45S5 (composition $45\text{SiO}_2\text{--}24.5\text{Na}_2\text{O--}24.5\text{CaO--}6\text{P}_2\text{O}_5$ (wt%)), are interesting materials for bone tissue engineering applications as they enhance osteoblast adhesion, differentiation of progenitor and mesenchymal stem cells and they can improve revascularization^[1]. Coating a titanium alloy with 45S5 is thus of interest to provide prosthetic material with bioactivity and as a result improve the bone bonding ability at the implantation site.

Only sparse studies have been reported on the deposition of sol-gel based 45S5 coatings and commonly used nitrate precursors cause sodium nitrate crystallization^[2], resulting in a loss of sodium in the glass network. Nitrates also need to be eliminated at high temperature as present strong toxicity to the cells. However, investigation of glass network homogeneity is severely lacking.

In this context, a new nitrate-free system has been developed and crack-free spin-coated coatings have been obtained for both as-deposited and thermally treated materials. Their elemental homogeneity is remarkably improved though the use of acetate precursors. Different phases have been obtained after glass heat treatment. Structural and chemical characterizations of each phase will be presented. Also, to conclude on the relevance of such materials for prosthetic implants, effects of the coated titanium substrates on biological and osteoconductive properties will be exposed.

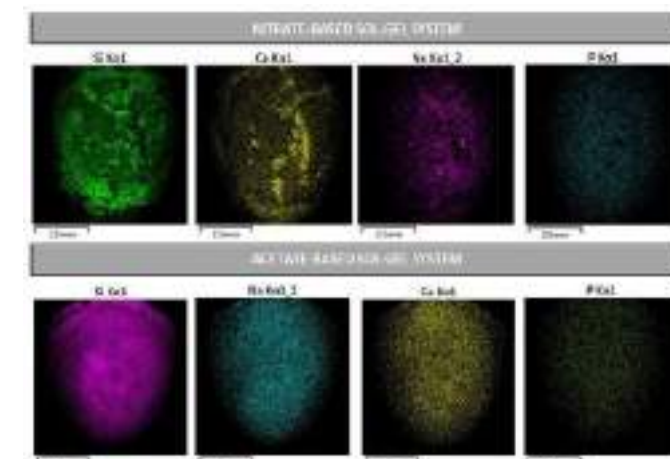


Figure 1. EDX analysis demonstrating the improved glass homogeneity of as-deposited 45S5 coatings through the use of acetate instead of commonly used nitrate precursors

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Doped LSCF as a stable electrode for solid oxide fuel cells

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Abstract: Solid oxide fuel cells (SOFCs) are a promising next generation system to produce energy without greenhouse gas emissions. To increase their efficiency, a particular attention must be paid on the development of cathode materials. Lanthanum strontium cobalt ferrite, $\text{La}_x\text{Sr}_{1-x}\text{Co}_y\text{Fe}_{1-y}\text{O}_{3\delta}$ (LSCF) is one of the most developed cathodes used in the high temperature solid oxide fuel cells. It exhibits high catalytic activity as well as good mixed electronic-ionic conductivities [1,2]. One of the critical issue for the practical application of LSCF cathodes is its performance degradation due to the Sr segregation and migration at the electrode/electrolyte interface that create resistive undesired Sr-phases [3,4]. Several doping on LSCF cathode were carried out to solve this problem and to increase its performances.

In this work, various doping (Nb, Mn, Ti, Cu...) on the B-site (Co/Fe) are proposed to reduce Sr-segregation. All compounds were prepared by sol-gel-like method, and their crystalline structures, microstructures, dielectrically properties and complex impedance were investigated systematically in order to obtain single phase compounds with the cubic structure. The results show a better stability of the cathode material after several annealing for various doping.

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The Beauty behind Hydrogen Production – Titania Nanoparticle-Based Aerogels as Photocatalysts

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Abstract: Our planet is struggling. The growing population demands an increasing amount of energy. This energy mainly originates from the consumption of fossil fuels releasing a lot of greenhouse gases, which contribute to the climate change. To solve the energy and global warming problem, new renewable energy sources need to be found and the abundantly available energy of the sun needs to be harnessed. Hydrogen is a good alternative to fossil fuels. Its production via photocatalytic methanol reforming converts solar energy into chemical energy. Unfortunately, the efficiencies of photocatalysts used for this process are still far too low for commercial applications and most of the more efficient systems reported in literature operate in liquid phase [1].

Using aerogels allows us to do photocatalysis at the gas-solid interface. Working at the gas-solid interface has some advantages compared to reactions in liquid phase: no solvent absorbs light, which would lead to a decrease in efficiency, no deposits from the liquid contributes to the deactivation of the photocatalyst, and the final products do not have to be separated from a liquid medium. Using aerogels with their large surface areas and high open porosity greatly increases the interaction between gas and photocatalyst compared to powders and thin films [2,3].

TiO_2 is the most reliable photocatalytic material due to its stability, non-toxicity, and low cost. However, the fast electron-hole recombination and the photocatalytic activity only in the UV range prevent hydrogen production rates of more than some micromole per gram of photocatalyst and hour of illumination ($\mu\text{mol g}^{-1} \text{h}^{-1}$). The combination of different metallic co-catalysts with TiO_2 improves the efficiency of the hydrogen production process. The metal nanoparticles trap the photocatalytically-generated electrons and, therefore, provide a spatial separation for the charge carriers and prevent their recombination [1].

Here, we report the synthesis of TiO_2 nanoparticle-based aerogels containing metal co-catalyst nanoparticles. The aerogels are fully crystalline monoliths of macroscopic size. They were produced by controlled destabilization of the corresponding nanoparticle dispersions within a 3D-printed polymer scaffold. The scaffold increases the otherwise very low mechanical stability of the aerogels. TiO_2 and metal nanoparticles were prepared by liquid phase routes in organic solvents. By fabricating our aerogels with a bottom-up approach from pre-synthesized nanoparticles as building blocks, we can easily combine different materials and nanostructures within one monolith (Figure 1). The incorporation of metal co-catalysts like Pd, Cu, and PdCu alloy nanoparticles into the TiO_2 aerogels results in a significant improvement of the photocatalytic activity. More than 200 times higher hydrogen production rates could be measured in the TiO_2 -Pd system (with a maximum rate of $1035 \mu\text{mol g}^{-1} \text{h}^{-1}$) compared to the co-catalyst-free TiO_2 system.

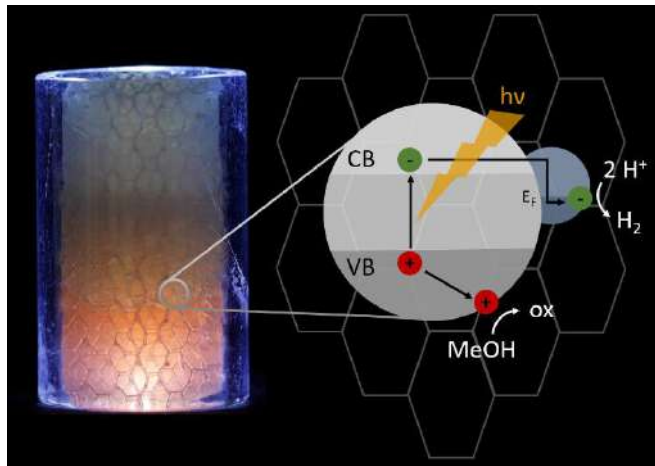


Figure 1. A TiO_2 nanoparticle-based aerogel containing metal nanoparticle co-catalysts and the scheme of the photoexcitation process displaying the simplified reaction mechanism of methanol (MeOH) reforming resulting in the generation of hydrogen and different oxidation products (ox).

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ABSTRACTS OF POSTERS SPEAKERS

Sol-Gel Synthesis of Non-Siliceous Glasses and Structural Characterization by Solid State NMR

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Abstract: Sol-gel glasses are an attractive area for both fundamental and applied research owing to their potential and actual use as catalysts, bioactive materials, photonic devices, and solid electrolytes. As some of these applications cannot be realized with glasses prepared by traditional melt-cooling, a fundamental understanding of structure-property relations in this research field is an important research objective. Nuclear magnetic resonance (NMR) spectroscopy offers an element-selective, inherently quantitative and experimentally very flexible approach for the structural elucidation of non-crystalline materials. While magic-angle spinning NMR is very suitable for characterizing short-range order in these glasses, advanced dipolar NMR experiments such as Rotational Echo Double Resonance (REDOR) methodology offers quantitative insights into the intermediate range order in these systems at the sub-nanometer scale. Examples to be discussed include numerous mixed network former glasses containing Al_2O_3 , B_2O_3 , and P_2O_5 , for which aluminium lactate is found to be a very suitable precursor. By monitoring the structural evolution occurring during the sol->gel->glass transformations NMR can also yield important mechanistic information, which is useful for optimizing the synthesis parameters. In addition, detailed structural studies as a function of glass composition reveal the underlying principles of glass formation in these systems.

Support by the Deutsche Forschungsgemeinschaft and FAPESP 2013/07793-6 (São Paulo, Brazil) is most gratefully appreciated

Metformin-Functionalized Mesoporous SBA-15 Nanocomposite as Feasible and Cost-effective Catalyst for Reduction of p-Nitrophenol to p-Aminophenol

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Abstract: Nitro-aromatic compounds are a class of aquatic contaminants that create hazards to the environment. 4-Nitrophenol, used for industrial purposes such as manufacture of pesticides, causes many problems to humans upon inhalation or ingestion that there have been many efforts to reduce its harmful effects. Ordered mesoporous silica nanomaterials (MSNs) feature a number of important characteristics which enable the feasibility of selective functionalizations on their exterior and interior surfaces, making them applicable in sorption, separation, sensing, drug delivery, and catalysis. The present work was aimed to synthesize an organic-inorganic hybrid material with catalytic properties, containing Metformin immobilized onto the surface of mesoporous silica (SBA-15) through covalent attachments. The structural and surface characteristics of the hybrid material were investigated by various techniques; SEM, FTIR, XRD and BET-surface analysis. In order to reduce nitro-aromatic compounds to less harmful amines, the SBA-15/metformin hybrid was used as a catalyst in the reductive removal of 4-nitrophenol in aqueous solutions. The reduction process was monitored by using UV-visible absorption spectroscopy. The results showed that the SBA-15/metformin hybrid material exhibited an excellent catalytic activity towards the reduction reaction, and the entire reaction was complete within a few minutes at room temperature.

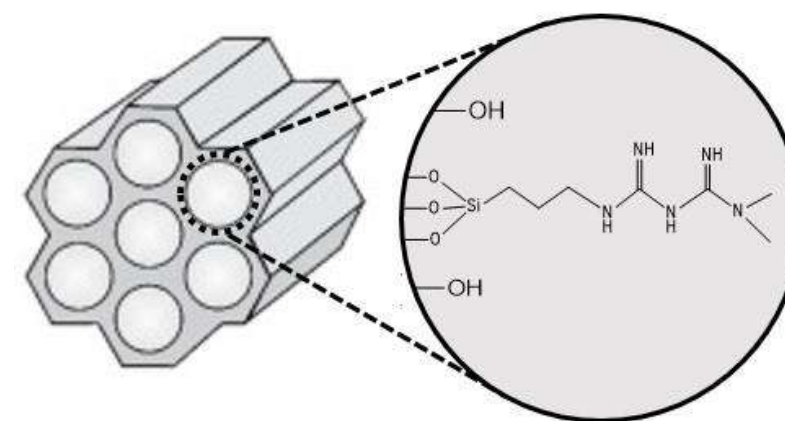


Figure 1. Schematic of SBA-15/Met.

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Sol-gel synthesis and characterization of the iron oxides magnetic nanoparticles for various applications

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Abstract: Magnetic nanoparticles of iron oxides (magnetite, maghemite) are currently in great demand in medical technology, electronic engineering and agriculture. In particular, they are promising material as a black pigment for electronic ink in the electrophoretic displays. In regard to the electrophoretic displays, the magnetite particles must meet the following requirements: the particle size must fit the nanometer range, the particle size distribution must be narrow, they must have spherical shape and a smooth surface. In addition, the particles must form stable suspensions in non-polar solvents. In recent years, the prospects for the use of nanoparticles, including magnetic iron oxides, in agriculture have been actively explored, but the requirements for their properties are not well understood yet.

The purpose of the present study is to synthesize nanosized particles of magnetite and maghemite and to modify their surface with oleic acid ($C_{17}H_{33}COOH$) and silicon dioxide to improve suspension stability in various solvents and biocompatibility with plants. The synthesis of core-shell particles $Fe_3O_4@C_{17}H_{33}COOH$, $Fe_3O_4@SiO_2$, $Fe_3O_4@γ-Fe_2O_3$, $γ-Fe_2O_3@C_{17}H_{33}COOH$, and $γ-Fe_2O_3@SiO_2$ will be carried out. The structure and properties of the obtained composite particles will be analyzed using various methods such as X-ray diffraction, SEM, low-temperature nitrogen adsorption, DLS and IR. Stable suspensions for the use in the electronic ink and agrotechnologies will be obtained with the use of the abovementioned composites. Electrophoretic activity data and effect of these particles on the seed germinations will be reported.

The sound of silica: ultrasonic monitoring of silica sol-gel materials for tamper indicating purposes

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Abstract: The development of ultrasonic monitoring techniques for use with silica sol-gel materials for the purpose of tamper indication presents a novel set of challenges. Tamper indication is an approach that can be adopted to monitor the containment or boundary of an item or area of interest, and in the field of nuclear arms control verification, this could include facilities, verification equipment or nuclear weapons.

Due to the responsive reaction of silica sol-gel to environmental change, it can be used as a visual indicator of tampering. Ultrasonics has been used within the field of structural health monitoring (SHM) due to its high sensitivity and non-destructive nature. The combination of these techniques has not been fully explored, so the aim of this project is to develop a highly effective and accurate interdisciplinary method of tamper indication. Metastable sol-gel formulations will show shrinking and fracturing upon solvent evaporation, but critically ultrasonics will provide continuous monitoring of the sol-gel material during the storage of dismantled equipment allowing invisible changes arising from tamper attempts to be identified.

This poster provides an overview of the capabilities of using ultrasonics to monitor the degradation of sol-gel formulations during simulation of a tamper, and other physiochemical techniques used to corroborate the data obtained.

The behaviour of $\text{ZrO}_2\text{-Y}_2\text{O}_3$ coatings deposited on 316L steel in the SBF

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Abstract: Metallic biomaterials are widely used as implants and materials for the reconstruction and regeneration of tissues and bones. About 3/4 of implants are made of metals thanks to their excellent mechanical properties and good biocompatibility [1]. On the other hand, they have insufficient corrosion resistance in the environment of body fluids, which leads to the release of metal ions harmful to the body. This leads to the mechanical weakening of the implant and at the same time to inflammatory changes in the living body [2]. In order to improve the properties of metals, protective and bioactive layers are usually applied on implants. In most cases, ceramic materials such as silicon oxide, zirconium, aluminum, hydroxyapatite and many other materials are used as coatings for implants, which improves implant properties [3]. Since the composition of ceramic materials is very similar to that of human bones they are more readily acceptable by the living body than metals. Ceramic materials do not undergo corrosion in body fluids and owing to the possible formation of apatite ceramic on their surface improve adhesion between the tissue and the implant.

The $\text{ZrO}_2\text{-Y}_2\text{O}_3$ layers were applied to 316L steel. The application of the layers was based on the sol-gel technique. The coating solutions were obtained from zirconium(IV) butoxide and yttrium(III) nitrate. As the solvent, butanol was used. Acetic acid and nitric acid were used to accelerate the reaction. Layers were applied on a dip-coater with the ascent rate: 1.7 mm/s. The samples after each applied layer were dried at 100°C. After 24 hours, they were subjected to a thermal treatment at 300°C.

Research showed that yttrium oxide additions in three-layer coatings deposited on steel 316L cause changes in the morphology and topography of the surface layer as a result of an increase in roughness. By adding the yttrium layer, the surface of the coatings is non-uniform. The surface is characterized by visible islands where yttrium accumulates. Scratch tests showed good adhesion of the layers to the metal substrate. The obtained samples show bioactive properties in the simulated body fluid environment through the growth of apatite ceramics (EDS). Samples coated with $\text{ZrO}_2\text{-Y}_2\text{O}_3$ layers increase the polarization resistance twofold during SBF exposure to the uncoated substrate in polarization tests.

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Gel materials on the basis of disperse sodium hydro silicate for carbonate and terrigene collectors conditions

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Abstract: Currently, most of the world's largest developed oil fields, in particular in the Republic of Belarus, are entering late stages of production, and their residual reserves are classified as hard-to-recover. A highly efficient method of involving such facilities with additional oil production into operation is the use of physico-chemical methods of stimulating the reservoir aimed at increasing the filtration resistance of the washed channels through their treatment with solutions of gel-forming compositions.

The aim of the research was the development of gel-forming compositions effective in technologies of enhanced oil recovery at elevated temperatures in contact with the rock of different mineralogical composition.

The compositions of gel-forming compositions obtained on the basis of an ecologically pure large-tonnage product produced – dispersed sodium hydrosilicate (GOS) were studied. The technological efficiency of the preparation of the solution of the composition in two stages is shown. The analysis of the effect of a series of organic modifiers depending on their structure and activity on the gelation processes of solutions of the compositions was carried out. The features of obtaining coagulation-stable multicomponent gel-forming compositions based on dispersed sodium hydrosilicate have been studied. The influence of the modifier structure and the concentration ratios of the components on the gelation rate of the mixtures and the physicomaterial properties of the formed gels is established. The optimization of the compositions. Experimentally substantiated the promise of using sulfamic acid as an effective GOS acid modifier, due to a set of criteria taking into account the geological features of the object of impact: obtaining a solution of a composition with low viscosity (1.15-1.30 mPa·s), selectivity of waterproofing works, high structural and mechanical characteristics (strength up to 47 kPa) and thermal stability of the gel, as well as the possibility of its destruction under certain conditions and complete removal from the reaction zone. The effect of temperature on the kinetics of the gelation process of the optimized composition, the structure and strength of the gel formed is investigated. Analyzed the physicochemical processes occurring in the system.

The peculiarities of the process of gelation of the composition in contact with the carbonate rock (limestone, dolomite) and terrigenous (has a sandy base with inclusions of quartz, feldspar and products of their chemical transformation) are studied. Samples of the composition were injected with ground rock (10 g per 10 cm³ of liquid) obtained by grinding the core and screening fractions of 0.07–0.25 mm; 0.25-0.50 mm and 1.0-2.0 mm. It has been established that, depending on the composition, the rock can be both the initiator of the gelation process and significantly reduce the gelation time. Obviously, the rock particles are active gelation centers. Analysis of the penetration curves showed practically identical structural and mechanical properties of gels formed in contact with carbonate or terrigenous rock of the same fraction. However, a decrease in the dispersion of the rock of the same mineralogical composition leads to an increase in the strength of the gels, which is caused by an increase in the area of interfacial interaction.

Thus, the developed gel-forming compositions based on modified disperse sodium hydrosilicate can be effectively used in enhanced oil recovery technologies with various mineralogical rocks to increase oil production and restrain the rate of watering of production wells.

Synthesis and structural characterization of $\text{LaSrAl}_{1-x}\text{Cu}_x\text{O}_{4-\delta}$

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Abstract: A set of novel oxygen-deficient $\text{LaSrAl}_{1-x}\text{Cu}_x\text{O}_{4-\delta}$ cuprates was synthesized for various values of x ranging from 0 to 1 using a conventional sol-gel process [1] followed by high-temperature calcination under O_2 gas flow. The structure and electrical properties of the so-obtained black powders was determined, respectively, by powder X-ray diffraction and by impedance spectroscopy. All compounds adopt the K_2NiF_4 -type tetragonal structure with space group $I4/mmm$ [2]. The observed variation of the structural and electrical properties of $\text{LaSrAl}_{1-x}\text{Cu}_x\text{O}_{4-\delta}$ with the substitution level are discussed in terms of the Jahn-Teller distortion of the $(\text{Al}/\text{Cu})\text{O}_6$ octahedra and of the mixed valence character of copper.

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Keywords: cuprates, Rietveld refinement, K_2NiF_4 -type structure

Design of anisotropic xerogels for nonlinear optical applications

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Abstract: With the democratization of the use of lasers over the years, optical power limiting materials have gained more and more interest. These materials, allowing to lower the intensity of a transmitted light beam, find applications in fields such as camera or optical sensors protection, in fields such as aeronautics or transports. To design such hybrid materials, a silica-based matrix can be synthesized and doped with high concentration of nonlinear organic chromophores, allowing the production of a solid bulk material with strong absorbing properties with ultrafast activation, high damage threshold and high photoptic transmission. The co-addition of gold nanoparticles into the hybrid system allows an enhancement of the optical responses of the chromophores, through the controlled interactions between the molecules and the metallic nanoparticles. Thus, gold nanoparticles have been successfully coupled to chromophores in hybrid silica host materials to strongly enhance their nonlinear characteristics.

However, as some gold nanoparticles own anisotropic properties, because of their shape, the interactions between the chromophores and the nanoparticles could be modified depending on their relative orientation. In this work, we have developed a host matrix to allow us to understand and control the orientation of gold nanoparticles and chromophores. This new method will make it possible for us to study the interactions of the organic molecules and nanoparticles and their impact on the optical properties of our doped silica hosts. We thus expect to have access to the relationship between the structure of these materials and their optical properties.

Effect of density on the thermal conductivity of transparent cellulose aerogels

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Abstract: Biopolymer aerogels are a potentially more sustainable alternative to classical silica aerogels. The thermal conductivity of silica aerogels displays a characteristic U-shaped dependence on density with a minimum near 0.100 g/cm³. For many polyurethane aerogels, this minimum is shifted to even higher densities. In contrast, there have been reports on pectin [1] and nanofibrillated cellulose (NFC) [2] aerogels with a minimum in thermal conductivity at much lower densities of <0.050 and 0.017 g/cm³, respectively. If confirmed, the possibility for ultra-low density and ultra-low thermal conductivity insulation would be an exciting prospect. However, a more extensive pectin aerogel study showed a typical U-shaped curve, with an optimum density of 0.100 g/cm³ similar to silica aerogel [3]. For NFC aerogels, it is difficult to directly determine the density dependence of thermal conductivity because the sol viscosity limits the maximum NFC concentration and, hence, aerogel density. Plappert et al. circumvented this problem through the irreversible compression of low-density carboxylated NFC aerogels and observed a minimum in thermal conductivity for densities around 0.087 g/cm³ [4]. However, it is not clear if these compressed aerogels are equivalent to an aerogel with the same density, but prepared from a more concentrated sol. Here, we present thermal conductivity, mechanical, electron microscopy and BET data on NFC aerogels of variable density (from 0.005 to 0.027 g/cm³). Cellulose hydrogels were prepared by acid-catalyzed gelation of tempo-oxidized NFC sols in water (0.25 to 2.0 wt. %), solvent exchange to ethanol and supercritical CO₂ drying. The final aerogels are highly transparent with surface areas in the order of 450 m²/g and a high mesoporous volume of around 2 cm³/g. As expected, the mechanical properties display a strong, power-law dependence on density with a maximum compressive strength near 1 MPa. The thermal conductivity decreases monotonically with increasing density, from 37 mW m⁻¹ K⁻¹ at 0.005 g/cm³ to 28 mW m⁻¹ K⁻¹ at 0.027 g/cm³, without a clear minimum in thermal conductivity. This monotonic decrease indicates that the gas phase conduction is reduced progressively as density increases and average pore size decreases, but is not minimized, even at the highest investigated density. We report thermal conductivity values for a given density that are lower than those reported for compressed NFC aerogels [4], but confirm that, at least for our synthesis protocol, the minimum in thermal conductivity for NFC aerogels does not occur at the ultra-low density that has been suggested in another study (0.017 g/cm³) [2].

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Novel visible light-activated hybrid titania-based materials with different morphologies for photocatalytic application

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Abstract: Titania (TiO₂) is one of the most widely used photocatalyst in light harvesting systems. Notwithstanding, due to its large band gap (3.0 - 3.2 eV), this material only harvests 5% of the solar radiation (UV). We have pioneered a new strategy for enhancing the visible-light activity of titania-based materials. This approach consists on the in-situ incorporation of the dyes into the anatase framework during their synthesis. By using this strategy, a series of visible light-activated hybrid titania nanoparticles have been produced, showing a remarkable photocatalytic activity under both UV and visible light irradiation. Recently, we integrated our hybrid titania containing the RuII N3 dye into a photoelectrode of a low-temperature dye-sensitized solar cells (It-DSSC) to obtain the highest efficiency reported so far for titania-based It-DSSCs (8.75%). In the light of these studies, we decided to extend this approach to other morphologies, also using other organic compounds. In this study, we have synthesized a series of hybrid nanorods and nanoparticles with different anatase-torutile ratio using aminoacids and phenanthroline, among others. The hybrid nanorods prepared by incorporating L-tyrosine during their synthesis, showed a photocatalytic activity much higher than both control titania and the commercial TiO₂ P25 under visible light irradiation (Fig. 1)

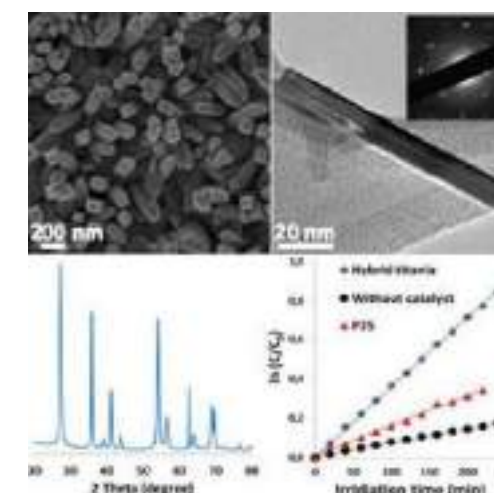


Figure 1. FE-SEM, TEM, Synchrotron X-ray diffraction and photocatalytic activity under visible light irradiation (R6G degradation) of the hybrid nanorods.

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Sol-Gel Method for the synthesis of Novel Phosphate based Bioactive Glass

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Abstract: Purpose:

The purpose of this study was to synthesize the novel phosphate based bioactive glasses by the sol-gel method at ambient temperature.

Materials and Method:

The phosphate based bioactive glasses formed by the evaporation induced self-assembly (EISA) method has improved composition and better bioactivity as compare to the glass formed by the other sol-gel methods. Mesoporous, uniform and well-ordered structure is achieved. EISA method is a modified form of sol gel method in which the surfactant is added as a structure forming agent. The spontaneous structural arrangement is formed by the non-covalent linkage between the glass component and the surfactant molecules. The surfactant is used according to the solvent solubility and it also determine the mesopore size and structure of bioactive glass. Bioactive glass which is more ordered and mesoporous exhibit more bioactivity then sol gel derived bioactive glasses.

Sol-gel EISA method was used to synthesize the novel phosphate based bioactive glass material at ambient temperature (25 °C) and the resultant product after aging was calcined at 600°C with the heating ramp of 1°C min⁻¹ for 6h in a furnace. The structural, physical and phase purity of resultant powder was carried out by Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive x-ray (EDX).

Results:

The peak assessment of FTIR spectra of phosphate based bioactive glass, the FTIR absorption results found to be sensitive in the region of 600-1400 cm⁻¹ for phosphate group in the form of ring, chain and terminal groups confirmed the crystallinity and exhibited asymmetrical and symmetrical stretching peaks of phosphate at 910 cm⁻¹ and 1125 cm⁻¹ respectively and after calcination the OH peak disappeared. The XRD pattern of phosphate based bioactive glass before and after heat treatment demonstrated intense peaks at 2θ values, the peak appeared at 24° corresponded to the P-O. In the XRD spectra of glassy materials a halo was seen instead of diffraction peaks. (SEM) images showed the fine dense nanoparticles size range from 350-450 nm. According to Energy Dispersive X-ray (EDX) spectra confirms presence of phosphate, Calcium, Sodium and some other minor trace elements.

Conclusion:

The ease of synthesis by the sol-gel method of these phosphate glasses made them clinically useful for promoting the regeneration. However, phosphate glasses can be produced at relatively

low temperatures, thus allowing the incorporation of drugs and bioactive macromolecules, which could have potent modulating effects.

Keywords: bioactive glasses, sol-gel method, dental materials, orthopaedic application

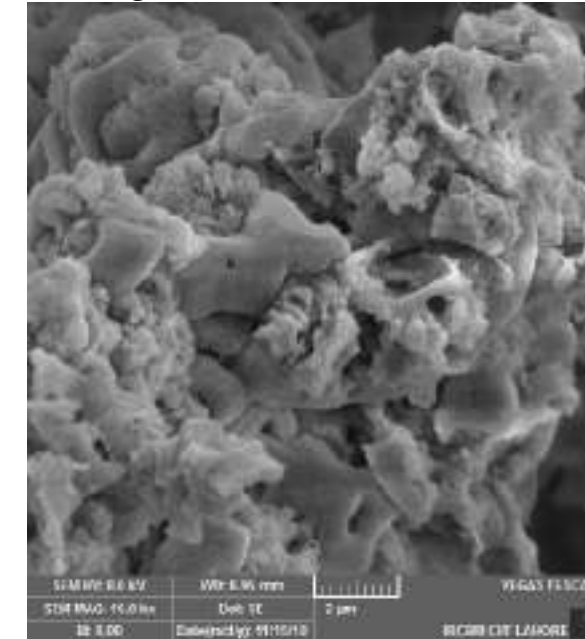


Figure 1.

The authors would like to acknowledge Engr. Faisal Manzoor for facilitation in SEM analysis.

Mesoporous organosilica nanoparticles derived from proline-valinol amides as recyclable catalysts for asymmetric aldol reaction

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Abstract: Sol-gel methods have been recognized as interesting procedures to prepare catalysts. The versatility of the sol-gel techniques allows the control of the texture, composition, homogeneity and structural properties in the production of tailored materials. Mesoporous organosilicas are frequently used as recyclable catalysts.¹ However, they are still limited by the lack of control on the morphology and particle size, and by the lower reaction rates found on these supported catalysts compared with the homogeneous counterparts. The ability to obtain silica nanoparticles improves the performances of bulk organosilicas. Following our interest on recyclable catalysts based on sol-gel methodologies,² we present herein our recent results concerning functionalized mesoporous silica nanoparticles derived from chiral proline-valinol amides as reusable organocatalysts in direct asymmetric aldol reactions.

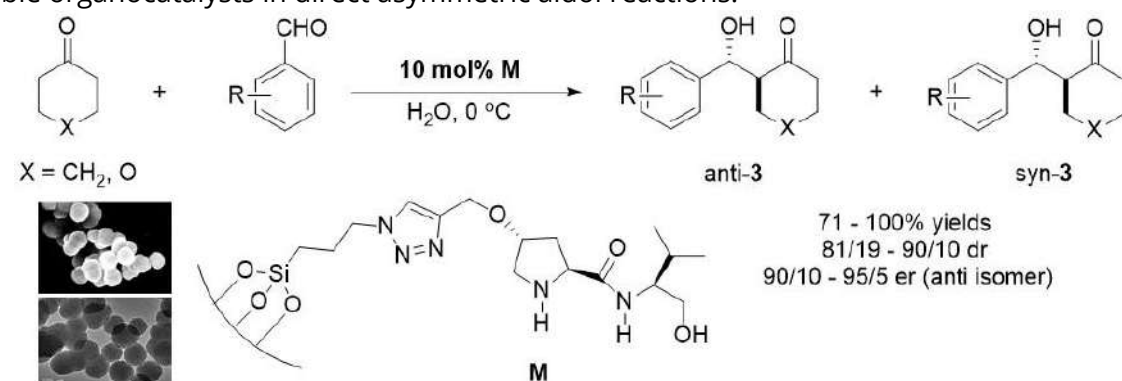


Figure 1. Example of a figure.

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When 19th century oil painters prepared organic/inorganic hybrid gels: physico-chemical study of "Gumtion"

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Abstract: Oil painting is composed of a pigment dispersed in a siccative oil. Frequently, the artists used to add a medium to their paint in order to modify its texture and drying properties. During the 19th century, British painters developed a particular medium with surprising rheological properties made of siccative oil (mainly composed of triglycerides), mastic resin (composed of triterpenoids and a polymer fraction) and lead acetate trihydrate ($\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$). The so-called "gumtions" form gellike materials in a relatively short time, outperforming the existing paint media. They would provide, at least according to the manufacturers, all the properties required for the art of painting.

While the unique properties of Gumtion gels were known from two centuries, their formation mechanism and their chemical structure remains unclear. Beyond fundamental aspects, the characterisation of these materials is crucial to develop adapted strategies for the conservation of works of art.

Here, we contribute unveiling the chemical and structural processes involved in the formation, drying and ageing of Gumtions. As a first step, by reproducing various historical recipes, we investigated the rheological properties of the gels as well as their organization at the mesoscopic scale. Moreover, the interaction between lead acetate and resin mastic triterpenoids has been clarified.

To deepen the understanding of the chemical interactions between the gel components, we focused on simplified gel formulations containing oleanolic acid (commercial triterpenoid) and a lead compound (acetate trihydrate or oxide). They are investigated at different scales by spectroscopic (FTIR, MAS-NMR) and supramolecular analyses (Cryo-TEM, SAXS). The use of these complementary techniques gives an overview of the gel's structure and formation, that is the interactions between lead and acidic groups of the resin allowing lamellar organization dispersed in a continuous phase.

Finally, we took advantage of typical methodology developed for sol-gel materials to study the Gumtion gel and its constituents shaped as thin film in order to mimic painting-like conditions. Their optical and structural evolutions as function of the environmental conditions were investigated by spectroscopic ellipsometry.

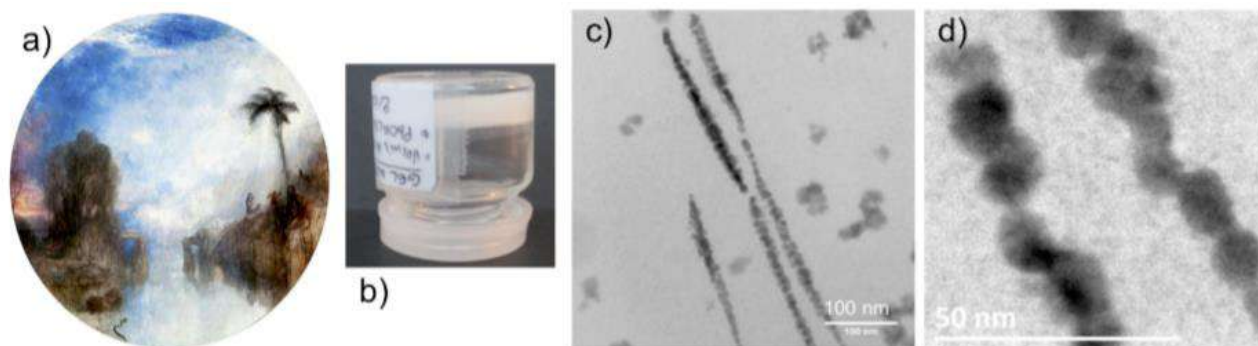


Figure 1. "Dawn of Christianity" painted by J. M. W. Turner in 1841 (a); a model gel (b); cryomicrographs of the model gel showing a lamellar organization (c, d).

Preparation of 2,5-Bis(triethoxysilylvinyl)pyridine and Its Application to Reverse Osmosis Membrane

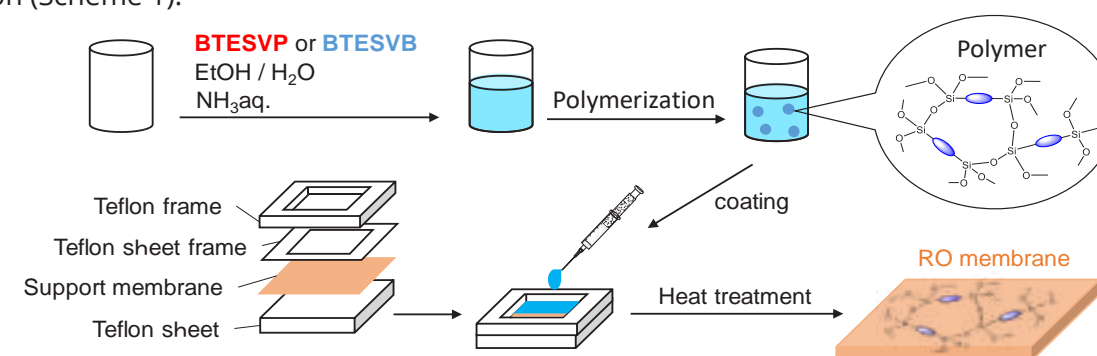
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Abstract: Reverse osmosis (RO) membranes such as polyamide are very useful to separate pure water from sea water, but these membranes are sensitive to chloride-based detergents. Organo-bridged polysilsesquioxanes have attracted as highly resistant RO membranes; however, this membrane shows low water-permeability. To improve water-permeability, we focus on bridged polysilsesquioxane with hydrophilic organic group. In this work, we will report the preparation and separation ability of RO membrane using 2,5-bis(triethoxysilylvinyl)pyridine(BTESVP) as raw material.

BTESVP and 1,4-bis(triethoxysilylvinyl)benzene(BTESVB) as a comparative target were synthesized⁽¹⁾ and reverse osmosis membranes were prepared by hydrolysis polycondensation reaction (Scheme 1).



Scheme 1. Preparation of polymer solution and reverse osmosis membranes membrane

Both the BTESVP and BTESVB RO membranes have very high NaCl rejection ratios of over 95%. Moreover, BTESVP showed water permeation rate more than twice compared to that of BTESVB (Fig.1). This is because BTESVP is more hydrophilic than BTESVB due to the hydrophilicity derived from the pyridine ring at the crosslinking site, as supported by the water contact angle measurement. Thus, the RO membrane improving water permeation rate by imparting hydrophilicity was prepared.

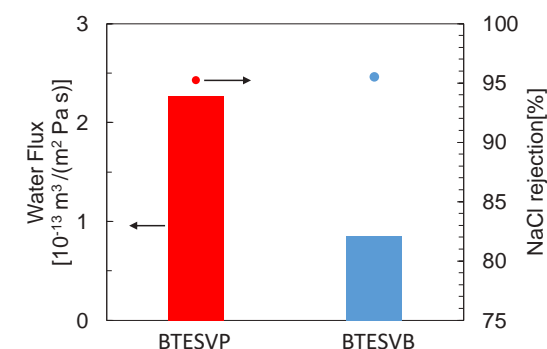


Figure.1 Performance evaluation of RO membrane.

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Sol-gel barrier layers with lower oxygen permability

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Abstract: Flexible films with high barrier properties against oxygen and water are currently in the focus for applications in an increasing number of technical fields e.g. electronic, optical devices, and packaging. In this research work, functional coatings, based on hybrid organic/inorganic materials, are being developed to combine the polymer flexibility and ease of processing with the rigidity, thermal stability and barrier properties of inorganic materials. The focus is to obtain low-temperature barrier layer on flexible substrate.

The main properties are required for electronic devices coating materials to ensure its durability are UV, oxygen, and water barrier [1,2], transparency, anti-reflectance [3], flexibility, affordable cost, and electrical isolation [4]. One of the ways in production barrier layers is using chemical vapour deposition or plasma deposition technics to lower gas permeability of polymer films [5,6].

Here, functional sol-gel-based materials were synthesized at room temperature by the hydrolysis and polycondensation of precursors, such as silicon alkoxides and organically modified metal alkoxide, under controlled conditions. In our laboratory study, the silica-based layers were deposited by a spin-coating method on flexible polymeric support.

Surface morphology (AFM) and surface performance (OM, SEM), hydrophobic properties (CA) and structural properties (FT-IR with ATR mode) were examined and compared for all samples prepared using different precursors. The oxygen transmission rates of obtained coating layers were analyzed.

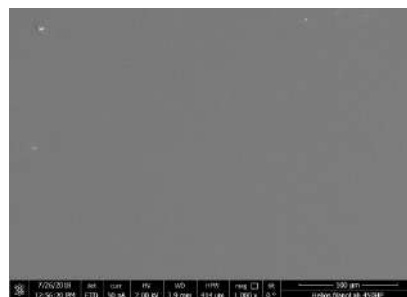


Figure 1. The Scanning Electron Microscope image of the surface of selected sample.

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Modeling and intensification of aerogel particles production processes

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Abstract: Aerogels are nanostructured material, which has a low density from 0.005 to 0.5 g/cm³, high porosity up to 99%, high specific surface area up to 2000 m²/g. The structure of this material is a combination of meso- and macropores in different ratios. Due to the specified properties, aerogels can be used as superinsulation, sorbents, carriers of active substances. Currently, the use of aerogels in the form of particles with specified characteristics is particularly relevant, since various functional and composite materials based on them can be produced.

The process of aerogel particles production includes three main stages: gelation and dispersion, solvent exchange, and supercritical drying. These processes are studied on the example of alginate aerogel production.

Gelation is carried out in an aqueous medium by reaction of the polymer chains of sodium alginate with calcium cations according to "egg-box" mechanism. For dispersion a number of methods are used: dripping and emulsion-gelation. In obtained hydrogel particles step-by-step solvent exchange on isopropanol is carried out. Then, to obtain aerogel particles, supercritical drying is carried out in a 250 ml apparatus at temperature 40 °C and pressure 120 bar with carbon dioxide flowrate 200 - 600 g/h. The dependences of the structural characteristics of aerogel particles on the parameters of the process of their production and the ratios of the initial materials are obtained. The dependences of the size of the obtained aerogel particles on the method of dispersion and its parameters are established. It is shown that an increase in the concentration of the initial sodium alginate solution leads to an increase in the size of the resulting aerogel particles, while an increase in the concentration of calcium cations leads to a decrease in aerogel internal specific surface area.

Supercritical drying consists of several stages: pressurization, solvent displacement from the free volume of the apparatus, diffusional exchange of the solvent in the pores of the gel on supercritical carbon dioxide. For a comprehensive study of the process of supercritical drying of gel particles, a mathematical model was developed, based on the provisions of the continuum mechanics. As a result of the modeling the parameters of the supercritical drying process were selected, which allow its intensification. Two regimes of carbon dioxide flowrate at the stage of diffusional exchange was proposed. The first regime: stepwise reduction - carbon dioxide flowrate decreases in steps with decreasing of solvent concentration in the gel. The second regime: pulse change - a sharp change of carbon dioxide flowrate with time. The implementation of the first regime allows to reduce the amount of carbon dioxide, and the second regime allows to reduce the process time. In addition, the temperature effect was evaluated. The results obtained are confirmed experimentally.

Sol-gel electrospinning preparation of metal oxide nanofibers for *electronics* and photonics

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Abstract: Sol-gel electrospinning routes have been actively exploited for the synthesis of a variety of polymeric, metallic, and metal oxide nanofibers. The surface functionality of electrospun nanofibers could be greatly manipulated by the immobilization of metallic and metal oxide catalytic nanoparticles, graphenes, and functional polymers to provide greatly enhanced electrochemical, structural, electrical, and optical properties [1].

In this work we report on the study of the physical properties of metal oxide nanofibers, such as indium-zinc oxide (IZO), a material which is able to change its electrical resistance when exposed to UV or absorbed gases, vanadium dioxide (VO_2), a material with metal-insulator transition, and sodium-potassium niobate $\text{Na}_x\text{K}_{1-x}\text{NbO}_3$ (NKN), a material exhibiting ferroelectric and piezoelectric properties. The choice of these materials is conditioned by the fact that all of them exhibit phenomena interesting from the viewpoint of physics, viz. phase transitions, photo- and gas-sensory properties, and on the other side, they are all possess applied potentialities in oxide electronics and photonics. Meanwhile, the implementation of these materials in the form of nanostructures can significantly modify the manifestation of these effects and improve the corresponding functional properties, which is important for technical applications.

The samples under study were obtained by means of electrospinning of corresponding gel precursor solutions containing metal compounds, namely, hydrated indium nitrate and zinc acetate dehydrate, vanadium acetyl acetonate, and sodium and potassium acetates with niobium ethoxide and erbium nitrate pentahydrate, respectively, in case of IZO, VO_2 , and NKN:Er nanofibers [2-4].

It is shown that the highest sensitivity to UV is observed in the IZO nanofiber samples at the indium content of about 50 at.% [2]. The photocurrent increment with respect to the dark current is more than 4 orders of magnitude. The response and recovery times are 60 and 500 sec., respectively. The obtained vanadium oxide nanofiber samples demonstrate the metal-insulator transition at $T_t \sim 60^\circ\text{C}$ and electrical switching with an S-shaped I - V characteristic. In the NKN nanofiber samples, Er doping with the concentration of 2 at. % provides readily detectable room-temperature broad-band photoluminescence. Impedance spectroscopy and static electrical tests revealed ferroelectric properties and electric field induced resistance switching [4].

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Synthesis and some properties of isotopically enriched SiO_2 with high chemical purity

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Abstract: High-purity Si isotopes are promising materials for many areas of science and technology, for example for spintronics and metrology [1]. A promising direction in the field of research of isotopically enriched substances is to obtain and study the physicochemical properties of optical materials based on quartz glass with a modified isotopic composition of Si and O atoms compared to natural ones. Based on calculations some publications [2] suggest a significant dependence of the optical properties of quartz glass on its isotopic composition (there is supposed to decrease the refractive index and reduce optical loss). However, information about the preparation and properties of such glasses in the literature is very limited. The probable cause of this is the scarcity and high cost of isotopes and the possibility of isotopic dilution of silicon and oxygen. Therefore, the task to obtain and study the properties of such samples is of fundamental and practical interests.

One of the common techniques of acquiring glasses is the sol-gel process in which alkoxides are hydrolysed yielding a gel then converted to a glass [3]. The advantages of the sol-gel process are the relative simplicity and the ability to use small quantities of the reagent. It is especially important while working with difficulties to obtain isotope-enriched substances as well as due to their expensiveness. The starting compound for the separation of silicon isotopes is the silicon tetrafluoride which is converted to the silicon tetrachloride via reaction with the aluminium chloride [4]. The purpose of the present work is to obtain and study the properties of the isotopically enriched glassy SiO_2 from SiCl_4 .

SiCl_4 , consisted of isotopically enriched silicon or silicon of natural isotopic composition, ethanol dried by metal Ca and deionized water were used to obtain high-purity isotopically enriched silica glass. To reduce the amount of impurities SiCl_4 and ethanol were purified by distillation. The amount of impurities were of magnitudes: for SiCl_4 $n \cdot 10^{-5}$ - $n \cdot 10^{-4}$ wt. %, for the ethanol - $n \cdot 10^{-6}$ - $n \cdot 10^{-5}$ wt. %, for the water – less than $n \cdot 10^{-7}$ wt. %. The elemental and isotopic compositions were studied by the inductively coupled plasma mass spectrometry (Thermo Finnigan Element-2). To obtain SiO_2 a tetraethoxysilane was prepared by adding SiCl_4 to the vigorously stirred ethanol in the fluoroplastic pot. $\text{Si}(\text{C}_2\text{H}_5\text{O})_4$ was hydrolyzed by ethanol-water mixture ($\text{Si}(\text{C}_2\text{H}_5\text{O})_4:\text{C}_2\text{H}_5\text{OH}:\text{H}_2\text{O} = 1:4:4$). The obtained solution then was cast to the fluoroplastic forms for the gelation. Then the gel was dried by heating to obtain glassy SiO_2 . The inductively coupled plasma mass spectrometry showed no significant isotopic dilution of silicon-28 and silicon-29 in $^{28}\text{SiO}_2$ and $^{29}\text{SiO}_2$. X-ray phase analysis indicated no reflections from the crystalline phase in X-ray patterns of the amorphous strip, though it showed the halo pattern region, characteristic of the amorphous materials and present within the range of angles of $5^\circ \leq 2\theta \leq 60^\circ$ degrees. Transmittance spectra of the acquired samples were registered on the spectrophotometer Shimadzu UV-3600. In the present work spectra of the silica glass based on $^{\text{nat}}\text{SiO}_2$, $^{28}\text{SiO}_2$ and $^{29}\text{SiO}_2$ are given and discussed.

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Cancer theranostic agent based on tantalum oxide nanoparticles: synthesis and characterization

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Abstract: Cancer nanotechnology is an emerging branch of science that strives to develop new methods of therapy and early diagnostics. Higher efficiency could be achieved due to operation at molecular or cellular levels. There is a novel approach in this field – theranostics (therapy+diagnostics) – that involves design pharmaceuticals which combine both therapeutic and diagnostic capabilities. It represents a further step forward towards personalized medicine.

Tantalum oxide nanoparticles are a perspective platform for developing multimodal theranostic agent because they inherently possess biocompatibility, radiosensitising properties (therapeutic capability) and X-ray contrast performance (diagnostic capability). An additional imaging capability could be achieved by doping oxide matrix by rare-earth elements that give nanoparticles adjustable luminescent properties, including upconversion ones. The upconversion luminescence has advantages when compared with the conventional fluorescence since near-infrared (NIR) excitation light causes minimal photodamage, induces practically no autofluorescence background and can penetrate biological tissue much deeper. This enables to design a converter for the radical destruction of malignant cells for enhanced radiotherapy, which at the same time offer dual imaging capabilities (luminescence and X-ray diagnostics).

In this regard, the developing of the synthesis procedure of undoped and lanthanide (Eu, Er, Yb)-doped Ta₂O₅ nanoparticles was performed. The influence of different synthesis conditions (for both solvothermal and sol-gel methods) on the properties of the obtained materials was investigated. The phase composition, morphology, surface properties and thermal behavior of obtained materials were studied by XRD, TEM, FTIR, BET, TG/DSC. Photoluminescence measurements were performed on thermally annealed doped nanoparticles with the use of mercury lamp and NIR laser as sources of excitation. The effect of electrolyte concentration and pH on the stability and colloid-chemical characteristics of sols were examined thoroughly by microelectrophoresis, dynamic light scattering and potentiometric titration. In Vitro Cytotoxicity (MTT-test) and In Vivo Acute Toxicity studies were performed for the obtained materials.

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Polymeric particles to determine infectious diseases *in vitro*

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Abstract: Functional polymer particles are widely used in many fields of science, such as biomedicine, electronics and the chemical industry. Lately cationic polymer particles have great interest among researchers. The size of the microspheres, the narrow particle size distribution, their surface properties in combination with the positive charge determine their unique properties and interest for further study. The ability to synthesize particles with desired properties can significantly expand the use of microspheres and use them in biotechnology, as carriers of immunoreagents or drug delivery.

In this regard, polymer monodisperse particles with surface aliphatic amino groups were obtained on the basis of methyl methacrylate and 2-aminoethyl methacrylate hydrochloride copolymers in the presence of cross-linking agents of various natures.

The diameter of the synthesized particles is 200-600 nm. The particles are aggregatively stable in a wide pH range (2-10). In this case, the inversion of the sign of the charge of the ζ -potential of the particles occurs in the alkaline region of pH, which indicates the predominance of amino groups over carboxyl.

Due to the aggregative stability of the particles, the preservation of the positive charge of the ζ -potential in the pH range, characteristic of physiological solutions and the presence of aliphatic amino groups in the surface layer, polymeric monodisperse particles are promising for attaching antibodies and antigens of infectious diseases for research in biotechnology and medicine.

The tick-borne encephalitis virus antigens were attached to the synthesized particles and latex agglutination reactions were carried out to determine the antibodies of the tick-borne encephalitis virus *in vitro*. The results showed that for the synthesized particles, after 10 minutes of the reaction, a visually distinguishable precipitate was observed, classified on the scale of four crosses as 4+ (Figure 1). The reliability of the proposed test system is more than 95%, which significantly exceeds the results of the methods that used now. The proposed method also has high values of diagnostic sensitivity, specificity, and overall system accuracy.

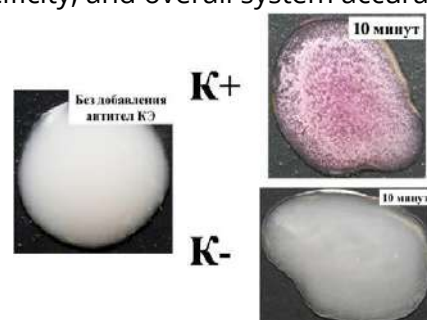


Figure 1. Positive and negative results when testing with the help of test systems

Thus it is possible to determine the presence of IgM and IgG tick-borne encephalitis immunoglobulin *in vitro* in human serum qualitatively and in less than 15 minutes without specific skills and equipment, and with minimal reagents.

Effect of hydrophilic polymers on architecture, stability and activity of biocatalysts based on living cells into sol-gel silica

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Abstract: One of the main attractions of sol-gel process is its potential for the development of new silica-organic materials (ormosil). In the materials of class I, organic molecules (such as polyethylene-glycol, polyvinyl alcohol, et al) are physically embedded in a silica network and play a primary role in forming the structure of silica-based matrix. Additives of PEG may improve biocompatibility by, e.g. improving the surface interactions between sol-gel matrix and living cell or protecting the cells from stresses of encapsulation. It's staying alive of living cells for biocatalysis or biosensing purposes. Biohybrid materials based on ormosil encapsulated yeast cells were synthesized through a one-step sol-gel route with base-catalyst (NaF) using tetraethoxysilane (TEOS) and methyltriethoxysilane (MTES) and polyethylene-glycol (PEG) with different molar weights polyvinyl alcohol (PVA) as a structure-controlling agent. The role of polymers in the 3D-structure biohybrids formation is associated with the ability of these polymers to form a mesh framework, with further producing an organosilica material and an intermediate layer of hydrogel around the cell walls. This ensures the targeted formation of an ormosil capsule by increasing the number of nucleophilic centers of hydrophilic polymers near the cell surface at neutral pH values. It was shown that in the process of one-step sol-gel synthesis from TEOS and MTES (85:15 ratio) film-type materials are formed with the addition of PVA, while pasty vitreous materials are formed when adding PEG [1]. These shells protect living cells from the effects of stressfull factors (UV, heavy metal ions) and ensure the viability of immobilized yeast during long-term storage at -18 °C (for a year). This research suggests the use of new hybrid biomaterials as biocatalysts (biofilters) and biosensing elements or surfaces (biosensors) [2, 3].

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Silicon polyethylene glycol as a new biocompatible precursor in sol-gel biomimetic mineralization of polysaccharides

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Abstract: Biomimetic mineralization is a process modeling biomineralization in living nature and resulting in the formation of hybrid materials with an unique structure and a set of new useful properties. Earlier we applied silicon tetraglycerolate as biocompatible water-soluble precursor for the preparation by the biomimetic sol-gel mineralization under mild conditions (in the absence of catalyst) of silicon-chitosan-containing transparent monolithic hydrogel with wound healing, regenerating, hemostatic and antimicrobial activity [1, 2]. In this case, chitosan accelerates gelation, and exerts a substantial effect on the biomimetic sol-gel mineralization resulting in the formation of polymeric silicon-containing 3D-network. I should be noted that other known biocompatible water-soluble polyolates [3], in particular, silicon tetrapolyethylene glycolate have not to our knowledge been investigated in the process of biomimetic sol-gel mineralization of polysaccharides. At the same time, their use shows promise in the sol-gel chemistry, since it allows the sol-gel processing to be carried out in aqueous solutions without toxic organic solvents and catalysts thus realizing the green chemistry methods.

In this work, we have demonstrated that in addition to silicon tetraglycerolate, a new water-soluble biocompatible polyolate precursors - silicon tetrapolyethylene glycolate can be successfully utilized in biomimetical mineralization of polysaccharides of various nature. By the example of chitosan (cationic), xanthan gum (anionic), and hydroxyethyl cellulose (uncharged) polysaccharides, an accelerating effect has been demonstrated on the gelation process and a stabilizing effect has been revealed on the hydrogels formed as transparent monoliths showing resistance to syneresis. Thus formed silicon-containing 3D-network of gels is found to be polymeric and appears to have ordered amorphous morphostructure, which can be explained as caused by the influence from the polysaccharides serving as templates for the structure. The presence of polyolate groups between silicon atoms in the polymeric network is characteristic of polyolate precursors only and is determined mainly by the nature of the precursor and by the contents of polyol and water in the system. The formation of polyolate groups is facilitated by the low reactivity of the precursor, by low water content, and also by polyol excess in the system. The sol-gel process utilized to obtain the silicon-polysaccharide-containing hydrogels runs under the mild conditions at room temperature, with no catalyst or any organic solvent to be used, and thus can be regarded as belonging to the green chemistry methods that show promise for biomedical materials applications.

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Hybrid sol-gel coating for dropwise condensation of pure steam

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Abstract: The condensation of steam occurs in many applications, like condensers of power plants and desalination plants. Promote dropwise condensation instead of the classic filmwise condensation is a solution to increase the efficiency of the process, with the aim of reduce the size of the heat exchangers and the investment costs. During filmwise condensation, the liquid layer adjacent to the wall introduces a thermal resistance that adversely affects the heat transfer. On the contrary, the dropwise condensation mode leads to higher thermal performance by inducing the breakage of the liquid film and replacing it with a big amount of randomly distributed droplets. The potential of dropwise condensation is based on the increase of the heat transfer coefficients by several times compared to those measured during filmwise condensation. Surface properties play a crucial role in determining the condensation mode, in particular dropwise condensation is promoted on hydrophobic surfaces. [1].

Hybrid organic-inorganic sol-gel silica thin coatings have a good durability on harsh environments, with high temperatures and high vapor velocities, and slight hydrophobic behavior, sufficient to promote dropwise condensation of pure steam. We have proven that the mixture of orthosilicate (TEOS) and alkoxysilane precursor containing organic groups, like methyl-triethoxy-silane (MTES) and phenyl-triethyl-silane (PhTES), is good promoter of such mechanism on aluminum substrate. A systematic analysis is performed to understand the potentials and the limits of using such coatings. Sol-gel coating optimization procedure is presented, in terms of reagents ratio and baking temperature. Moreover, a thermal analysis in a proper experimental apparatus has been performed with different heat fluxes to test the potential of this films in the thermal industry.

From experimental data a homogeneous and mechanical resistant film with mean thickness of 250 nm is successfully synthesized over lapped aluminum substrate. Steady-state dropwise condensation is achieved obtaining a heat transfer coefficient up to $200 \text{ kW m}^{-2} \text{ K}^{-1}$ at 3.5 K wall subcooling, which is about 15 times higher than the heat transfer coefficient measurable during filmwise condensation on the untreated aluminum sample, for a time over 10 h of pure dropwise condensation mode. All samples analyzed present a gradual deterioration of properties, producing a hybrid condensation mode before arriving at a pure filmwise condensation that persists for a period about 5 times longer respect to pure dropwise condensation. This period is still characterized by higher heat transfer coefficient respect to classic condensation mode.

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Electrochemical properties of anode materials $\text{Li}_2\text{ZnTi}_3\text{O}_8/\text{C}$

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Abstract: Nowadays lithium zinc titanate ($\text{Li}_2\text{ZnTi}_3\text{O}_8$) is considered as a very promising anode material for lithium-ion batteries. The main disadvantages of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ are low electronic conductivity and lithium ion diffusion coefficient. In order to improve its electrochemical performance several approaches have been proposed: reduction of particle size or conductive additives incorporation. This will shorten diffusion pathways providing fast movement of lithium ions and conductivity improvement. The main purpose of this work is the synthesis of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ -based materials with different particle size and their electrochemical performance study. Lithium zinc titanates were prepared by sol-gel method followed by heat treatment at different temperatures. Obtained materials were characterized by X-ray diffraction, impedance spectroscopy, scanning electron microscopy, Raman spectroscopy and electrochemical performance study.

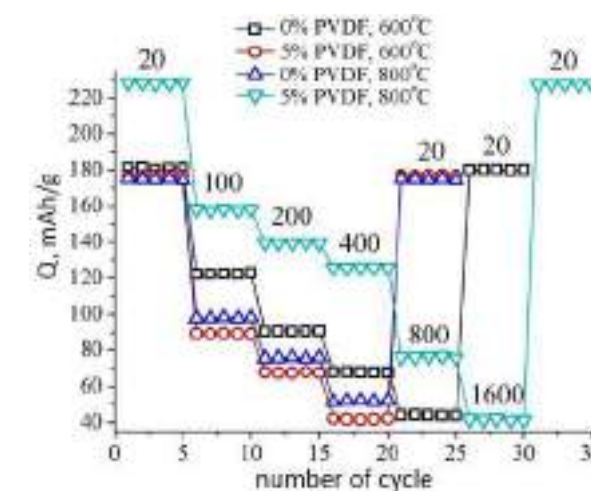


Figure 1. Changing the discharge capacity of lithium zinc titanate samples during cycling.

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Platinum Free Thermally Curable Siloxanes for Optoelectronic and Photo-functional Devices

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Abstract: Polysiloxanes for applications in the area of optical devices are usually based on two-component platinum catalyzed cross-linked or irradiation curable epoxy materials.¹ Here we report the synthesis and properties of a novel one-component siloxane that can be thermally cured showing similar tailorable properties like commercially available encapsulation systems without using a noble metal catalyst.^{2,3} The pre-curing material is formed by an acid catalyzed condensation reaction of trialkoxysilanes (TAS), dialkoxysilanes (DAS), and alkoxy-terminated polysiloxanes (Figure 1a). NMR, TG and DSC analysis of the formed compounds reveal that the materials are partially cross-linked gels. The obtained compounds can be thermally cured at temperatures between 160 and 200°C (Figure 1b). Depending on the composition a tunable hardness, refractive indices of 1.494 – 1.505, as well as a temperature stability up to 443°C were obtained (Figure 1c, 1d). These extraordinary properties make these materials to ideal systems for optoelectronic applications. Additionally, organic fluorescence dyes can be covalently or non-covalently integrated into the polymer matrix to form fluorescent encapsulations or films, which protects the dyes from photobleaching. Hence, the materials are perfectly suited for high-performance LEDs or photo-functional devices like luminescent solar collectors.

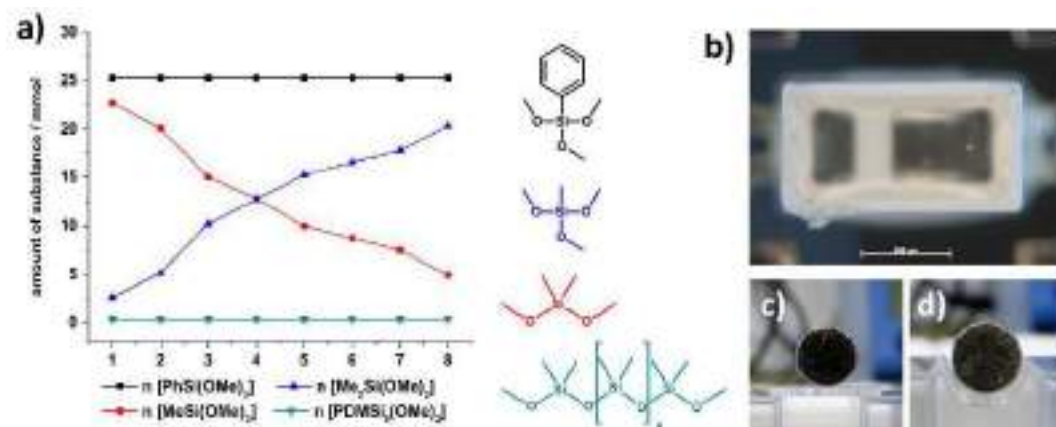


Figure 1. a) Subsequent substitution of a trialkoxy- by a dialkoxysilane monomer in the formulation. b) LED leadframe with the casted and cured gel. c)-d) A hard and a soft sample of the cured materials weighted with a cylinder for hardness demonstration.

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The use of ASPEN Plus for the optimization of acid catalyzed hydrolysis polymerization process of TEOS

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Abstract: Sol-gel process is a flexible solution process for producing advanced materials in many industries. Odor problems caused by hydrogen sulphide also have been treated using a gel produced by sol-gel technology. While TEOS, water and nitric acid used as primary chemicals for the hydrogel, several other inhibitors and bactericides have been added to the gel in order to make the gel function properly for the requirement of suppressing Sulphur Reducing Bacteria (SRB). In this study, the main focus was to optimize the hydrolysis-polymerization process for this system using ASPEN Plus software in order to achieve efficient production at the end. The gelation time of the hydrogel reduces as the temperature of the final solution increases. To maintain a convenient residence time and to obtain the established gel, temperature control is essential in the first reactor. In order to control the temperature, thermodynamic conditions of the process has been taken into consideration. ASPEN Plus simulations have been performed in order to observe the outlet variations in the hydrolysis reactor with respect to the reactor temperature and heat duty. The kinetic coefficients have been taken from reference (1) & (2) which considered similar conditions. It has been revealed that maintaining 1.5-1.66 kJ/sec heat duty generate the required temperature range of 28°C-70°C in the outflow with above 93% TEOS consumption.

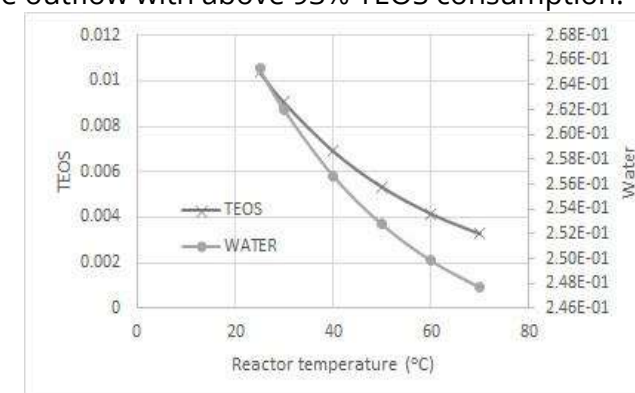


Figure 1. Outflow reactants mole fractions vs. reactor temperature.

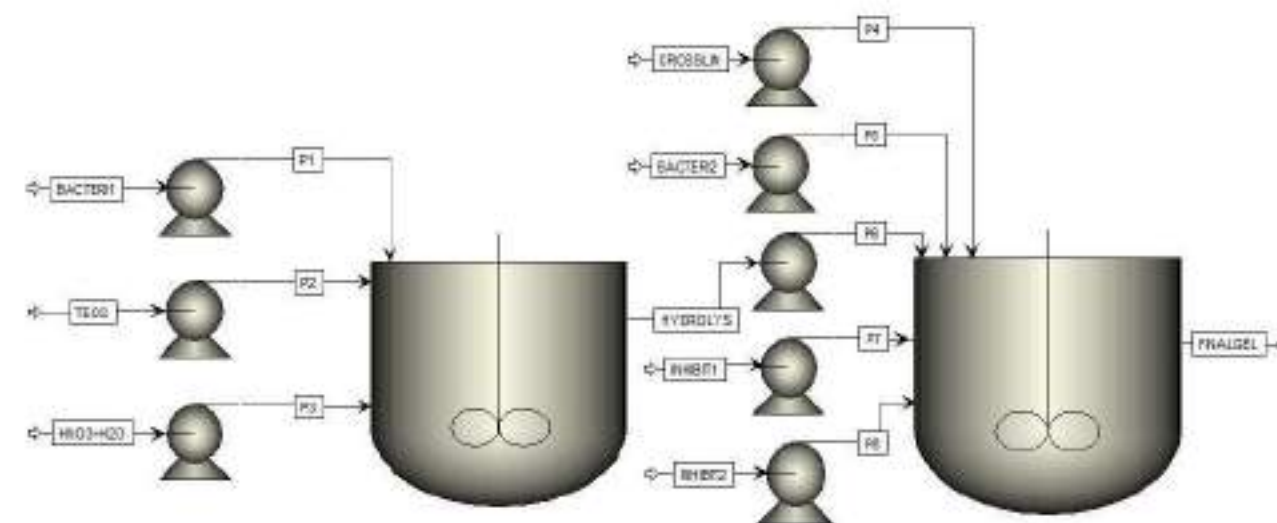


Figure 2. Continuous flow process for production of the gel.

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Molecular Design of Hybrid Porous Titanium Phosphonates

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Abstract: The ability to design materials with control over their assembly at nanoscale is one of key challenges in synthesizing tailored hybrid materials. The advent of periodic mesoporous organosilica (PMO) ushered in creation of hybrid materials based on porous metal phosphonates. Metal(IV) phosphonate based metal organic frameworks (MOF) with their applications in solid acid catalysis, proton conduction and metal sorption, are characterized by layered motifs and pore sizes lying generally in the microporous region. In contrast, mesoporous titanium phosphonates are mainly based on polyfunctional phosphonic acids that forms an amorphous network rather than a layered structure¹. There is a need in understanding how the organophosphonic linkers interact with metal alkoxides in the presence of porogenic templates.

In this work, we aim to combine the controlled assembly of molecular units as in MOFs with supramolecular templating to yield a mesoporous hybrid material. We achieve this by performing a partial in-situ hydrolysis of diphosphonate ester into an acid that reacts with titanium alkoxide². This way, the kinetics are more controlled due to the relatively slow rate of hydrolysis of the phosphonate ester when compared to the condensation of titanium alkoxides and phosphonic acids. The TGA thermograms of hybrid materials synthesized from titanium butoxide (TBT) with propylene diphosphonic acid (PrDPA) and its tetraethyl ester (TEPD) in the presence of CTAB as the template is shown in Figure - 1. The decomposition of the organic entities that comprises the template and the organic fragment of the phosphorus precursor are leaving the structure in a different manner depending of the use of ester or acid. In the case of hybrids with TBT and TEPD, spectroscopy evidences a weak interaction of the phosphoryl oxygen with the metal center (with weight loss around 350°C). For hybrids based on TBT and PrDPA, strong Ti-O-P have formed that increase the temperature at which the organic fragments that are lost around 450-480°C.

In conclusion, we control hydrolysis of the ester groups of organophosphonic linkers into an acid via the HCl/H₂O ratio, allowing to regulate its reaction rate with the titanium precursor to yield hybrid material with controlled condensation.

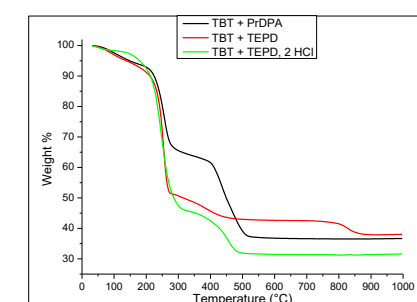


Figure1. TGA of hybrid materials synthesized from TBT with PrDPA, TBT with TEPD, and TBT with TEPD under reflux (90°C for 6 hours).

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Functionalization of silica synthesized by sol-gel process with PDLLA via “grafting to” method

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Abstract: Due to its properties of biodegradability and biocompatibility, polylactide has been first designed for the medical field, in particular for tissue reconstruction by tissue engineering. However, for this kind of application, its mechanical properties are too low. The addition of silica has been proposed to reinforce the mechanical strength of this biopolymer. The main challenging aspect to realize this nanocomposite is to achieve a good dispersion of nanofillers in the polymer matrix. An effective method to improve compatibility between inorganic particles and polymer matrix relies upon the preparation of PLA grafted silica nanoparticles. To form a network structure with PLA matrix, molecular weight of these grafted chains has to be superior to the critical entanglement molecular weight (CEMW) of 8.5 kDa [1].

This work is dedicated to the functionalization of sol-gel silica by the “grafted to” method. A recurrent problem with this method is the great dependence of the grafting density on the molecular weight of the PDLLA chains. When weight is above the CEMW, grafting densities greater than 0.001 chains/nm² of silica are difficult to achieve [1]. To increase grafting density of PDLLA chains, these chains were firstly synthesized via ring opening polymerization with Sn(oct)₂ as catalyst and with a organosilane (alkoxyde XSi(OR)₃), the (3-Aminopropyl)triethoxysilane (APTES) as initiator, instead of a classic protic compound. This process led to the formation of PDLLA capped with three terminal functions Si-O-CH₂-CH₃. The resulting polyester was then dissolved in tetrahydrofuran under inert atmosphere to prevent hydrolysis of Si-OR functions. After dissolution, silica was synthesized by sol-gel reaction by mixing prehydrolysed tetramethyl orthosilicate (TMOS), dissolved polymer, water and APTES followed by three days of gelation at 65°C. Finally, these nanoparticles were washed several time with methylene chloride and cycle of centrifugation to remove unbound PDLLA and APTES. GPC and ¹H NMR have confirmed the targeted molecular weight of PDLLA of 11 kDa with a monomer conversion closed to 100%. FTIR measurement and solid ²⁹Si NMR have confirmed the covalent attachment of PDLLA chains on silica surface. BET analysis, performed after calcination of silica at 400°C, gave a specific surface of 350 m²/g. Finally, TGA allowed us to calculate a grafting yield of 25 % and a grafting density of 0.035 chains/nm² in a reproducible and manner.

As a conclusion, our chemical strategy has been demonstrated successful to increase significantly the grafting density of polyester chains on silica according to a reproducible methodology easier to apply compared to former publications [1][2].

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Protein encapsulation in silica gels by sol-gel process for bone reconstruction application

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Abstract: Over the last years, bone repair has increasingly gained in importance. Temporary porous matrices, called scaffolds, are attractive matrices in order to support and control the spatial organization of stem cells intended to be grafted to promote bone reconstruction. Various materials have been proposed for the conception of scaffolds, like ceramics, polymers, and metals. Nevertheless, studies have shown a lack of cell differentiation, bone production, and bone integration at the surface of these materials. The aim of this study is the adjustment of the surface functionalization of hydroxyapatite via sol-gel coating of silica to promote the local sustained delivery of Bone Morphogenic Proteins (BMP). In this optic, the influence of the functional groups present at the surface of silica pores on the release kinetics of a model protein (i.e. Soybean Trypsin Inhibitor, STI) and on its activity have been studied.

The encapsulation of STI was assessed adopting two alternative methods: (1) the impregnation of already synthesized silica gels in the protein solution (i.e. ex situ method), and (2) the direct incorporation of the protein during the gel synthesis (i.e. in situ method). For the ex situ method, tetraethylorthosilicate (TEOS) was used as main silica precursor and 3-(2-aminoethylamino)propyltrimethoxysilane (EDAS), (3-aminopropyl)trimethoxysilane (APTMS) or phenyltrimethoxysilane (PTMS) as nucleating agents in alcoholic medium and under basic conditions. After drying and/or calcination, the gels were impregnated in a STI solution for 3 days. For the in situ method, tetramethylorthosilicate (TMOS) served as silica precursor after hydrolysis under acid conditions. The nucleating agents were also EDAS, APTMS, or PTMS. The textural properties were characterized by nitrogen adsorption and mercury porosimetry. The point of zero charge was determined via a method of equilibrium pH at high loading. The release kinetics of the protein and its inhibitory activity were analyzed in vitro on a 3 months period.

The results of the textural analysis revealed that ex situ gels presented a porous funnel-like structure (micro, meso, and macropores) while in situ gels presented a micro and mesoporous structure. The in vitro release profile of STI has also been shown to be significantly affected by the functionalization strategy. For the ex situ method, the release kinetics highlighted a burst observed during the first 24 h of incubation, due to the STI adsorbed at the surface of the SiO₂ particles. This burst was followed by a plateau for the calcined samples and by a continuous release for the dried samples. The inhibitory activity decreased after 4 weeks of incubation to a low value (i.e. around 30 %) for the dried samples and was equal to 0 in the case of the calcined samples. These differences could be explained by the sign difference of the charges present at the surface of the pores. Indeed, we can anticipate that the negative charges existing at the surface of the calcined samples should reinforce their interaction with the protein in contrast to the dried samples which bear positive charges at their surface. Accordingly, the entrapment of the protein would be less reversible for the calcined silica with a possible decrease in inhibitory activity. Regarding the in situ method, a continuous release were observed over the first 24 h followed by a plateau due to the proteins entrapped in closed pores. Interestingly enough, STI released after 4 weeks of incubation was still mostly active (i.e. around 80 %).

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Sol-gel synthesis of nanocrystalline PbS/TiO₂ composite

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Abstract: Titanium dioxide is a compound actively applied to solve such technological problems as the environmental friendly and energy-saving technologies. The TiO₂-based materials are widely used in the field of alternative energy as a matrix of the photoactive layer of solar electrochemical cells [1]. The contact between two semiconductors in composites is proposed for improvement the photoactive characteristics of TiO₂. In this regard, an actual task is to create composites based on TiO₂ and semiconductor nanoparticles with a smaller band gap. For enhancing the spectral sensitivity in IRregion the TiO₂ is doped by PbS nanoparticles [2].

In this work, an original sol-gel method for obtaining nanodispersed two-phase TiO₂ samples doped with PbS nanoparticles was suggested. For the first time, the hydrolysis reaction of titanium (IV) n-butoxide Ti(OBu)₄ was carried out in an aqueous colloidal solution of PbS nanoparticles. This approach provided the in situ sensitization of TiO₂ and the formation of a PbS/TiO₂ nanocrystalline composite. The obtained PbS/TiO₂ samples were studied by X-ray diffraction, optical spectroscopy, electron microscopy and elemental analysis.

Thus, the proposed method of synthesis allowed obtaining the nanocrystalline PbS/TiO₂ composite in a neutral aqueous solution at low temperature and atmospheric pressure, without additional heating of xerosols at high temperatures or using ultrasonic and aggressive media treatments. The composite consists of anatase and brookite nanoparticles with 0.5 at.% PbS clusters.

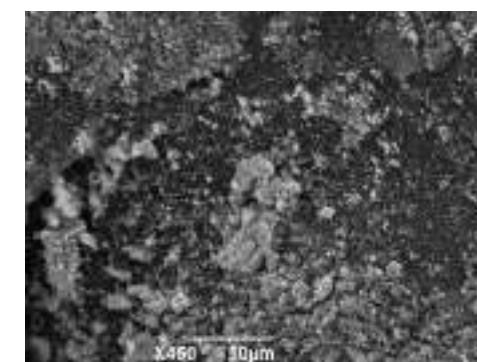


Figure 1. Scanning electron microscopy image of nanocrystalline PbS/TiO₂ composite

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Preparation of New Sol-Gel derived Siloxane-PEO-PLA hybrids for Biological Applications

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Abstract: Poly(lactic acid) (PLA) is a particularly interesting polymer for biological applications due to its biocompatibility, low toxicity and biodegradation properties. However, the obtention of hybrid inorganic-inorganic materials containing PLA is a challenge, due to the pronounced hydrophobic character of this polymer and its tendency to crystallize, which prejudices both miscibility with other organic or inorganic phases and favors fast degradation with time. The sol-gel process offers the possibility to obtain a three-dimensional hybrid network consisting of siloxane nanoparticles interconnected by hydrophilic polyoxyethylene (PEO) and hydrophobic polylactic acid (PLA) chains. For this purpose, PLA chains presenting hydroxyls groups at their extremities have been synthesized in order to react with a silicon alcoxyde containing an isocyanate group, which also reacts with PEO chains presenting amine groups at their extremities. In a second step, the resulting hybrid precursor containing urea and urethane bridges between PEO or PLA chains (respectively) and silicon species is hydrolyzed using NH_4F as a catalyst. Three different $[\text{PLA}]/[\text{PEO}]$ ratios (0.25, 1 and 4) have been employed, in order to investigate how the more hydrophilic or the more hydrophobic character of the resulting hybrids gels affect their structural and physicochemical features. Hybrid monoliths without cracks has been obtained, as shown in Figure 1. The success of precursor synthesis was confirmed by Infrared Spectroscopy (FTIR), which evidenced the disappearance of the vibration of the isocyanate group at 2500 cm^{-1} , whereas the bands associated to urea and urethane groups are distinctively present. ^{29}Si CP/MAS Nuclear Magnetic Resonance (NMR) spectrum of the hybrid material displayed characteristic T2 and T3 peaks of the siloxane phase, whereas Small-Angle X-ray Scattering (SAXS) results show an interference peak located around 1.6 nm^{-1} (attributed to the spatial correlation between siloxane nanoparticles) and another peak located around 3 nm^{-1} (attributed to the long period between PLA lamellas in PLA crystalline phase). The resulting interparticle distance d and long period L can be determined by the position of the peaks maximum and are 3.9 nm and 2.1 nm , respectively. X-ray diffraction (XRD) evidenced that PLA crystallization has been strongly reduced in the hybrid network by comparing with pure PLA. This result, combined with the improved optical and mechanical properties of Siloxane-PEO-PLA hybrids due to the presence of the inorganic siloxane nanoparticles and the homogeneity of this material up to nanometer scale, is very promising for future biological and pharmaceutical applications.



Figure 1. Siloxane-PEO-PLA monolith.

Enhancements of electrical and mechanical properties of silica aerogel by embedded CNT

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Abstract: Silica aerogel is one of the most well-studied and widespread aerogels. Silica aerogels have a number of unique properties, such as high specific surface area (1000 m²/g) [1], high porosity (85-99.87 vol.%) [2], low density (0.03-0.35 g/cm³), low coefficient of thermal conductivity (up to 0.008 W/(m·K)) [3]. Silica aerogels have a huge potential for use in various applications, for examples, catalyst carriers, gas sensors, acoustic and thermal insulations. However, the use of aerogel in specific areas involves the solution of complex problems to improve its properties, for examples, structural strength and hydrophobic of the material are necessary using aerogel as thermal insulation, structural strength and electrical conductivity of the material are necessary using aerogel as a gas sensor. As is well known, silica aerogel is a dielectric and mechanical brittle material. Aerogels consisting of two or more different materials are the most promising [4], for example, aerogels with embedded carbon nanotubes (CNTs).

During production of hybrid aerogels with nanotubes, CNTs tend to form aggregates due to the action of van der Waals forces. The formation of aggregates affects hybrid aerogels' structure and, as a result, their characteristics. Control of the aggregation process allows producing materials with required properties. The distribution of nanotubes in a material is influenced by various factors: surface's chemical composition, dimensions, synthesis method, concentration of nanotubes [2]. In addition, the type of polymer matrix and its physicochemical properties also affect the uniformity of distribution. As it is known from the literature survey, the following approaches and their combinations are used to obtain a uniform nanotubes distribution: mechanical methods (calendering, use of ball mills, homogenization, ultrasonic treatment) and use of surface-active substances (surfactants). Functionalization of CNT surface can also improve distribution.

This work is devoted to the mechanisms of structure formation and enhancements of electrical and mechanical properties of silica aerogel by embedded CNT.

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Innovative sol-gel routes for the preparation of highly efficient Ti-SiO₂ epoxidation catalysts

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Abstract: The simultaneous control over active site speciation and texture is a key for materials used as heterogeneous catalysts. Those features are known to rule respectively the intrinsic activity and the accessibility of the active sites, thus triggering intensive research on the design of efficient catalysts combining large pores, high specific surface area (SSA) and proper dispersion of the active species. Additional challenges include the resistance to water and the shaping of the materials for industrial flow processes. Herein, we present three examples of innovative sol-gel strategies which successfully address those challenges for the bottom-up preparation of structured Ti-SiO₂ epoxidation catalysts.

As a first example, we use the aerosolassisted sol-gel chemistry to prepare – in an easy and scalable way – hierarchically porous materials (4 mol. % Ti) with a sphere-like shell morphology (Fig. 1). The porosity is controlled at the three micro-, meso- and macro- levels by the use of a soft templating approach (evaporation-induced self assembly (EISA), Fig. 1a), combined with polymer beads as hard templates (Fig. 1c-d). The high SSA (up to 890 m².g⁻¹) and the pore architecture of these materials account for higher performance compared to conventional TS-1 zeolite (~ 3 times higher TOF, 96 % sel.).¹

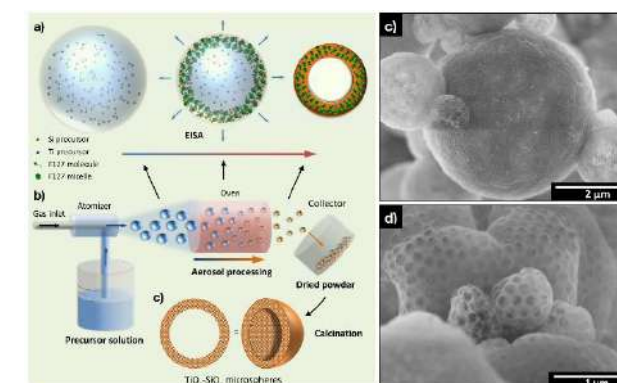


Figure 1. a) EISA mechanism; (b) schematic representation of the aerosol setup; c-d) SEM-FEG images of Ti-SiO₂ made by aerosol.¹

Moving further, we synthesize a macrocellular Ti-SiO₂ monolith foam using an emulsion-based templating technique (HIPE, Fig. 2). These monoliths are shown to possess high void fractions (ca. 85-90 %), with high Ti dispersion. This allows to perform epoxidation in continuous flow mode (Fig. 2), thus paving the way to process intensification in olefin epoxidation.²

Finally, as amorphous Ti-SiO₂ are sensitive to water, we investigate the role of surface hydrophobicity – via the grafting of methyl groups – on the performance of a mesoporous catalyst (6 mol. % Ti, 1020 m².g⁻¹) prepared by non hydrolytic sol-gel. We show that, in the presence of an excess of water in the solvent (25 % vol.), we can increase both the activity and the selectivity of the catalyst.³

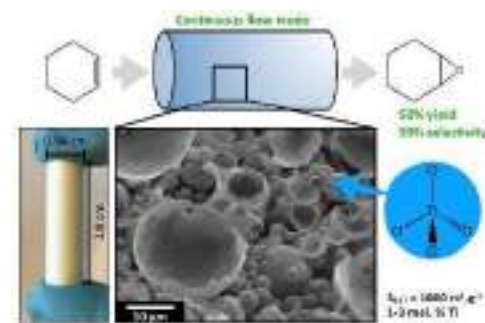


Figure 2. Incorporation of titanium in HIPE monolith and its consecutive use in continuous flow epoxidation.²

Thus, we present an overview of innovative preparation methods based on sol-gel chemistry that lead to efficient Ti-SiO₂ catalysts with tunable texture, pore architecture, Ti loading, surface properties, and also with possible scale-up and use in flow processes.

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Heavy metals removal from water by bacterial biofilm grown on sol-gel particles

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Abstract: Recent years application of biological alive and dead organisms became an encouraging solution, considering their capability to adsorb and remove different pollutants, including heavy metals. This process of biomass or certain biomolecules to bind and concentrate selected ions or molecules from aqueous solutions is called biosorption. Silica gels are another group of metal adsorbent that are found to be effective due to their highly porous structure and capability to be doped with different organic, inorganic and biomolecules. These gels are prepared from a solution of various precursors (metal alkoxides) via the sol-gel process, which is a room-temperature technique for synthesizing glass like materials and ceramics with preset structural and chemical characteristics. In our research we studied the combination of these two sorbent materials, in order to get an even more effective biosorbent for remediation of heavy metals from aqueous solutions. In this regard, two remarkable bacterial species were chosen as heavy metal removals: *Paenibacillus mucilaginosus* (former *Bacillus mucilaginosus*) and *Deinococcus radiodurans* (DR) (the first one produces abundant amount of EPS and the second one is a radioactive and desiccation resistant bacteria). Both bacteria were grown as attached biofilms with sol-gel particles as support. Owing to its transparency it was possible to dope the silica support with heavy metal detectors, in this case PAN (1-(2-pyridylazo)-2-naphthol), which can help in visual detection of metal binding in situ, via color change. The present study showed that sol-gel together with bacterial biofilms had higher maximum adsorption capacity than sol-gel alone. Comparison of the two bacterial biofilm strains revealed that sol-gel-DR complex demonstrated higher adsorption capacity for copper and cobalt removal, while sol-gel-BM had higher capacity for cadmium ions. Moreover, the adsorption capacity changed depending on metal ion type and its specific properties. The adsorption kinetics for all experimental heavy metals followed a pseudo-second-order kinetic and the equilibrium data best fitted the Freundlich isotherm. When comparing the linear and non-linear forms of adsorption isotherms, significant differences were not detected, and in both cases, adsorption followed Freundlich model with higher R² values and smaller standard errors.



Figure 1. Sol-gel color change after heavy metal interaction.

In situ FTIR study of silica polycondensation in a system containing PEO and TEOS

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Abstract: Fourier-transform infrared spectroscopy (FTIR) spectroscopy is a useful technique for investigation of the stages of the sol-gel process. Many FTIR studies have been devoted to hydrolysis of alkoxy silanes, yet the condensation reaction was not well characterized. Most of these studies used films or gels after heat treatment and removal of solvents [1, 2]. However, silica microstructure in gelling systems depends on the H₂O/TEOS ratio [3, 4]. Analysis of swelling gels in the FTIR region is a difficult task. Attenuated total reflection (ATR) is a sampling technique used in conjunction with infrared spectroscopy which enables samples to be examined directly in solid or liquid states without drying. ATR FTIR can be well used for *in situ* investigation of silica microstructure in swelling silica gels.

In this work the evolution in time of sol-gel systems containing water, nitric acid, tetraethoxysilane and various amounts of polyethylene oxide will be discussed. ATR FTIR method was used with special temperature-controlled sealed cell in contact with a diamond crystal. Main absorption bands are related to Si-OH (960 cm⁻¹) and Si-O-Si groups (1000-1250 cm⁻¹). The 1250-1000 cm⁻¹ region includes the transverse-optical and longitudinal-optical Si-O-Si modes as well as some important information about linear or cyclic structure [1, 2, 5]. The concentration of Si-OH groups decreased due to the polycondensation reaction and the formation of Si-O-Si bonds. As the reaction progressed, the broad absorption band at 1110-1250 cm⁻¹ with a peak at 1140 cm⁻¹ decreased and shifted to higher frequencies. With the rise in vibration frequency, the Si-O-Si intertetrahedral angles increase [2, 5]. This can be explained by deformation of Si-O-Si bridges. Therefore, the shift towards large wavenumbers was associated with a looser structure with large siloxane rings. However, with the evaporation of solvent during the sol-gel reaction the spectrum varied greatly (Fig. 1, spectrum 3).

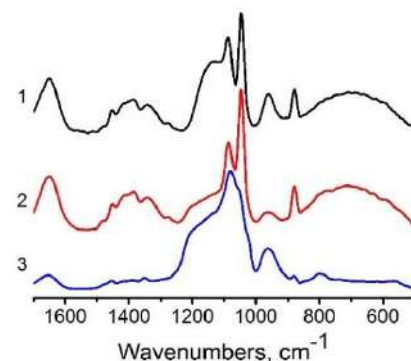


Fig 1. FTIR spectra from sol-gel system after reaction of 0.5 h (1), 23 h (2), and partly dried gel (3).

Therefore, the microstructure of the gel depends on the water content. The ATR FTIR method was proposed as an approach to studying the formation of microstructure of the gel.

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Preparation and properties of microporous materials using organic bridged polysilsesquioxanes

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Abstract: Silicon-based porous materials often contain mesopores or macropores, so that the mechanical strength is reduced due to the low density. The thin film prepared by the sol-gel method of alkoxy silane was found to decrease the refractive index by heat treatment because pores are formed by the decrease of alkoxy groups¹⁾. On the other hand, the thin film of organic bridged polysilsesquioxane has high mechanical strength due to the high bridged-density including cyclic structures in the polymer²⁾. In this study, we investigated the preparation of porous materials with high mechanical properties.

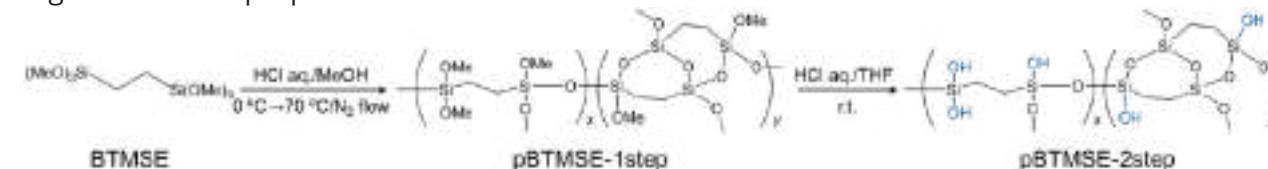


Figure 1. Preparation of pBTMSE-1step and pBTMSE-2step.

BTMSE was polymerized by the sol-gel reaction with water in methanol using HCl aq. as a catalyst at 70 °C under nitrogen flow. Polymers with high molecular weight including many cyclic structures and methoxy groups (pBTMSE-1step) were obtained. Water and an acid catalyst were added to pBTMSE-1step and further stirred to obtain a jelly gel (pBTMSE-2step) in which residual methoxy groups in the polymer were converted to silanol.

Spin-coating films were prepared from both polymers and the refractive indices were measured. The refractive index was 1.42 for pBTMSE-1 step and 1.45 for pBTMSE-2step. In addition, the surface hardness of the thin film of pBTMSE-1step was lower than that of pBTMSE-2step by pencil hardness test. These results suggested that methoxy groups remaining in the polymer acted as a template and decreased the density of the thin film.

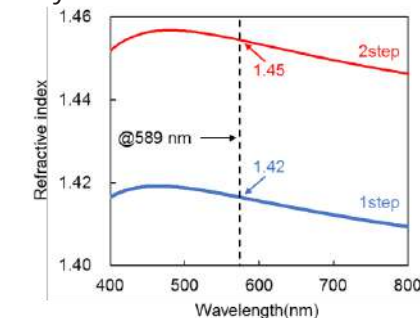


Figure 2. Refractive index of pBTMSE films.

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Modified voltammetric, impedimetric and optical behavior of polymer- assisted sol-gel MgFe_2O_4 nanostructured thin films

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Abstract: Different transition metals due to their multiple oxidation state have been investigated as electrode for electrochemical capacitors and for energy storage applications. Some of the transition metals show extremely good electrochemical performance although they are so expensive and environmentally poisonous such as RuO_2 so they are not good candidate for electrochemical capacitors. Comparing to the simple metal, oxide spinel ferrite (MFe_2O_4 M=Fe, Cu, Mn, Co) have better electrochemical activity and greater electronic conductivity. Since polymers can change the porosity of electrode surface and improve the electrochemical performance, we investigated the effect of polyethylene glycol (PEG) and polyvinylpyrrolidone (PVP) on physical properties of sol-gel prepared magnesium ferrite (MF) thin films. The X-ray diffraction (XRD) results showed the formation of cubic spinel magnesium ferrite for all samples. The surface morphology of films changed and average surface roughness decreased by polymer addition. The height-height correlation function and fractal dimension were evaluated using cube counting and triangulation methods from atomic force microscopy (AFM) images. The refractive index and extinction coefficient of MF thin films decreased by adding polymer while the band gap value increased from 2.24 to 2.72 eV. The PEG addition enhanced the electrochemical performance while PVP addition didn't have significant effect on cyclic voltammetry (CV) of magnesium ferrite thin films. The sample with highest value of PEG showed the maximum specific capacitance (68.5 mF cm^{-2}) and the smallest charge transfer resistance (565Ω) among all samples.

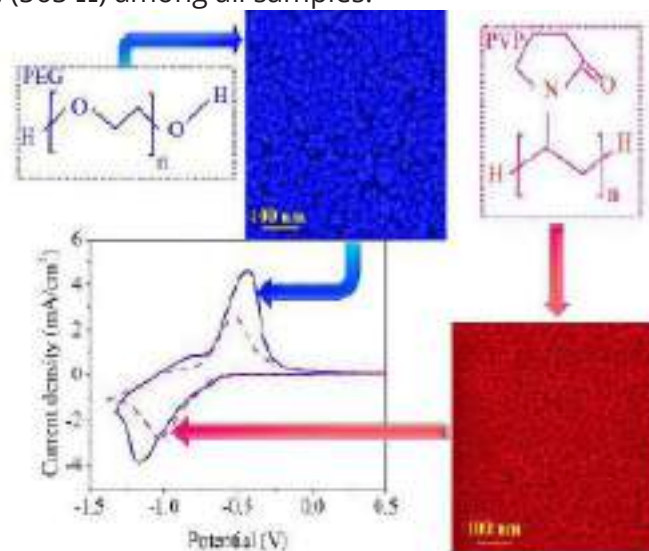


Figure 1. effect of PEG and PVP on morphology and electrochemical properties of thin films

Resilient, Fire-retardant, Robust Polyimide-Polyvinylpolymethylsiloxane Composite Aerogel prepared via Stepwise Chemical Liquid Deposition

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Abstract: Resilient, fire-retardant, robust polyimide-polyvinylpolymethylsiloxane (PI-PVPMS) composite aerogels have been prepared via stepwise chemical liquid deposition (SCLD). The synthesis is based on the formation of PI-PVPMS cross-linked network structure with (3-aminopropyl)trimethoxysilane (APTMS) as a coupling agent to provide reactive sites on the backbone. We successfully realize the PI in-situ growth on the whole super-flexible PVPMS gel skeleton with this simple method. The effect of APTMS amount and deposition time on the properties of final samples was also deeply investigated. The resultant PI-PVPMS composite aerogels show excellent mechanical and thermal properties. They can support at least 10000 times of their own weight and can recover 20% from a compressive strain of 60%. For the thermal behavior, the native PVPMS aerogel burns drastically and becomes ash after being subjected to an alcohol lamp outer flame of around 650°C for 5 min. On the contrary, PI-PVPMS composite aerogels can maintain their structural integrity even after 30 min, indicating the superior fire-resistant property. These results together with the simple synthesis process demonstrate the potential for construction materials using PI-PVPMS composite aerogels. Furthermore, the SCLD synthesis method could also be applied to prepare other composite aerogels, especially for those containing complex polymer.

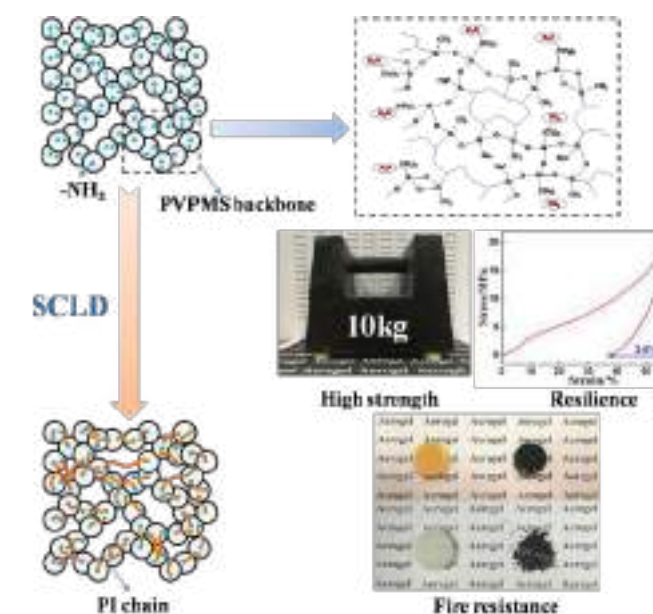


Figure1. The skeleton structure and properties of PI-PVPMS composite aerogel.

Glycerohydrogel materials based on chiral chitosan-containing sol-gel systems

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Abstract: In the work, silicon-chitosan-containing glycerohydrogels based on chiral chitosan polysalts and silicon tetraglycerolates were obtained by the sol-gel synthesis. The influence of the synthesis conditions and the organic ligand's nature on the gelation kinetics, structure and features of the chiro-optical properties of the materials obtained was studied.

Sol-gel technology using pharmacologically active precursors and chiral structure-forming templates is one of the promising areas for designing biocompatible hydrogel materials with a unique stereostructure and a set of novel functional properties, in particular, with controlled sites of complementary-specific interactions.

The aim of the work was the sol-gel synthesis and study of the properties of chitosan-containing glycerohydrogels (monoliths and thin-film plates) based on optically active salt forms of chitosan and silicon tetraglycerolate ($\text{Si}(\text{C}_3\text{H}_7\text{O}_3)_4 \cdot n\text{C}_3\text{H}_8\text{O}_3$).

The following reagents were used: chitosans (CS) with a viscosity-average molecular weight $M_\eta = 30\text{--}200$ kDa, a degree of deacetylation $\text{DD} = 70\text{--}80$ mol % (Bioprogress Ltd., Russian Federation), poly(vinyl alcohol) (PVA) $M_w = 80\text{--}100$ kDa with a weight-average molecular weight of 90–100 kDa and a 95–99% basic substance content (Sigma Aldrich, USA); *L*- and *D*-iso-ascorbic acids (Meligen Corp. and Khimreaktiv Corp., Russian Federation), glycolic acid (GIA, Sigma-Aldrich, USA), silicon tetraglycerolate (IOS UrB RAS, Russian Federation). To obtain glycerohydrogels in the form of monoliths, water-acid solutions of chitosan were mixed with a glycerol solution of $\text{Si}(\text{C}_3\text{H}_7\text{O}_3)_4$ with/without NaCl, 1 wt.% and left for the sol-gel reaction to proceed at a temperature within 4–37°C. PVA was additionally introduced into the system to obtain thin-film plates. The plates were formed by pouring the mixed composition onto a horizontal silicone substrate at $20 \pm 2^\circ\text{C}$ and leaving for 1–2 days. The gelation time of monoliths was fixed according to the loss of fluidity of the system, and that of plates was fixed by the formation of a film structure, easily detached from its substrate.

The effect of the gelation conditions and the nature of the organic ligand on the (rheo)kinetics of the process was evaluated. It was established that an increase in temperature, pH, M_η of CS and the introduction of a salt electrolyte accelerates gelation. The time of reaching the gel point in equiconcentrated systems increased in the row chitosan hydrochloride → glycolate → ascorbate →. In the case of chitosan ascorbate, with the same pH value, the sol-gel process kinetics was determined by the isomeric form of the acid residue. The *D*-derivative had a retarding effect as compared with the *L*-acid. The plates based on chitosan *D*-ascorbate had higher mechanical strength and elasticity under uniaxial tension, and a smaller value of Young's modulus. The results obtained are explained by differences in the chiro-optical characteristics of the sol-gel systems. E.g., chitosan *L*- and *D*-ascorbates differ in the wavelength of the dichroic band maximum and the values of its specific ellipticity, the sign of specific optical rotation (+ and -), the type of dispersion curves (anomalous and smooth ones), and the morphology of the condensed phase (anisodiametric particles with bright pronounced optical anisotropy and tightly packed spherical confocal domains). Using IR spectroscopy, X-ray diffractometry, atomic force and electron scanning microscopy, it was shown that the glycerohydrogel structural framework was formed by interpenetrating networks of organic and inorganic ($\equiv\text{Si} - \text{O} - \text{Si}\equiv$) nature coated with a shell of amorphized silicon-containing structures.

In vitro and *in vivo* studies of the biomedical properties of our sol-gel systems showed no cytotoxicity, high biocompatibility, antibacterial, anti-inflammatory and wound-healing activity, most pronounced for the glycerohydrogels based on chitosan *D*-ascorbate. In addition, the latter ones had an immunotropic effect on the effectors of the innate immunity of microorganisms.



The impact of pores surface on physical properties and phase transition of porous glass-based ferroelectric nanocomposites

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Abstract: The results of FTIR, XRD and differential scanning calorimetry (DSC) studies of empty MAP and MIP porous silica matrices and these matrices filled from the melt by binary mixtures of $K_{1-x}Ag_xNO_3$ ($x = 0.05, 0.10$) are reported in comparison with those obtained for bulk salts in the temperature range of structural phase transitions. Scanning electron microscopic data of the studied empty MAP and MIP glasses confirmed differences in the pore surface texture associated with the presence of silica gel. Accordingly XRD and FTIR all samples contain crystalline phase of KNO_3 and $AgNO_3$. It has been revealed that intensity of crystalline phase of KNO_3 depends on pores size and total ration of $KNO_3/AgNO_3$ in impregnation solution. The results of calorimetric investigation of porous glasses filled with binary mixtures of $K_{1-x}Ag_xNO_3$ ($x = 0.05, 0.10$) are presented. The results shown that in the $K_{1-x}Ag_xNO_3$ nanocomposites anomalies associated with phase transitions were detected. An influence of the mean value of pores sizes on the ferroelectric phase transition temperatures of $K_{1-x}Ag_xNO_3$ nanocrystals embedded into the porous matrices was determined. The impact of pore surface structure and silica gel on the properties of ferroics nanocomposites will be discussed.

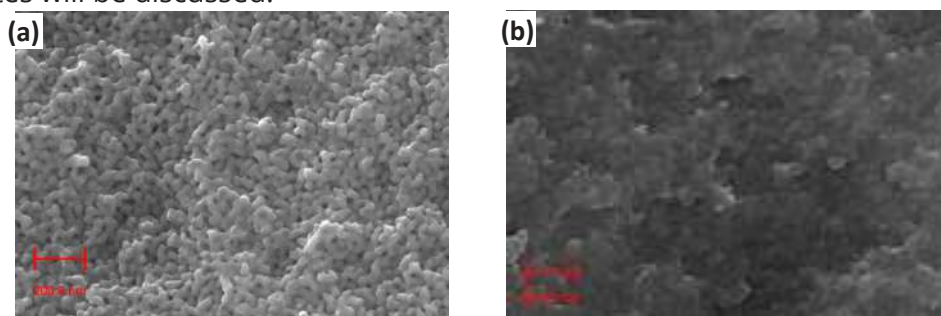


Figure 1. SEM images of empty MAP (a) and MIP (b) porous glass.

The authors are grateful and acknowledge the efforts of dr G. Golovina and M. Girsova (Institute of Silicate Chemistry, Russian Academy of Science, St. Petersburg) for FTIR measurements.

Sustainable hybrid aerogels made of tannin and silica

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Abstract: Over the last decades organic and biopolymer aerogels have evoked increased interest, with resorcinol-formaldehyde based gels being the most intensively studied ones as they show excellent materials properties and are suitable precursors for carbon gels⁽¹⁾. By simply altering the sol-gel processing parameters, the pore structure as well as the overall porosity can be deliberately adjusted, resulting in gels of interest for a wide range of applications starting from thermal insulators to electrode materials. However, resorcinol as well as formaldehyde represent costly and environmentally harmful reagents. Therefore, green and cheaper alternatives have been investigated over the past years. Instead of resorcinol, the usage of the polyphenolic tannin, which is a natural, sustainable and low cost material, has been reported allowing the preparation of highly porous tannin-formaldehyde gels⁽²⁾. Nevertheless, still toxic formaldehyde is used and hence alternative bio-friendly precursors have to be found in order to obtain a fully sustainable class of aerogels.

In this work, the synthesis as well as the characterization of an innovative hybrid aerogel system made of the tree extract mimosa tannin and a glycol based silica precursor, namely tetrakis(2-hydroxyethyl)orthosilicate (EGMS) or water glass is presented. Highly porous, homogeneous hybrid tannin-silica aerogels have been prepared by adjusting the sol-gel processing conditions. The resulting materials are thoroughly investigated regarding their chemical structure and composition and synthesis-structure relationships will be discussed in detail. In addition, to the substitution of resorcinol and formaldehyde, hybridization of tannin with silica might be a sustainable alternative for porous carbon and/or silicon carbide gels. Furthermore, the tannin/EGMS system is expected to allow simple functionalization using organofunctional silanes.

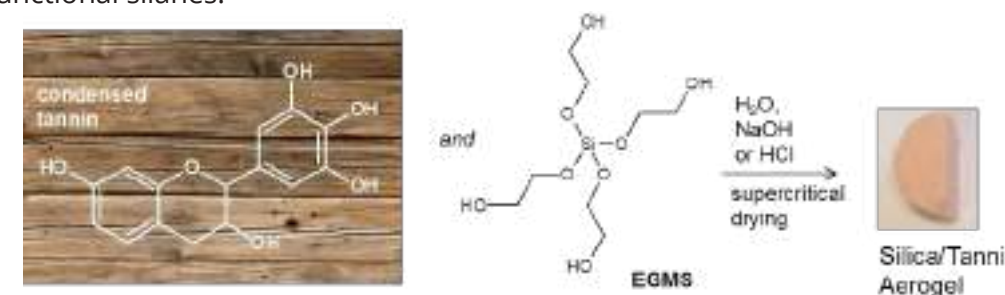


Figure 1. A sustainable hybrid aerogel made of Prorobinetinidin (condensed tannin) and tetrakis(2hydroxyethyl)orthosilicate (EGMS).

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Combined first principles and experimental insights on Eu-, Ho-, Yb-doped $\text{Bi}_2\text{Ti}_2\text{O}_7$

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Abstract: Doped bismuth titanate pyrochlores may be interesting as materials with high dielectric constant, low leakage current, mixed electronic-ionic (proton) conductors, photocatalytic systems under visible lights, and photoluminescence materials. Rare-earth elements have the suitable ionic radius, charge state for substitution Bi-atoms in $\text{Bi}_2\text{Ti}_2\text{O}_7$ and formation of the stable doped pyrochlore compounds. Moreover, chemical synthesis methods (e.g. co-precipitation) can realize metastable conditions in order to obtain new pyrochlore compositions with high dopant content.

Ab initio calculations were performed by means of the DFT using the PAW method as implemented in VASP. The generalized gradient approximation for exchange-correlation potential in the PBE form was used. Doping in the pyrochlore structure was simulated by the substitution one Bi (Ti) atom to one dopant atom (Eu, Ho, Yb) within the $\text{Bi}_4\text{Ti}_4\text{O}_{14}$ cell, which corresponded to the 25 at.% substitution. The cut-off energy of 500 eV and k-mesh $8 \times 8 \times 8$ were used. The geometry optimization was performed until the forces on the atoms became less than 0.5 meV/Å. The calculations of the total and partial DOS, the band structure, dielectric and optical parameters for the pyrochlore models have been carried out after the geometry optimization.

The pyrochlore-type compounds $\text{Bi}_{2-x}\text{M}_x\text{Ti}_2\text{O}_{7-8}$ (M = Eu, Ho, Yb) were obtained via co-precipitation method in the fine powder state. According results of DFT calculations the substitution of Bi-atoms by the dopant atoms is an energetically favorable process, rather than Ti-substitution. This fact is in agreement with the synthesis of doped pyrochlores with appropriate element composition and previously observed results [1]. Detail descriptions of the homogeneity regions for doped compounds, the study of the distribution dopant atoms in the crystallographic pyrochlore sites, thermostability, morphology, optoelectronic properties, dielectric behavior of doped BTO are presented based on the comparative results of ab initio and experimental study.

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Monitoring and control of the aging of a hybrid sol-gel formulation for the protection of polymeric materials

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Abstract: Sol-gel protective transparent coatings on polymeric substrates such as polycarbonate or PMMA have been widely studied for optical lenses, electronic components or construction materials. The improvement of resistance to scratch damage is an important property that it has been studied modifying the surface by the deposition of sol gel coatings. For the development of this functional films the combination of inorganic and organic precursor in a single-phase material provides unique possibilities to tailor the mechanical and optical properties. These hybrid materials combine the most important properties of their constituents, like high transparency (glasslike), low processing temperatures (polymer-like), sufficient thermal stability (silicone-like), and are easily accessible because of an unique availability of the respective precursors (commercially available metal alkoxides and organo(alkoxy)silanes).

Hybrid silica coatings based on 3- glycidoxypropyltrimethoxysilane (GLYMO), tetraethylorthosilicate (TEOS) have been selected for the development of sol-gel coating. By means of the addition of GLYMO, the epoxy silane creates an organic matrix that blends with the inorganic SiOSi matrix formed from the TEOS. The combination of the blended matrix results in coatings with good adhesion to substrates and improved mechanical properties obtaining scratch resistant surfaces.

During this work, the monitoring of the hybrid sol by means of different techniques and control of the reactions associated with ageing, in order to determine the optimum moment for the deposition of the coating is studied. Spectroscopy such as FTIR provides versatile tool to investigate hydrolysis and condensation reactions of organo(alkoxy)- silanes. Parameters such as a viscosity or surface tension of the sol have been also studied with a rheometer and Du Nouy method.

Synthesis of graphene-zirconia nanocomposites

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Abstract: Nanocomposites based on graphene and zirconia attract attention of the developers and researchers of new materials because they have unique physicochemical properties: high specific surface area, improved electrical and thermal conductivity, high (photo/electro)catalytic activity. Composites based on graphene and zirconia are intended for the development fuel cells (catalyst support), solar cells, supercapacitors, electronic devices, catalyst systems (Fischer-Tropsch synthesis, hydroprocesses, synthesis/decomposition of ammonia, photocatalysts for environmental protection (decomposition of organic dyes and solvents), thermal barrier coatings, biocompatible matrix for protein immobilization, transistors (advanced gate dielectrics). One of the main challenges in the production of graphene-based composites is homogeneous dispersion of graphene and metal-oxide in the material volume without the formation of structural defects. The purpose of this study was to develop a method for the mild conditions synthesis of nanocomposites based on oxygen-free graphene and nanocrystalline zirconia, the crystalline size of which does not exceed 10 nm. It combines sol-gel synthesis and ultrasonic exfoliation of graphene sheets from the surface of synthetic graphite in an organo-inorganic acidified medium. Available zirconyl nitrate was used as sources of metal. In the carried out research, it was shown that during the formation of graphene-zirconia composite structures from the mixture of as-prepared Zr-containing sol and graphene suspension, graphene sheets take part in the formation of the hybrid structure. At a gelation stage, they prevent coarsening of the sol particles. In the following stage, graphene is the texturing agent in formation of overall nanocomposite structure. As a result, isolated crystallites of zirconia are incorporated into graphene sheets (Figure 1). There is no chemical interaction between graphene and zirconia, which indicates the formation of van der Waals system. The work is supported by RFBR, Grant No: 17-02-00759_a.

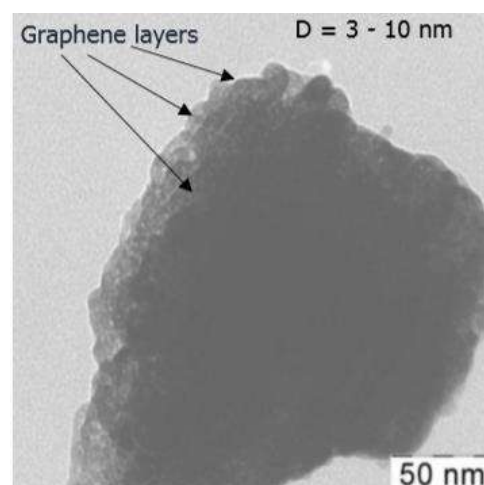


Figure 1. TEM image of the graphene-ZrO₂ composite calcined at 500°C.

Porous MgF₂-NiF₂ binary fluorides as hydrogenation catalysts

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Abstract: Nickel-containing catalysts are applied on a large scale in chemical industry in many reactions of organic synthesis including hydrogenation of nitro compounds, alkenes, alkynes, aromatic compounds, carbonyl compounds, nitriles, as well as in ammonolysis of alcohols and methanation reactions. The most frequently used nickel-containing catalysts are Raney nickel and nickel on different supports. Nickel is usually introduced onto supports by the precipitation method or by impregnation of a support with a nickel salt-containing solution.

The NiF₂-MgF₂ binary fluorides used in our research were prepared by the precipitation from a solution of a mixture of nickel nitrate(V) and magnesium nitrate(V) with ammonium fluoride solution. The obtained precipitate of binary fluorides was subjected to the treatment with hydrogen flow at 500°C. As a result of it, a part of NiF₂ undergoes reduction to metallic nickel, whereas MgF₂ is stable in this conditions and no reduction of this compound was observed. Magnesium fluoride makes a support on which the nickel metal is deposited.

Depending on the initial composition of NiF₂-MgF₂ binary fluoride mixture and reduction temperature, the total content of nickel metal was in the range of 5-50 wt.% as determined by XRD analysis. The surface area of metallic nickel ranged from 0.5 to 25.0 m²/g of catalyst as determined by means of hydrogen chemisorption.

The obtained catalysts have been studied in the reaction of toluene hydrogenation to methylcyclohexane. The catalyst containing 85 mol% NiF₂ and 15 mol% MgF₂ was the most active and its activity exceeded that of a commercial Raney nickel catalyst.

The way of nickel catalyst synthesis developed in this study is very simple, because it does not require the introduction of a support and enables a precise control of nickel metal content. The NiF₂-MgF₂ catalyst, in contradistinction to Raney nickel, is not pyrophoric and can be stored in air for a long time without a loss of activity.

The work was supported by grant no. POWR.03.02.00-00-1020/17 co-financed by the European Union through the European Social Fund under the Operational Program Knowledge Education Development.

Three-dimensional Graphene aerogel attached with polar compounds for High performance Li-S Battery

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Abstract: Lithium-sulfur (Li-S) batteries are promising alternatives to conventional Li-ion batteries in terms of outstanding theoretical specific capacity (1675 mAh g^{-1}), low cost and environmental benignancy [1]. However, their practical applications are deterred by a series of technical challenges, especially the dissolution and migration of intermediate lithium polysulfide (Li_2S_n with $4 \leq n \leq 8$) in organic electrolyte during charge and discharge processes. The “shuttle effect” lead to the low sulfur utilization, anode corrosion, large capacity decay and the poor coulombic efficiency [2]. Nano-structure and chemical adsorption of cathode material hold a great promise in mitigating polysulfide shuttling problem. Here, we design and synthesize composite materials consisting of three-dimensional (3D) graphene aerogel (GA) and polar compounds uniformly dispersed on the graphene sheets as sulfur (S) hosts by a facile hydrothermal method. As a result, the hybrid materials with 70 wt% of S loading exhibit a high initial discharge capacity, a high rate capability, and a superior cyclic stability. The excellent electrochemical performances of these hybrid materials could be ascribed to the synergistic effects of two aspects: (1) the structural support, physical confinement for S and strong electrical conductivity of 3D interconnected mesoporous GA; (2) the chemical interactions towards the S species of polar nanocomposites. Such architecture design paves a new way to synthesize well-defined sulfur hosts to tackle the challenges for high performance Li-S batteries.

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Sol-gel revitalization of porous refractory ceramics

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Abstract: The honeycomb structured supports (Fig. 1) are widely applied in heterogeneous catalysis, in separative processes (filtration, adsorption), etc. If the mentioned porous bodies are manufactured using refractory ceramic precursors (powders) or enter in the refractory state after proceeding, it appears often difficult to fulfil these supports with chemically bonded active components because of their surfaces are drastically deprived from functional active centers being able to be involved into the reactions of ion exchange (for instance, as Bronsted acid (BA) centers $\equiv\text{E}-\text{O}-\text{H}$ acting as H^+ ion exchangers). We suggest applying the sol-gel (SG) method for making the surfaces of refractory porous ceramics highly hydrophilic (Fig. 2) and able to promote the H^+ ion exchange reactions. In particular, it may be seen that several layers of activated alumina $\gamma\text{-Al}_2\text{O}_3$ (for example – 5) deposited using the SG technics on the surface of a refractory honeycomb lozenge constituted by $\alpha\text{-Al}_2\text{O}_3$ completely reverse the surface acidity type: the initial refractory surface multi-layered with γ -alumina deposits manifests a domination of BA-centers [1] (Fig. 3) obligatorily required for its efficient chemical modification using some widely used industrial technics, such as wet impregnation in aqueous solutions, epitaxial deposition, CVD-ML (ALD), SG and so on. A variant of the SG method implemented in this work was partially inspired by [2], but the protocol was profoundly revised and simplified. It will be described in details in the final text.



Figure 1. Honeycomb lozenge.

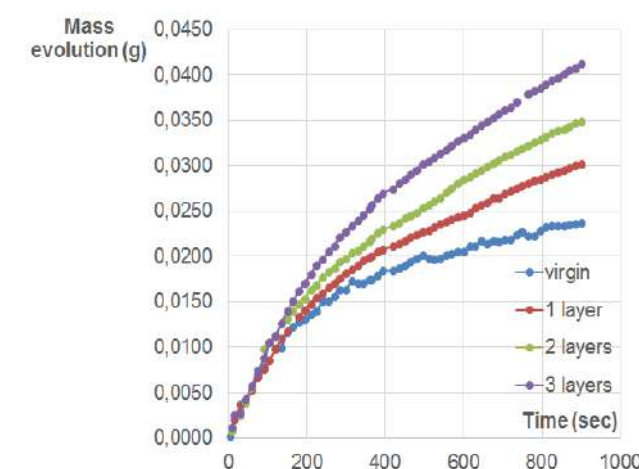


Figure 2. Adsorption isotherms of water vapor at the surface of a virgin refractory honeycomb lozenge constituted by $\alpha\text{-Al}_2\text{O}_3$ (Fig. 1) and at the lozenges modified with 1, 2 and 3 layers of activated alumina $\gamma\text{-Al}_2\text{O}_3$; test conditions: temperature – $24.3\text{-}24.4^\circ\text{C}$, air relative humidity – $34.2\text{-}34.7\%$ (at the left).

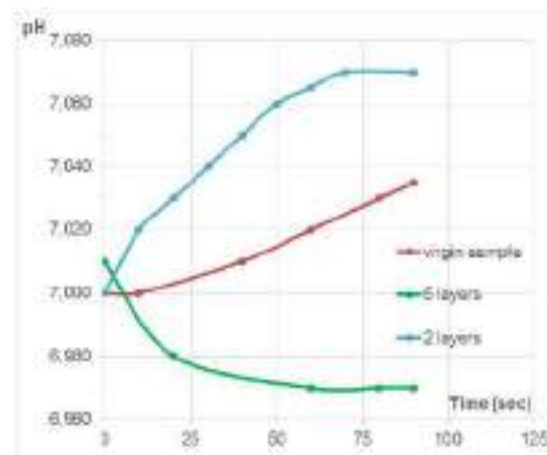


Figure 3. Evolution of the pH index in agitated suspensions "water – powdered solid material" [1] (at the right).

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Aramid-zirconia nanocomposite coating with superior corrosion protection of stainless steel in saline media

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Abstract: In marine based industries, stainless steels corrosion resistance requires continuous surface improvement and enhanced protection by utilizing new surface coatings. In this study, a thermally stable aramid-zirconia nanocomposite has been successfully prepared via the sol-gel process to produce zirconia network structure bonded with the polymer chain. The synthesized nanocomposite was fully characterized via different techniques such as: transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS). The investigated nanocomposite (using 10% zirconia) was coated on the stainless steel surface through a facile and effective spin coating method to examine its protection to steel alloy in saline solution (3.5 % NaCl). The aramid-zirconia nanocomposite coating has been found to provide an outstanding corrosion resistance to steel surface which led to protect it against the corrosive marine environments. The electrochemical impedance measurements were performed to evaluate steel resistance against dissolution in chloride solution in the absence and presence of the investigated nanocomposite showed corrosion protection efficiency of 96.3 % using three coated layers of the nanocomposite. Also, the potentiodynamic polarization plots showed pronounced decrease in the corrosion current values which confirm the formation of the passive layer for mitigating the corrosion reaction and ions diffusion. The water contact angle of bare stainless steel and the aramid-zirconia coated stainless steel were found to be 14° and 125°, respectively confirming the hydrophobic nature of the investigated coating. On the other hand, the results obtained from the electrochemical and surface techniques were used to clarify the protection mechanism. The aramid-zirconia nanocomposite coating showed remarkable protection performance by controlling the charge transfer at the interface between the steel alloy and the electrolyte which prevent the alloy dissolution.

Porous microspheres for chemical immobilization

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Abstract: In this work, an adapted sol-gel method combined with emulsion technology is presented. It involves a controlled phase separation by spinodal decomposition phenomenon, which occurs within the tiny droplets of the emulsion, leading to a varied portfolio of customized macroporous microspheres (microscaffolds) for advanced functionality materials.

This work is part of a Technology Platform on Microencapsulation and Immobilization, where functional microspheres or core-shell microcapsules, either with hybrid composition, or with hybrid or multifunctional performance are developed. Their custom-tailored morphology, porosity and organic functionality enable the entrapment and grafting of a variety of chemical species, which can be further assisted by low vacuum conditions. The “loaded” microscaffolds can be used not only for an application where a slow release of the entrapped compound is needed, but also for an application in which the compound loss is unwanted, i.e. an anchored active chemical is desired. They are potentially useful in applications ranging from antifouling coatings to photocatalysis.

As an example, silica-epoxy hybrid microscaffolds are herein reported (Figure 1), exhibiting a “wormlike” morphology¹. They were developed by sol-gel processing combined with a microemulsion (water-in-oil) technique, using as Si precursors, tetraethylorthosilicate (TEOS) and 3-glycidyloxy propyl trimethoxysilane and were subsequently impregnated with a biocide (Econea[®]), which was recently approved by EU Regulator (BPR) as a safe biocide. The reaction between the secondary amine of Econea and the oxirane ring of the silica-epoxy microscaffold resulted in the entrapment and partial grafting of the biocide. The presence of Econea[®] within the microscaffolds was revealed by infrared spectroscopy, thermogravimetric analyses (TGA) and scanning electron microscopy (SEM-EDX). The release of Econea[®] from the scaffolds when immersed into salted water was followed by TGA and their biocidal effect was assessed against *Staphylococcus Aureus* bacteria showing very promising results and revealing a hybrid antifouling performance, based on contact and biocide release mechanisms. These findings lead to a more environmental friendly antifouling strategy, able to combine a more efficient, long-lasting antifouling performance in water-immersed structures, together with non-toxic properties.

Other case studies will be presented, as well as new findings on the emulsion stability and the mechanisms involved in the microscaffolds’ production steps.

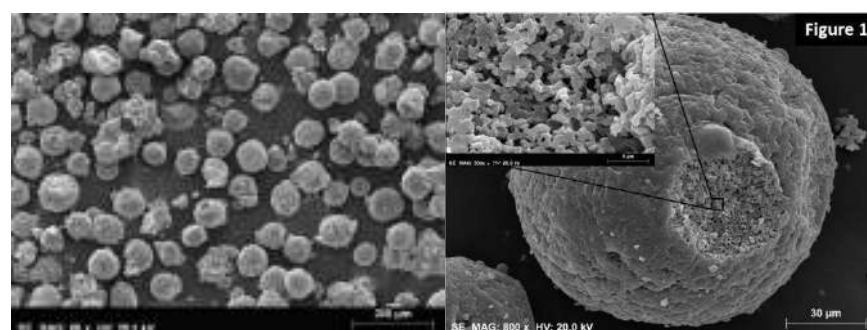


Figure 1: Photomicrographs of the silica-epoxy microscaffolds, where the inset reveals the worm-like macroporosity used for active chemical entrapment and immobilization.

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Synthesis of hydrophobic polysiloxane aerogels directly in scCO₂

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Abstract: Aerogels are porous materials with extremely low density, high specific surface area, large porosity and very low thermal conductivity. There are several classes of aerogels: inorganic, organic and hybrid organic-inorganic. Among them the most popular aerogels are silica-based aerogels, non-silica inorganic aerogels, carbon aerogels and polymeric aerogels such as polysiloxane.

For aerogels preparation special methods which generally are based on sol-gel process with the next supercritical drying are used. Another alternative method for obtaining aerogels is carrying out the process of gelation directly in scCO₂ (DSGSCF - "Direct Sol-Gel process in SuperCritical Fluid"). This approach favorably differs from the "classic" one because it does not have a high-cost process of supercritical drying. Replacing the solvent with "volatile" CO₂ makes the solvent removal stage relatively easy, avoiding costly drying processes or solvent removal, that is very important when processing materials based on polymers.

In this work we have described a new method of the synthesis of hydrophobic polymeric aerogels based on vinyl- and thiol-containing siloxanes^[1] and cyclosiloxanes, which is carried out directly in the scCO₂ media (figure 1). The applying of this approach significantly decreases costs for producing aerogels by removing the drying step.

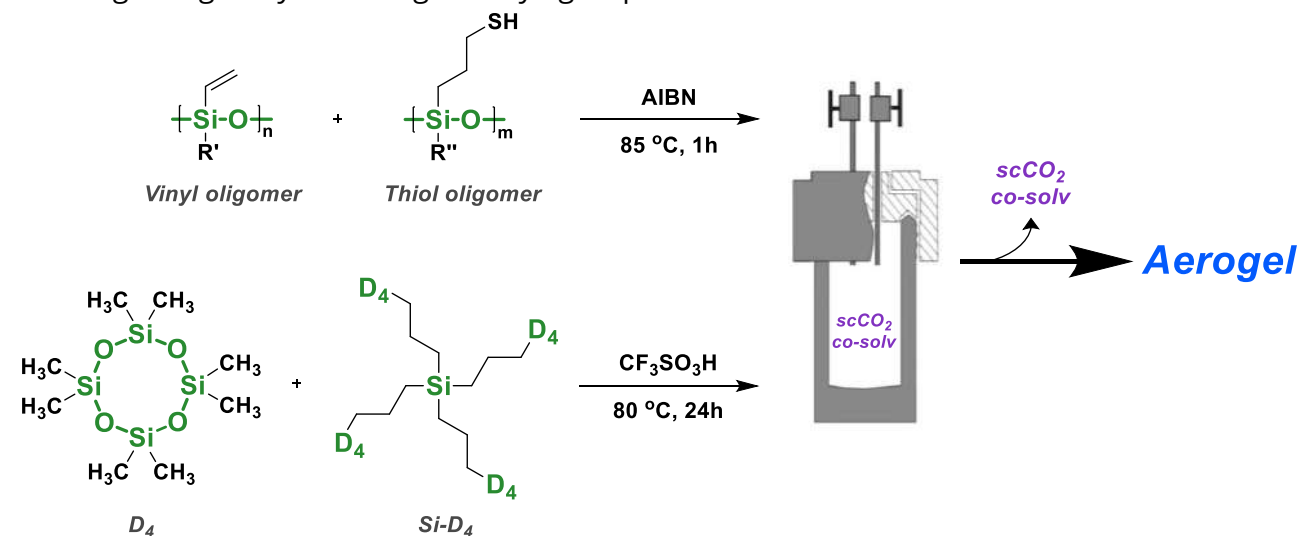


Figure 1. Synthesis of polysiloxane aerogels directly in scCO₂.

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Iridium supported on aluminum oxo-fluorides – characteristics and hydrogenating properties

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Abstract: Metal fluorides have attracted more attention since last decade, because of their potential applications to catalysis, ceramics, optics and energy-storing systems. For our point of view, their catalytic applications seem to be encouraging fact which the metal fluorides become an attractive alternative to oxide supports.

The aim of the presented work was the preparation of iridium catalysts (1wt.% Ir) supported on binary AlF₃-Al₂O₃ systems and investigation their catalytic activity in the hydrogenation of toluene. The catalytic activity was compared with catalysts supported on AlF₃ and Al₂O₃ supports. The binary supports were obtained by sol-gel and suspension methods in the reaction of aluminum nitrate or ammonium aluminum carbonate hydroxide (AACH) with an aqueous solution of HF. The obtained gels were calcined under air at 500°C for 4h. The influence of the aluminum precursor on the physicochemical properties of supports was studied. The prepared supports and catalysts were characterized by XRD, N₂ adsorption/desorption measurements, TPR-H₂. The mean size of metal particles was determined by H₂ chemisorption measurements.

The combination of two phases 50AlF₃-50Al₂O₃ led to obtaining the support characterized by great surface area (Figure 1), and pore structure promoted the catalytic activity in the hydrogenation of toluene (Figure 2).

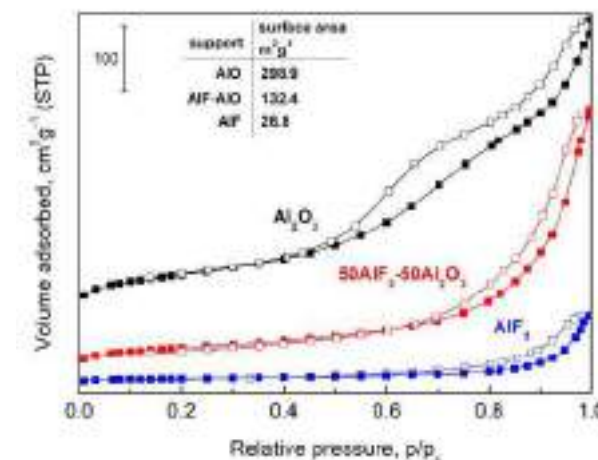


Figure 1. Nitrogen adsorption-desorption isotherms and BET surface area of supports obtained by suspension method calcined under air at 500°C for 4h.

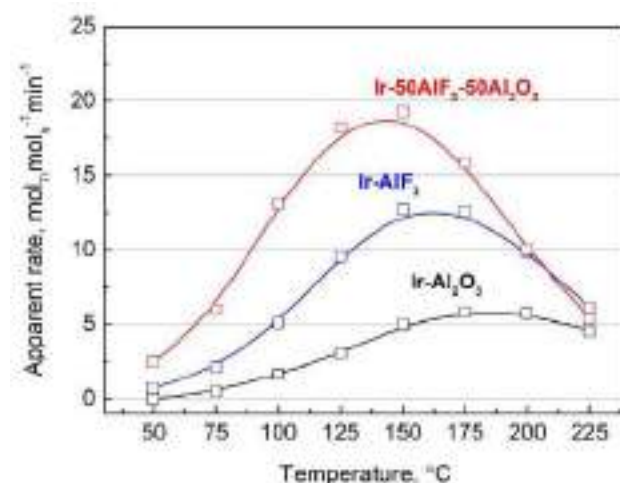


Figure 2. The effect of support on the apparent rate of hydrogenation of toluene as a function of temperature. Activation of catalysts: 400°C, H₂ = 100cm³min⁻¹, 2h; Reaction: cTI = 0.75molcm⁻³, H₂ = 50cm³min⁻¹.

The work was supported by grant no. POWR.03.02.00-00-I023/17 co-financed by the European Union through the European Social Fund under the Operational Program Knowledge Education Development.

Ex situ infrared and Raman spectroscopy of electrochromic vanadium-alkoxide-based films

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Abstract: Alkoxides of various transition metals can be effectively used for the production of sol-gel films with electrochromic properties. For example, vanadium(V) tri-n-propoxide oxide in isopropanol offers the possibility of preparation of crystalline V₂O₅ when thermal treatment is performed at temperatures above 300 °C. Such preparations are suitable for deposition on electronically conductive glass substrates, but the use of flexible polymeric substrates demands the preparation of films at lower temperatures, i.e., not above 250 °C. In order to prepare low-temperature V-oxide films (150 °C) with embedded V₂O₅ nanocrystallites, we adopted the preparation route. Namely, commercial V₂O₅ powder was introduced into vanadium-alkoxide-based sol and milled in order to decrease the size of agglomerates to the nanometer size. The optical quality of films prepared from such dispersions is very good and enables their application in flexible electrochromic devices.

The properties of sol-gel crystalline V₂O₅ films prepared at 400 °C and also low-temperature V-oxide films (150 °C) were compared using various techniques. SEM and AFM micrographs confirmed that the surface of low-temperature V-oxide films is slightly more rough compared to crystalline V₂O₅ films. TEM micrographs showed the presence of V₂O₅ nanocrystallites in the low-temperature V-oxide films. Electron energy-loss spectroscopy (EELS) confirmed the higher amount of vanadium atoms in 4+ state in the initial low-temperature films in comparison with crystalline V₂O₅ films. Electrochemical techniques in the safe potential range were applied to demonstrate the optical changes in both types of films that are related with the transformation of vanadium sites between 5+ and 4+.

The insight into changes that occur in the films during electrochemical cycling can be followed by using different vibrational spectroscopies. From this reason we used three coupled techniques *ex situ*: (i) near grazing incidence angle infrared reflection-absorption technique, (ii) IR absorbance technique and (iii) Raman spectroscopy. Each coupled electrochemical-spectroscopic technique is characterized by certain limitations, but also possesses certain advantages which will be disclosed. The results of both IR techniques (i, ii) showed consistent characteristics; that are the red shift of the vanadyl mode and the gradual disappearance of the bridging V-O-V band. The Raman spectra (iii) revealed that the vanadyl band was red shifted, but also split into two components. The observed changes of vanadyl modes are consistent with the literature reports on increase in the interlayer distance of V₂O₅ layers. The paper will show the possibilities of all three coupled techniques in investigation of sol-gel electrochromic films.

The research leading to these results was funded by the Slovenian Research Agency (Project L2-7630).

Changes in the properties of silica thin films applied on polymers according to structure modifications

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Abstract: One of the biggest advantage of the sol-gel method is possibility to influence on materials properties by changing synthesis parameters, like used reactants, solvents, pH of reactions, aging, thermal treatment etc.. While, the dependencies between synthesis parameters, resultant structure and finally properties of pure silica coatings are well known and described, the modifications of the silica network by functionalization with organic groups still bring plenty of opportunities to obtain new materials with desired parameters.

In this study the Authors by modification of silica structure with variety of organic groups affect the properties of coating materials striving to obtain materials with the best combination of barrier and mechanical properties according to idea presented in Figure 1. The introduction of organic groups to silica aims to enhance the mechanical properties of the most dense structures, which are too fragile to can be applied in case of pure silica. The barrier properties of obtained materials were measured with different gases with the smallest kinetic diameters and deformations causing cracking of the coatings were determined. The mechanical examinations were also supplemented by the scratch resistance and adhesion measurements. Moreover, physicochemical properties showing the materials structure were determined and collated with the barrier and mechanical properties changes. The additional novelty of the research is the type of used substrate – results for coatings deposited on polymeric materials are limited, however chosen substrate is very attractive due to its exceptional properties, e.g. light weight, elasticity and opens up new application possibilities, especially for devices which require to be flexible. The low temperature processing has been used during syntheses.

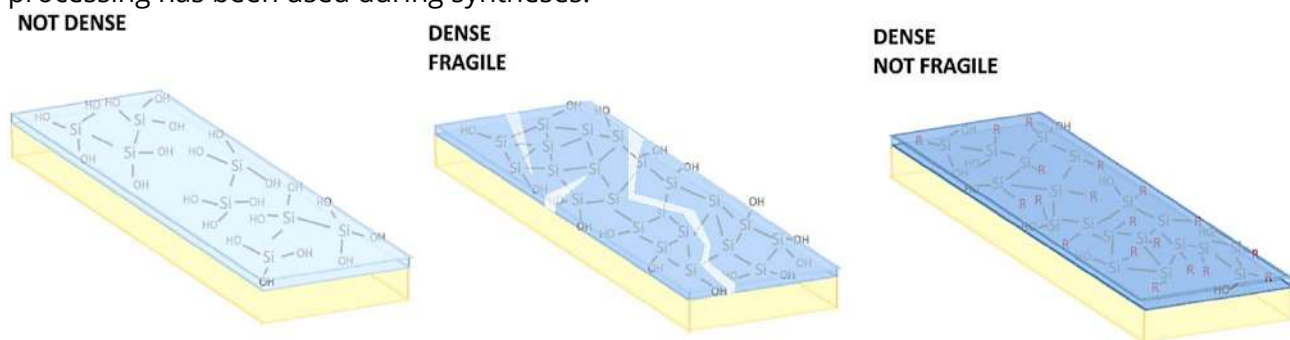


Figure 1. The idea of silica structure modification influencing the properties of coating.

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Metal-organic framework-silica aerogel composites: advance materials for absorption, separation and catalysis

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Abstract: Metal-organic frameworks (MOFs) combining the well-defined structural characteristics, large surface areas, tunable surface properties and pore size are promising candidates for separation and purification of liquid mixtures. MOFs are mostly obtained in the form of fine powder with wide size distribution of micron particles that are extremely difficult to shape into larger pellets. Unfortunately, in this form it is almost impossible to use the metal-organic frameworks in catalysis, adsorption and chromatography under the flow regime on a commercial scale due to high drag, material loss and etc. This circumstance blocks the development and implementation of any efficient processes based on these materials in real processes under flow regime and blanks the most advantages and unique properties of the MOFs. Therefore, it is a real challenge to find the adequate approach for packing of MOFs in a shape suitable for continuous flow processes).

We proposed the novel universal approach for the synthesis of MOFs silica aerogel composites via sol-gel method and subsequent drying in supercritical CO₂ to minimize the deterioration of the individual properties of MOF and silica aerogel structures and tune its properties to be acceptable for flow mode. This approach is based on the adding MOFs powder as a suspension into a pre-synthesized SiO₂ sol just before gelation [1]. Such an approach allows using less acid and bases for the hydrolysis and polymerization of silica precursors that preserves the MOF structure as well as microspores of final composites. The set of various MOF-silica aerogel composites based on different MOFs (HKUST-1, Fe-BTC, ZIF-8 and UiO-67) was synthesized. As an example, figure 1 shows composites HKUST-1@SiO₂, ZIF-8@SiO₂ and HKUST-1&ZIF-8@SiO₂. We also coupled the sol-gel and emulsion methods for the synthesis of MOF@SiO₂ aerogel composites for the first time directly into the pellets, which can be used in continuous flow processes without any further treatment [2].



Figure 1. Photography of monolithic MOF@SiO₂ aerogel composite.

The HKUST-1@SiO₂ composites are suggested for the efficient separation of unsaturated hydrocarbons from saturated aliphatics by liquid phase chromatography. This is the first time MOF based composites are used for the separation of organic molecules by conventional column chromatography [1]. It was found that the HKUST-1@SiO₂ pellets catalyze isomerization of styrene

oxide to phenyl acetaldehyde with high selectivity in a flow reactor [2]. Thus, the proposed approach for synthesis of MOF composites creates the potential to use a wide range of MOFs in continuous flow catalysis.

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Enzyme Immobilization on Ordered Mesoporous Materials

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Abstract: In the last decades, concerns about the hazards of carcinogenic compounds found in indoor air have risen. Among those compounds, formaldehyde, which is well-known to be found in paints, tobacco smoke, open fireplaces, insulating foams, lacquers, glues, varnishes, paper and household products, is of grave concern. With the aim of removing formaldehyde from indoor air, our work focused on the immobilization of an enzyme (FDH) catalyzing the following reaction in the presence of NAD⁺ as an enzyme cofactor: $\text{H}_2\text{CO} + \text{H}_2\text{O} + \text{NAD}^+ + \text{FDH} \rightleftharpoons \text{HCOOH} + \text{H}^+ + \text{NADH} + \text{FDH}$

One of the main challenges in this work was to preserve the activity of an enzyme immobilized in a harsh environment and to maintain its activity for a long time. Ordered mesoporous silica and periodic mesoporous organosilicates materials have shown to be good candidates. They offer a large specific surface area and their physico-chemical properties as well as their structural properties can be tailored during (or after) their sol-gel syntheses [1,2].

FDH was produced and protein-engineered to have a His-Tag sequence, allowing purification on a Ni²⁺ chromatography column. Pure FDH was successfully immobilized on different supports and its activity was assessed by UV-Vis spectrometry of NADH. The immobilization was characterized by solid state ²⁹Si NMR and by IR spectroscopy while enzyme loading was characterized by TG-DSC. The geometrical properties of supports were characterized by Hg porosimetry, nitrogen adsorption/desorption, TEM (cf. Figure 2) and by small-angle X-ray scattering. Altogether, these results allowed us to investigate relationships between the activity of immobilized enzymes and the environment provided by their supports.

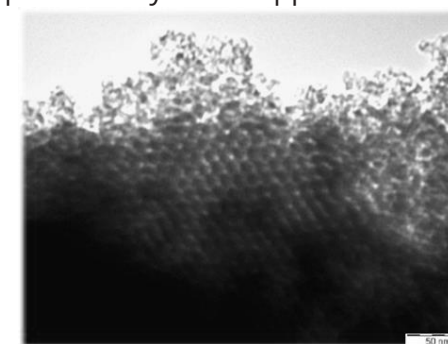


Figure 2. Transmission Electron Microscopy image of a modified SBA-15 powder. A swelling agent was added during the synthesis to expand the pores of the material allowing the enzyme to enter the pores. The ordered hexagonal structure is preserved.

Glutathione-Responsive Hydrogels with Thiol-Based Crosslinking for Designing Controlled Drug Release Devices

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Abstract: Bio-stimuli-responsive soft materials have been subject to intense study from a standpoint of their possible application to smart drug delivery and release devices. Glutathione (GSH) is well known as a cellular reductant that influences the antioxidant defense and nutrient metabolism of cells and regulates cellular events. Several intracellular compartments such as cytosol, mitochondria, and nucleus contain a high concentration of GSH (2-10 mM), which is 100-1000 times higher than that in extracellular fluids (2-10 μ M). Moreover in tumor cells the GSH concentration is at least four times higher compared to normal tissues. Therefore, chemical components (or chemical bonds) that easily make a response to the millimolar range of GSH concentration in the intracellular compartments of tumor cells are helpful for constructing an excellent system for the controlled drug release. From the significance of designing GSH-sensitive materials, we report the preparation of hydrogels with cross-linkages making cleavable in the presence of higher concentration of GSH.

GSH-sensitive hydrogels was synthesized from alkyl- (or aryl-) thiol-functionalized 4-armed poly(ethylene glycols) (PEG) and maleimide-functionalized 4-armed PEG. The thiol functional groups with different pK_a values as a hydrogel cross-linker were judiciously selected to enable microenvironment-controlled degradation of hydrogels and controlled release of drug molecules.

Hydrogels from alkylthiol-functionalized 4-armed PEG have no degradable functional groups and are expected to serve as a non-degradable material. On the other hand, a lower pK_a of arylthiol-based cross-linkages undergo degradation via click bond cleavage, which induces thiol exchange reactions in the presence of GSH providing a reducing microenvironment. The hydrogels were successfully formed by mixing precursor solutions of thiol-functionalized 4-armed PEG and maleimide-functionalized 4-armed PEG at a ratio of 1:1. Then, we evaluated the degradation behavior of hydrogels by mass loss experiments in the presence of GSH. The results confirm that the linkages formed from arylthiol undergo thiol exchange at a GSH-rich microenvironment. In order to demonstrate the utility of this GSH-sensitive degradable system for selective release, 100-nm sized fluorescent liposomes were entrapped within the hydrogel as a model drug delivery vehicle. Since the size of liposomes is around 10 times larger than the estimated size of the network of polymer hydrogels, the release of liposomal vesicles was expected to be promoted by the hydrogel degradation. The release of liposomes in response to appropriate stimuli causing degradation of the cross-linkages was monitored in solution by fluorescence spectroscopy. The hydrogels with alkylthiol-based cross-linkages exhibited a limited release of liposomes in incubation with 10 mM GSH solution. On the other hand, a clear rapid GSH sensitive release was observed in the hydrogels with arylthiol-based linkages. The rapid release can be attributed to the cleavage of the succinimide thioether linkages and the consequent thiol exchange reactions that occur in the presence of GSH. Although we will make a more detailed report on our presentation, we also designed disulfide bond-based hydrogels that could be used to regulate GSH sensitive degradation kinetics for a variety of pharmaceutical or medicinal applications.

These unique GSH degradable hydrogels designed in this study are promising for local drug release of therapeutic devices in GSH-rich microenvironments such as cancer tissues.

Aerogel Contribution to the Energy Efficiency in Industry - Cluster of German Federal Ministry of Economic Affairs and Energy

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Abstract: In order to devise a long term strategy regarding aerogels development, German experts from industry and academia have formed a community of interests supported by BMWi (German Federal Ministry of Economic Affairs and Energy) and PTJ (Project execution organization Jülich). The main goals of this cluster are:

- Investigation of aerogels manufacturing from low-cost, sustainable raw materials and blends
- Adjustment of product quality with regard to the energy efficiency of material synthesis.
- Development of online process surveillance techniques.
- Scale-up and optimization of existing processes to manufacture organic, inorganic and hybrid aerogels, based on suitable models.

Currently the following joined projects in different application fields are part of the cluster:

AeroFurnace (ZAE Bayern, SGL Carbon Group, FCT Systeme GmbH): Main goal of this project is the development of carbon based aerogel insulation materials for high temperature applications (>1500 °C). Synthesis of nanoporous carbon composites is optimized with respect to their thermal insulation performance and materials are scaled-up from lab size to industrial scale to provide a novel thermal insulation that outperforms commercial graphite fiber based insulations by a factor of 2 to 5.

AeroPROcast (DLR, Bosch Rexroth AG): Within this project technical routines for the production of resorcinol-formaldehyde and carbon aerogels will be developed and transferred from laboratory to pilot plant scale. Used as sand core additives in metall casting, these aerogels prevent many casting defects and therefore reduce the casting rejection which leads to an increase of energy efficiency.

NAFT (TU Dresden, PlasmaChem): This project focuses on the synthesis of gels and aerogels from noble metal nanoparticles, which are suitable for the cost-efficient and well established inkjet printing technique. By printing the aerogels in layers, highly efficient (electro) catalysts and sensors with extremely large surface areas are formed, allowing for the smallest possible noble metal utilization in a broad range of applications.

AeroKonti (TUHH, BASF): Aim of the project AeroKonti is the development of a pilot scale continuous process for the production of aerogels via supercritical drying with CO₂. Continuous techniques and their technical realization are to be elaborated for each particular process step, aiming on minimization of energy and material requirements for the aerogel production.

In our presentation we introduce the current projects and provide an outlook to additional activities in progress of the cluster such as Round Robin tests for structural and thermal properties as well as the establishing of tools to monitor and thus optimize the different steps upon aerogel processing, such as the sol-gel transition and in particular supercritical and ambient pressure drying.

Enhanced luminescence in Tb³⁺/Eu³⁺ co-doped sol-gel materials containing PbF₂ nanoparticles

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Abstract: Energy transfer process is a promising strategy to improve the emission efficiency of wide range of phosphors doped with optically active rare earth ions (RE³⁺). In such process, the excitation energy could be transferred from an excited state of sensitizer (donor) to a nearby unexcited activator (acceptor). Indeed, energy transfer phenomenon is considered as an interesting topic for many scientists [1,2]. One of the most promising research areas for the use an energy transfer between RE³⁺ ions is production of multi-color or white-emitting phosphors [1].

Materials mentioned above could be easily obtained by a sol-gel method. The advantages of sol-gel method include high purity, ability to forming many shapes, atomic-scale mixing, large compositional flexibility, and low-temperature of this process. Preparation at room temperature makes it easy to include inorganic and organic additives.

In this work, the nanocrystals PbF₂ co-doped with Eu³⁺ and Tb³⁺ ions were derived via controlled heat-treatment of appropriate precursor samples synthesized by low-temperature sol-gel technique. The DSC/TG, XRD as well as IR-ATR techniques were used to structural characterization of prepared sol-gel materials. The optical behavior of prepared sol-gel samples was evaluated based on photoluminescence excitation and emission spectra as well as luminescence decay analysis from the ⁵D₀ (Eu³⁺) and ⁵D₄ (Tb³⁺) excited states. The series of luminescence lines located within reddish-orange and green spectral range were registered and were originated from Eu³⁺ and Tb³⁺ optically active ions, respectively. Upon direct excitation of Eu³⁺ ions at 393 nm, only the characteristic transitions from the ⁵D₀ state of Eu³⁺ ions were observed, but upon excitation of Tb³⁺ ions at 351 nm the characteristic transitions from both the ⁵D₄ state of Tb³⁺ and the ⁵D₀ state of Eu³⁺ were registered. This is a direct proof that energy transfer Tb³⁺ → Eu³⁺ in silica sol-gel materials occurs. Emission originating from the ⁵D₀ state of Eu³⁺ ions upon excitation through an indirect way (λ_{exc}=351 nm) is quite long-lived in comparison to that one obtained under excitation at 393 nm.

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Synthesis parameters of silica aerogels responsible for changes in mechanical properties

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Abstract: Aerogels are exciting porous materials characterized by many unique properties collected in one place, e.g. high porosity, large specific surface area or low thermal conductivity. One of the most prominent groups are silica aerogels which synthesis based on the sol-gel process of the silicon alkoxides. During hydrolysis and condensation reactions of silica precursor, next the aggregation and clusters' formation, and then the aging process of the gel, the growth of silica particles and creating of the final spatial silica network take place.

The sol-gel synthesis allows for quite extensive and well control of the structural parameters of the aerogels. Their structural variations can be described by changes in density, porosity or the particles size and their connectivity. It is noteworthy that these internal alterations indirectly result from the gelation time. From the point of view the brittle nature of the native silica aerogels each of the structural modification has a significant influence on mechanical properties. Tetramethoxysilane (TMOS) based silica aerogels considering synthesis parameters such as TMOS:solvent molar ratio, base catalyst concentration and the size of the hydrocarbon chain in alcohol (solvent) have been prepared. The significant impact of these synthesis variables on the gelation time has been noticed (Fig. 1 and Fig. 2). Mechanical tests based on uniaxial compression to ensure Young's modulus values as the measure of aerogels' flexibility have been carried out. Parallely, the structural changes in terms of the specific surface area, mean pore size, porosity and with scanning electron microscope observations have been examined. Finally, we connected the synthesis parameters with gelation time and structural changes, and further with mechanical properties of the native silica aerogels.

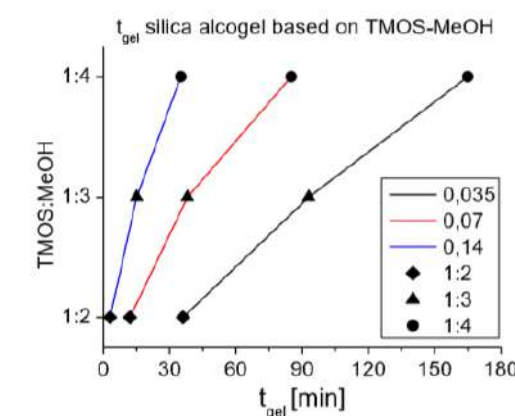


Figure 1. Gelation time of TMOS-based alcogels in dependence on molar ratio silica precursor (TMOS) to methanol (MeOH) (1:2 - squares, 1:3 - triangles, 1:4 - circles) and on catalyst (NH₄OH) concentration (0.035 M - black line, 0.07 M - red line, 0.14 M - blue line).

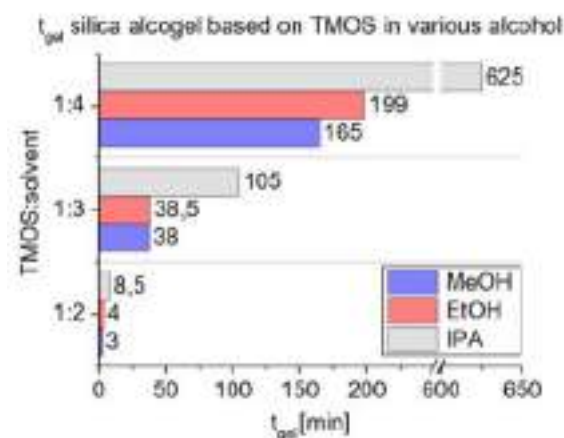


Figure 2. Gelation time of TMOS-based alcogels in dependence on used solvent: methanol (MeOH, blue), ethanol (EtOH, red) or isopropyl alcohol (IPA, grey), and TMOS:solvent molar ratio (1:2, 1:3 and 1:4).

Cold-Sprayed TiO_2 and Ag- TiO_2 coatings produced using sol-gel amorphous powders

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Abstract: The newest trends embrace utilization of titanium dioxide, well-known for its availability and photocatalytic potential, in various environmental applications. It is significant to emphasize the growing importance of TiO_2 in self-cleaning, water purification and water splitting. Not only does it become attractive worldwide for scientific research but also can be commercially exploited. Taking into account the industrial applications, the distinctive feature for best photocatalysts is possibility of covering large surfaces of wide range of substrates. Having Cold Spray (CS) compared with different coating technologies it meets all the requirement. Using CS it is possible to manufacture mechanically stable coatings on diverse substrates for a large-scale production. Mechanism of CS itself bases on the impact of solid particles of desired material on the substrate. In the spray process, the powder particles are characterized by high kinetic energy and while approaching the substrate they deform and in that way adhere to the substrate. Previously, the method was not particularly recommended for ceramics since it impedes deposition of coating. Currently, it has been developed that the utilization of appropriate agglomeration [1] or/and the amorphous form [2] of feedstock powder can lead to deposition of homogenous anatase coatings.

In the presented paper, the alternative feedstock powder has been suggested for cold spraying. In order to fabricate the powder the sol-gel method was employed. For that reason it was possible to obtain amorphous form of titanium dioxide aggregated adequately and what is especially interesting chemical modification of TiO_2 with silver ions was also possible. The detailed SEM, Raman and XRD measurements clearly demonstrated that during the process of low pressure cold spraying amorphous titanium dioxide was transformed into crystalline anatase form and what is more silver ions were reduced to the metallic form.

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Siloxane-based nanocomposites with up-conversion properties

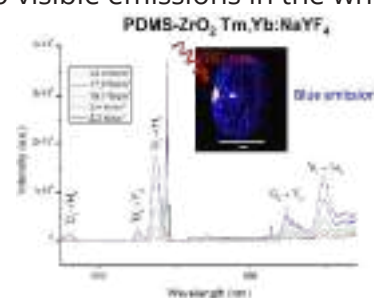
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Abstract: Polydimethylsiloxane, PDMS, is a widely used silicon-based polymer due to its transparency, low autofluorescence, biocompatibility, water repellence, easy-to-shape, flexibility when sticks tightly to glass or another substrate. Thus, PDMS-based nanocomposites are envisaged as tactile or pressure sensors, microheaters, biosensors in microfluidic systems, volumetric full-color three-dimensional displays or photonic micro membranes.^[1] The development of composite materials based on a combination of transparent PDMS and optically active species, such as lanthanide-doped NaYF₄ nanoparticles (UCNPs, as up-converting nanoparticles) can pave the way to advance in smart optical technologies^[2]. However, a good match of the refractive indices between polymer and UCNPs is necessary, and more importantly, undesired nanoparticle's aggregates inducing light scattering should also be avoided. An original way to solve both issues is by crosslinking PDMS linear chains with metal oxo-domains (M_xO_y, M:Ti, Zr, Nb and Ta) generated in-situ during the PDMS polymerization from molecular precursors through an accurate control of the sol-gel kinetics.^[3] The presence of these hydrophilic oxometallic domains increases the refraction index of the polymer and helps the dispersibility of the up-conversion nanoparticles, resulting in transparent gels, easy to shape as bulk materials, fibres or films, which efficiently convert near-infrared photons into visible emissions in the whole volume.



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Studying Water Adsorption on Mesoporous Silica Films by ATR-IR Spectroscopy: Determination of Porosity and Structure of Adsorbed Water

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Abstract: At ambient conditions, all materials are covered by a few monolayers of water. However, the understanding of the water structures on different surfaces and especially in confined spaces as found in mesoporous materials is still object of intensive studies.¹ The surface-induced ordering that water experiences in the first monolayers at the pore surface and the needed film thickness to reach water's bulk properties is investigated with particular focus.² For studying the interaction of water with itself and/or a surface, mid-infrared (mid-IR) spectroscopy has proven an ideal method since it is very sensitive to water and gives information about the species states of hydrogen bonding.³

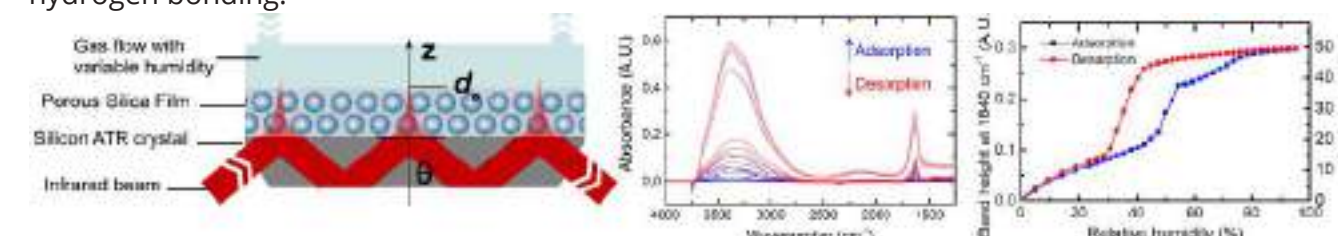


Figure 1. (left) Si ATR crystal coated with mesoporous silica film. Absorption takes place within the evanescent field of the totally reflected infrared light, which extends beyond the crystal and the film. (middle) FTIR spectra of water adsorbed into mesoporous silica film. (right) adsorption isotherm retrieved from IR spectra.

In this contribution, we present the combination of attenuated total reflection (ATR) mid-IR spectroscopy with mesoporous silica films for determining the growth and structure of water adsorbed into mesopores depending on relative humidity of the gas phase above the film (scheme of setup is given in Figure 1 left). The identification of different states of hydrogen bonding of the water molecules visible in the IR spectra enabled us to differentiate quantitatively between the first layers of surface-induced ordered water similar as in ice crystals and bulk water situated in larger distance to the pore surface (see shift in absorbance maximum in Figure 1 right upon increasing humidity and pore filling). In addition, quantitative analysis of the obtained spectra allowed for the retrieval of porosity and pore size distribution of the mesoporous film. The results were in excellent agreement with values obtained from ellipsometric porosimetry.

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Sol-gel preparation of nanocarbon – glass materials

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Abstract: Graphene has attracted intense research and industrial interest owing to its superior optical, electrical, and mechanical properties [1]. There are many works reported in the literature on polymer-graphene composites, but the use of graphene for preparing metal, ceramic and glass matrices composites is relatively new [2].

In the present work, the ternary system ZnO-B₂O₃-P₂O₅, undoped and co-doped with Dy and Tb oxides together with graphene oxide alcohol solution was studied by using the sol-gel method in order to obtain powders and thin films. The influence of composition, pH, temperature and time on sol-gel process is investigated, in order to obtain powders and thin films with desired properties.

Thin nano-structured zinc-boro-phosphate glass-graphene composite films are obtained by sol-gel method using spin-coating technique at different speeds. The speed of 3000 rot/min was chosen for best results. Since the thickness of the films influences the properties, ten layers (totalizing about 1 µm) were successively deposited on glass and silicon substrates. The sol-gel films were dried at several temperatures, between 150 and 400°C.

The structure and thermal properties of the zinc-boro-phosphate glass-graphene composite powders and films are investigated by Raman and FTIR spectroscopy. The quality of deposited films in terms of roughness, composition and surface defects is investigated by using SEM, EDAX and AFM.

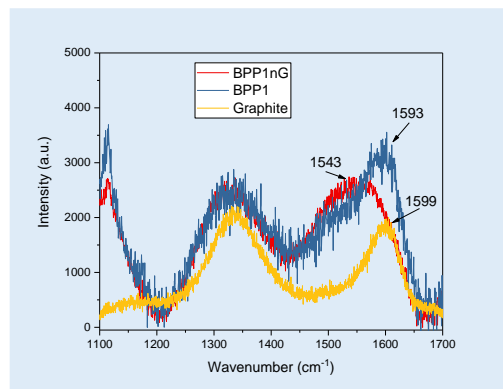


Figure 1. Raman spectra of glass (BPP1), graphite and composite (BPP1nG)

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SiO₂ Aerogels – Understanding of hygrothermal ageing

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Abstract: Retrofitting of residential buildings is a key lever to reduce the energy consumption in Europe, and therefore achieve the target lowering of greenhouse gas emission. In this task, super-insulation materials are complementary with traditional ones (glass wool, PUR...). SuperInsulation Materials (SIM), with a thermal conductivity below that of static air (4-20 mW.m⁻¹.K⁻¹), offer the opportunity to suitably insulate with a low thickness, thus avoiding the loss of habitable space. Their thermal efficiency relies on nanopores (< 70 nm). They mainly concern Vacuum Insulation Panels (VIP) where a core of silica powder with fibers is wrapped, under vacuum, in a protective aluminum seal, and SuperInsulation Materials at Atmospheric Pressure (SIAP), which are based on silica aerogels. In order to improve confidence in those high-end products and to adjust the synthesis regarding the desired applications, the understanding of silica ageing is required. This work is based on a wide panel of commercial products (aerogels, precipitated and pyrogenic silica) with differences in the chemical (hydrophilic silanols groups Si-OH, rather hydrophobic siloxane bridges Si-O-Si, hydrophobic functions Si-R) and structural properties (specific surface areas, particles and pores sizes...). They are aged in climatic chambers, with a control over the temperature (20-70 °C) and relative humidity (0-90 %RH), during different times (from few days to year), in order to distinguish mechanisms involved in the physico-chemical evolutions. The latter are tracked with tools such as gas sorption, TGA/DSC, FTIR, SANS, isostatic and oedometric compression, TEM and electron tomography. Aerogels ageing appears to be product specific with a common trend. Changes in the surface chemistry or in the surface functions environment (neighbor types and proximity) are thereafter followed by structural modifications. These include lowering of the specific surface area and shifting of the pore size towards higher values. Hydroxylation of the surface occurs by hydrolysis of either siloxane bridges, residual ethoxy groups or other hydrophobic functions. Displacement of matter via a water media previously physisorbed at the silica surface and a dissolution/precipitation process is identified as the main mechanism of structural evolution. The initial surface chemistry and pores size are two important factors in the further evolutions.

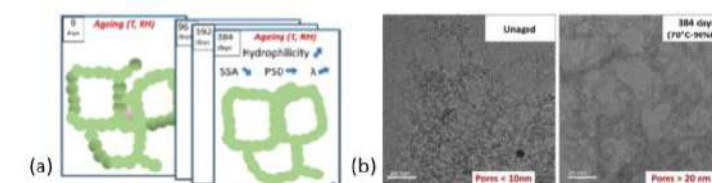


Figure 1. Schemas (a) and TEM micrographs (b) of the aerogel evolutions while ageing. The authors would like to thanks the ADEME (grant 1604C0019) for financial funding.

Mesoscopic computer simulation and theory of P-graft-H polymer dilute solutions

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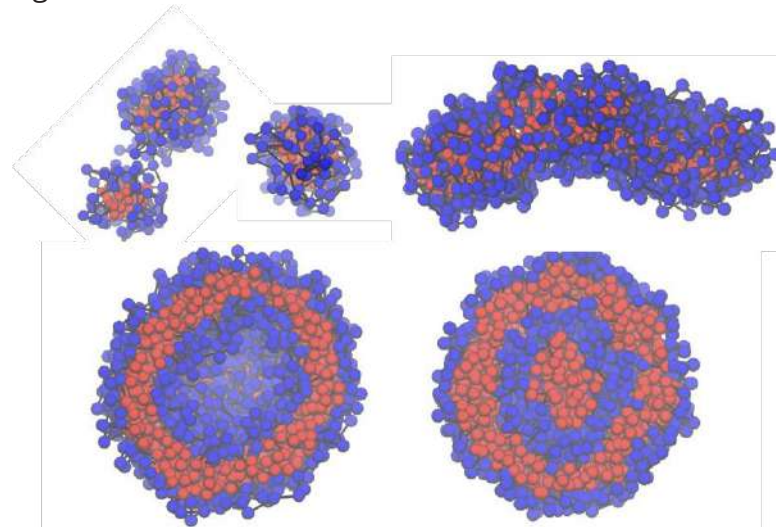
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Abstract: Amphiphilic homopolymers draw attention due to their ability to self-assemble and possible usage as nanoreactors, containers for targeted drug delivery, protein sensing devices, oil recovery agents. Solutions of amphiphilic homopolymers in aqueous and organic solvents were previously investigated in experimental works [1]. Single macromolecule with hydrophobic main chain and side polar groups has been studied by means of molecular dynamic simulations and analytic theory [2].

In the present work, dilute solutions of P-graft-H polymers with solvophilic backbone (P) and solvophobic (H) pendant groups were studied by means of dissipative particle dynamics (DPD) simulation method [3] and mean-field theory. With worsening solvent quality for P groups at high incompatibility of H groups and solvent, the following sequence of shapes of assemblies was obtained in computer simulation and theory: spheres, cylinders, vesicles (or lamellae), single onion-like aggregate in computer experiment or layered macrophase with alternating layers composed of H or P groups in theory. At moderate and low values of incompatibility of H groups with solvent, helix structure, tori, nanoworm, and hollow particles were also observed in computer experiment. The morphological diagrams were constructed.



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Analysis of the products of yttrium chloride hydrolysis obtained at different pH values

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Abstract: Synthesis of oxide nanoparticles with specified morphology for rare-earth elements and yttrium has aroused interest due to their unique electronic, optical, and magnetic properties. These compounds are used in high-performance luminescence devices, as phosphors, the reactants for synthesis of nanotubes, nanowires, and nanorods, as well as other functional materials. Besides, the catalysts on the basis of yttrium chloride and oxide are produced, which are used in synthesis of various organic compounds, in particular, biodegradable polymers. At the same time, the catalytic properties substantially depend on the method of obtaining oxides and yttrium oxyhydroxides.

In the present study the products of yttrium chloride hydrolysis were investigated. The compounds were obtained by the sol-gel method, both with and without hydrothermal treatment. The precursors were yttrium chloride and ammonium hydroxide with concentrations of 0.1 mol / L and 1 mol / L, respectively. The final pH values were 8.5, 9.5, and 10.

Analysis of micrographs of the samples obtained by the sol-gel method without hydrothermal treatment has shown that all samples have a layered structure. At the same time, the samples obtained at a pH values below the zero charge point (8.5 and 9.0) have similar morphological features. The sample obtained at pH above the zero charge point (9.5) has a slightly different, more dense, structure. Analysis of the obtained diffractograms for these samples has shown that all samples have the most intense reflexes in the 2θ range of 10 degrees, which indicates a large interplanar distance characteristic of layered materials. Thermal analysis of the samples has shown that with increasing the synthesis pH there is a tendency for decreasing the content of adsorbed carbon dioxide in the samples; this can indicate a decrease in the interplanar distance. A well-defined peak on the DTG curve in the temperature range of 820 ... 1120° C, which corresponds, according to mass spectrometry, to HCl cleavage, decreases with increasing pH. This is due to decreasing percentage of chloride groups and the corresponding increase in the content of hydroxyl groups in the samples obtained at higher pH values. A tendency to a decrease in the chlorine content has also been observed in the samples obtained by the sol-gel method with hydrothermal treatment. The samples obtained with hydrothermal treatment are characterized by high crystallinity. The morphological features are significantly affected by the hydrothermal processing of the samples. For the samples obtained with hydrothermal last stage, the formation of nanoscale plates has been observed, which tendency decreases with increasing pH (65 nm at pH 9.5, 20 nm at pH 10).

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Preparation of calcium phosphates via aqueous solution routes

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Abstract: Calcium phosphates have been widely used in biological applications. Among the calcium phosphates, hydroxyapatite (HA, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) and tricalcium phosphate (β -TCP, $\text{Ca}_3(\text{PO}_4)_2$) have received great attention due to their prominent bioactivity and biocompatibility. The materials are also promising candidates to remove hazardous chemicals with high reactivity for incorporating toxic or harmful substances. Various types of calcium phosphates can be utilized for a variety of applications due to differences in their physical and chemical properties. The calcium phosphates, pure HA, β -TCP and biphasic HA/ β -TCP, were synthesized by aqueous preparation routes of a precipitation and a hydrothermal process. In both processes, powders were formed by mixing aqueous solutions of calcium hydroxide ($\text{Ca}(\text{OH})_2$) and phosphoric acid (H_3PO_4). NaOH was used as a pH control agent. This work aimed to compare two preparative processes in the production of calcium phosphates.

In the simple precipitation process, the 85% of H_3PO_4 solution was dropped slowly into the 275 ml of 3.6 M $\text{Ca}(\text{OH})_2$ aqueous suspension solution. For the preparation of different calcium phosphates, predetermined Ca/P molar ratios of the precursor solutions of 1.40, 1.50 and 1.67 were set by the addition of H_3PO_4 solution to the continuously stirred $\text{Ca}(\text{OH})_2$ suspension at room temperature. The resultant precipitates were ball-milled right away with the mother solution up to 12 h. The synthesized powders after ball-milling process were dried at 70°C for 12 h. Unlike the other preparative processes for the calcium phosphates, there was no maturing (aging) and filtering (washing) process involved. In the hydrothermal process, the aqueous suspension solution prepared from the precipitation process was charged into a teflon-lined autoclave of 300 ml capacity with a fill factor of 80 vol%. Subsequently, the reactor was heated to temperatures between 80 and 130°C for 1 h. The reaction products were dried at 70°C for 12 h. The calcium phosphates powders including pure HA, β -TCP and biphasic HA/ β -TCP were prepared in both processes under various conditions. Single HA phase has been obtained by the precipitation process from the precursor Ca/P ratio of 1.67 with the ball-milling step for 6 h and by the hydrothermal method from the same solution for 1 h at 130°C (Fig. 1). The preparation processes offered advantageous features such as fast, convenient and economical routes for the synthesis of calcium phosphates, at higher precursor concentrations.

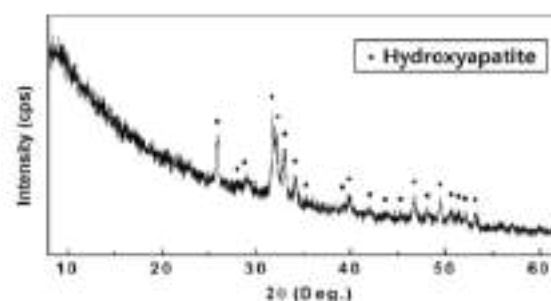


Figure 1. Hydrothermally synthesized hydroxyapatite (nanometer size) powders at 130°C.

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Dielectric properties of Core-shell nanostructures

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Abstract: Giant dielectric materials have become increasingly important, as their promising use in high-performance capacitive devices for microelectronic applications and high energy density storage. In recent years, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) with perovskite-related structure has attracted much attention because of its unusual giant dielectric properties. It has colossal dielectric constant of the order of magnitude close to 10^5 with weak temperature dependence (100 K – 600 K) in the frequency range from 100 Hz to 100 kHz [1-2]. However, the high low-frequency dielectric loss ($\tan\delta$) and the low resistivity hinder its practical applications. To clarify the origin(s) of the giant dielectric properties, related electrical properties of CCTO ceramics have been studied extensively. It has been confirmed that CCTO ceramics are electrically heterogeneous, consisting of semiconducting grains and insulating grain boundaries [3, 4]. On the basis of the results, an internal barrier layer capacitance (IBLC) effect seems to be the most plausible explanation for the giant dielectric properties of CCTO ceramics.

In this work, it is designed to coat the surface of CCTO powder by an insulating material like SiO_2 , Al_2O_3 ... to prepare composites ceramics with core-shell structure [5]. CCTO/(SiO_2 and/or Al_2O_3 ...) composite ceramics with core-shell structure were prepared by sol-gel-like method, and their crystalline structures, microstructures, dielectric properties and complex impedance were investigated systematically [6]. The results show that the properties of these ceramics are similar or better than CCTO properties attributed to the increasing resistance of the insulating grain boundary.

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Preparation of organic and carbon nano- and microspheres by a Stöber-like process

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Abstract: Organic nano- and microspheres were derived by a template free sol-gel process based on the reactants resorcinol and formaldehyde (RF). Subsequent pyrolysis of the organic spheres under inert gas provides carbon spheres with a diameter reduced by approx. 16% compared to the organic precursor.

The RF-system is commonly applied and extensively investigated for the synthesis of monolithic sol-gel derived organic aerogels and xerogels with porosities up to 99%. These highly porous organic aerogels are then used as precursors for carbon aerogels and xerogels. However, when the synthesis parameters in the RF-system are adjusted to low alkaline catalyst concentration and low mass content of resorcinol and formaldehyde in the starting solution, a Stöber-like [ref. 1] process takes place, i.e. the formation of individual spherical particles rather than the formation of a gel.

We investigated this RF-based Stöber-like process in detail to reveal the relationship between synthesis parameters and morphological/structural characteristics of the resulting particles [ref 2.]. Particle characterization was performed by scanning electron microscopy (SEM), dynamic light scattering (DLS), nitrogen sorption and small-angle-X-ray scattering (SAXS). Characterization reveals organic and carbon spheres derived therefrom with an average diameter that can be adjusted to be in the range between 30 nm and 5 μm with a relatively narrow particle size distribution (Figure 1). The diameter of 5 μm appears to be the upper size limit, while 30 nm spheres develop near the gelation limit, i.e. at the transition from dispersed particles to a bulk gel.

The approach provides access to the synthesis of spherical particles without the need for an assistance of templating and the related additional process steps.

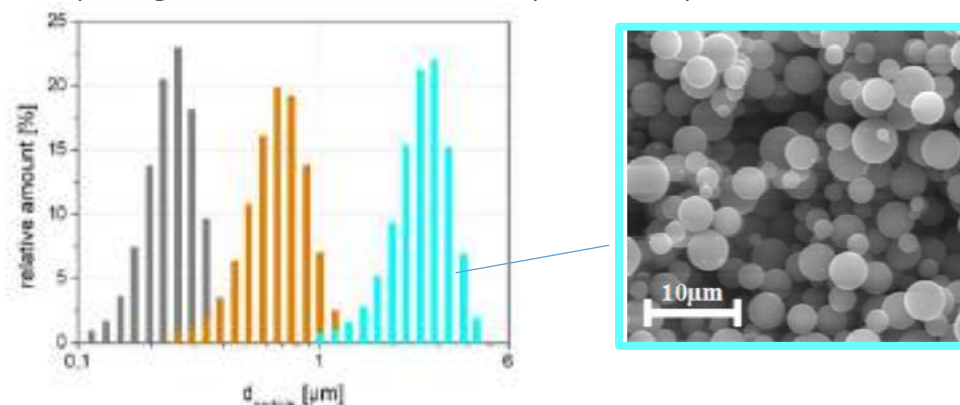


Figure 1. Left: Particle size distribution determined with DLS for 3 different carbon samples. Right: SEM picture of one of the samples prepared.

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Au Bipyramids@mSiO₂ Core-Shell Nanoparticles for Singlet Oxygen Photooxygenations in Continuous-Flow Microreactors

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Abstract: Gold nanomaterials display interesting plasmonic features with potential application in various fields depending on the size and shape of the metal nanostructures. Synergy between Au nanoparticles and chromophores can enhance the photophysical properties of nearby molecules¹. Au bipyramids (AuBPs) exhibit intense and well-defined plasmon resonance, easily tunable with the aspect ratio. In Rose Bengal-NPs systems for the production of singlet oxygen (¹O₂), it is now well established that the control of the dye-to-nanoparticle distance ranging from 10 to 20 nm is crucial to achieve the proper coupling between the plasmon resonance and the dye^{1,2}. We have developed AuBPs@mSiO₂ core-shell nanostructures to control the distance between metallic surface and photosensitizers in order to increase the production of ¹O₂ (metal-enhanced ¹O₂ production – ME¹O₂). An enhancement of ¹O₂ generation has been shown for the obtained anisotropic AuBPs and AuBPs@mSiO₂ in presence of RB using three indirect methods of ¹O₂ detection, namely Electron Paramagnetic Resonance (EPR) with TEMP as chemical trap *in situ* under visible photoexcitation³, photooxidation of the fluorescence probe anthracene dipropionic acid (ADPA), and photooxygenation of methionine to methionine sulfoxide in a continuous-flow microreactor⁴.

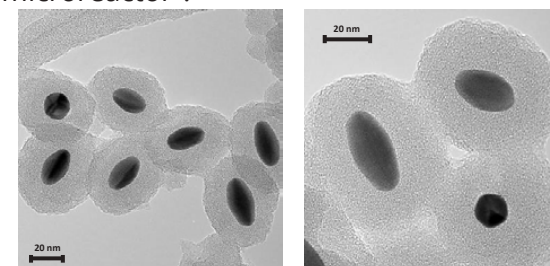


Figure 1. TEM images of AuBPs@mSiO₂ at 280kX and 490kX

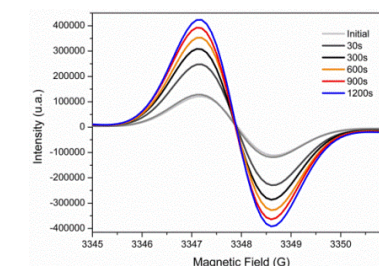


Figure 2. EPR/TEMP spectra of AuBPs@mSiO₂ in presence of RB under visible irradiation as a function of time

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Antireflective and low surface energy sol-gel coating stack design and field performance on photovoltaic application

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Abstract: Porous silica layers with outstanding antireflective (AR) durable properties have been prepared by acid-catalyzed sol-gel process in presence of organic phases as structure directing agents (SDA) and excess water, with the aim of offering a cost-competitive, easy up-scaling and high efficiency process that contributes to reduce current levelized cost of energy (LCOE) of concentrating photovoltaics (CPV). AR silica multi-layer stacks were first theoretically designed with the purpose of maximizing light transmittance that better matches with spectral response of multijunction solar cells considering that outstanding durability in terms of antireflective stability are also required. Silica porous coatings were grown by combining acid-catalyzed sol-gel route and evaporation induced self-assembly (EISA) method. The scanning of four types of organic/inorganic systems and the optimization of the water/alkoxide ratio allowed to select the coating that fulfilled specific thickness, porosity and optical constants (n , κ) with, in parallel, excellent results on sol stability. These properties were studied by ellipsometry, environmental ellipsometric porosimetry (EEP) and atomic force microscopy (AFM). Optical properties of both side AR coated glass were characterized by spectrophotometry, AR providing a 7.2 % (under the reference AM1.5 solar spectral irradiance) increase in transmittance over bare glass in the wavelength range 300 to 2000 nm.

Considering one of the external factors that may alter the optical properties of the system when operating outdoors, such as soiling, low surface energy properties were further searched, in order to obtain coatings capable to contribute against soiling adherence, without losing the AR properties. This property was implemented through two different routes: i) methyl-silylating post-treatment of porous coating (two-step process) and ii) formulation modification with low content of polyfluoroalkyl silicon alkoxides of different non-hydrolyzable fluoroalkyl chain lengths (one-step process). Low energy surfaces without detrimental effect on AR properties were obtained by both methods.

Considering others external factors that may alter the optical properties of the system when operating outdoors, such as harsh climate conditions and alkali ions diffusion from glass, several AR layer stack configurations were built with the most promising obtained coatings and several sintering temperatures. The aim was to achieve the most rational design, based on a proper trade-off between cost efficiency, processability, optical properties and reliability during real life operation. The assessment consisted of (i) an analysis of the optical transmittance, reflectance and refractive index (ii) hydrophobicity and effect of water absorption on the external porous coatings in relation to the results of accelerated aging tests following photovoltaics standards (IEC 62108) (iii) nanoindentation and nanoscratch analysis in relation to reciprocating abrasion test to assure the required robustness.

Most promising AR layer stacks were transferred from lab to industrial application, and thus permitted to study AR coating performance in field exposure conditions, since they were deposited on front glass sheet of PV mono-modules and exposed for one year. The current generated by the

modules was continuously monitored, thus providing a correlation between each AR layer stack properties and their behavior depending on irradiation, precipitation, moisture and temperature along test.

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Sol-gel synthesis of high-temperature glass-ceramics

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Abstract: One of the most important problem of modern materials science is the development of new materials that can be operated under the influence of high temperatures and various aggressive media. From this point of view, a great deal of attention is being devoted to glass-ceramics in the systems $\text{Sr}(\text{Ba})\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$. This is because the principal phases crystallizing in this systems: monoclinic strontium anorthite ($\text{SrAl}_2\text{Si}_2\text{O}_8$) and monocelsian ($\text{BaAl}_2\text{Si}_2\text{O}_8$) possess low weight (density: 3.08 g/cm^3 and 3.39 g/cm^3 , respectively) and high melting points (1650°C and 1760°C , respectively). However, low fracture toughness ($K_{1C} < 2.5 \text{ MPa}\cdot\text{m}^{1/2}$) significantly limits the use of these materials. A possible way to solve this problem is to modify of aluminosilicate glass ceramics with various fillers, such as particles of refractory zirconium and hafnium oxides. Their introduction may allow realizing the effect of transformational hardening of materials [1].

The preparation of modified aluminosilicate glass-ceramics by a sol-gel method is promising. The main advantage of the sol-gel method is the possibility of obtaining materials with a nanocrystalline structure and uniform distribution of modifying oxides in the glass-ceramic matrix, providing higher values of their mechanical properties.

In this work, sol-gel synthesis of strontium aluminosilicate (SAS) and barium aluminosilicate (BAS) glass-ceramics modified with additives of hafnium and zirconium oxides in the presence and without of a stabilizing yttrium oxide is carried out. The influence of the nature of modifying oxides on the processes of gelation, phase formation, sintering and the structure of materials has been studied.

It was established that the introduction of oxides in the series $\text{ZrO}_2 \rightarrow \text{HfO}_2$ in the presence and without of stabilizing yttrium oxide contributes to an increase in the rate of hydrolysis and condensation during the gelation of solutions, which leads to a reduction in the time of their gelation.

It was shown that the phase formation process of SAS and BAS glass-ceramics synthesized by the sol-gel method is complex. Crystallization occurs through the phase transformations of strontium and barium silicates into hexagonal and monoclinic forms of strontium anorthite and celsian. In all samples of the SAS system after heat treatment only the phase of monoclinic strontium anorthite is present. The simultaneous presence of both monoclinic and hexagonal forms of celsian in the samples of BAS system is observed, exclusion of the composition with zirconium oxide. Regardless of the nature of the base system (BAS or SAS) hafnium oxide is present in glass-ceramics in a monoclinic form, while surrounding the zirconium oxide particles with a glass-ceramic matrix partially stabilized the high-temperature tetragonal form of ZrO_2 even in the absence of yttrium oxide.

It was found that the introduction of modifying oxides into BAS glass-ceramics leads to an intensification of the sintering process. The presence of yttrium oxide enhances this effect. Synthesized samples are characterized by a fine-crystalline structure. The use of the sol-gel method made it possible to evenly distribute the grains of modifying oxides in the volume of glass-ceramics. It was shown that agglomeration of yttrium oxide is observed near zirconium oxide particles. This confirms the action of Y_2O_3 as a stabilizer of the tetragonal form of ZrO_2 in glass ceramics.

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Li₇La₃Zr₂O₁₂/LiCoO₂ - cathode for all-solid-state batteries

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Abstract: A battery is a device that converts the chemical energy contained in its active materials directly into electric energy through an electrochemical oxidation-reduction reaction. The battery is composed by an anode (the negative electrode) where, upon discharging, the oxidation reaction takes place, a cathode (the positive electrode) where the reduction reaction takes place, and an electrolyte (usually an organic, flammable liquid) that allows the migration of the ions between the electrodes. Currently, some research on this topic tends towards the manufacturing of flexible Li-ion micro-batteries for uses in microsystems. To do so, it is necessary to replace the widely used liquid electrolyte by a solid-type one because the flexible/micro configuration is not compatible with liquid electrolytes: (i) it is difficult to process microsystems with liquid electrolytes and (ii) the flexibility of the battery may lead to leakages. In addition, this replacement could also open the way to new battery types in order to solve the safety issues related to the use of flammable organic electrolytes in larger batteries.¹

Recently, a low-cost and energy-efficient spray-coating process of lithium cobalt oxide (LCO), *i.e.* a cathode material, has been developed in our lab to obtain flexible microelectrodes. As the final objective is to use a solid state electrolyte such as Gel Polymer Electrolyte (GPE) or Lithium Phosphorous Oxynitride (LiPON), the coating process still needed to be adapted to the production of solid state batteries. In fact, due to the presence of 50-60% porosity inside the cathode layer, the migration of the lithium ions is hindered, which leads to the decrease of the ionic conductivity. The main challenge was to use a nanostructured electrolyte such as Li₇La₃Zr₂O₁₂ (LLZO) to fill the LCO coating porosity (between 50 - 60 %) in order to improve the ionic conductivity of the layer without changing the electrochemical properties of the LCO, to finally be able to build an all solid-state battery.

Three different crystalline structures of LLZO can be synthesized. The first one, the high-temperature cubic phase (HT-LLZO), is obtained at temperature over 1000°C and is not stable at room temperature; the second one is the tetragonal phase (t-LLZO), which is obtained above 700°C; recently, Murugan *et al.*² have shown that a second cubic phase could be obtained at temperature below 700°C. Among these three polymorphs, the low temperature cubic phase (c-LLZO) has been chosen because it is possible to synthesize it using a low-temperature sol-gel process and because the obtained material is stable at room temperature^{3,4}. Moreover, c-LLZO (Figure 1) is a very promising material for solid state electrolyte applications due to its chemical stability in contact with Li metal and its relatively high ionic conductivity ($\sim 10^{-6}$ S/cm)⁵.

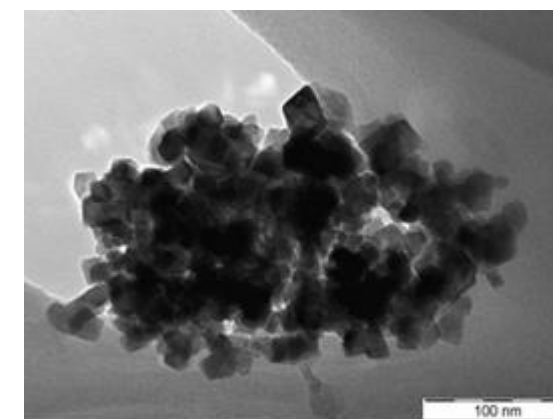


Figure 3 TEM image of cubic LLZO

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Synthesis of N-(anthracenylmethyl)imidazolium functionalized-silsesquioxane cages

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Abstract: Polyhedral oligomeric silsesquioxanes (POSS) have been considered as hybrid organic-inorganic materials that widely used in many prospective applications, for instance, chromofluorogenic chemosensors.¹ In previous work, 1-imidazolylmethylpyrene (IMPY) was used as a sensor for detection of explosive chemicals.² In this study, N-(anthracenylmethyl)imidazolium functionalized-silsesquioxane cages (AnIMSQ) was synthesized by nucleophilic substitution between N-(9-anthracenylmethyl) imidazole and silsesquioxane cage. The desired product will be characterized by ¹H, ¹³C and ²⁹Si-NMR and its photophysical properties will be further investigated.

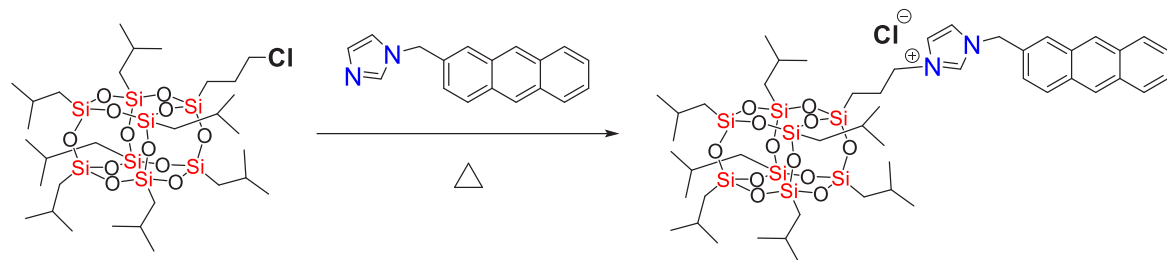


Figure 1. Synthetic scheme of N-(anthracenylmethyl)imidazolium functionalized-silsesquioxane cage.

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Anthracene-based functionalized silsesquioxane as dual functions: fluoride sensor and absorbent

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Abstract: Polyhedral oligomeric silsesquioxanes (POSS), prepared *via* sol-gel method, can be categorized as inorganic-organic hybrid materials. In this work, after fluorescent materials (anthracene) were cross-linked with octavinylsilsesquioxanes *via* Heck reaction to form anthracene functionalized silsesquioxane (AnSQ) polymer, which is an insoluble polymer and can be used as sensors and absorbents for anionic recognition. AnSQ polymer exhibits good selectivity to fluoride ion with fluorescence enhancing, giving low detection limit (0.12 ppb). Moreover, AnSQ polymer provides a high porosity with an excellent removal efficiency of fluoride up to 82 %.

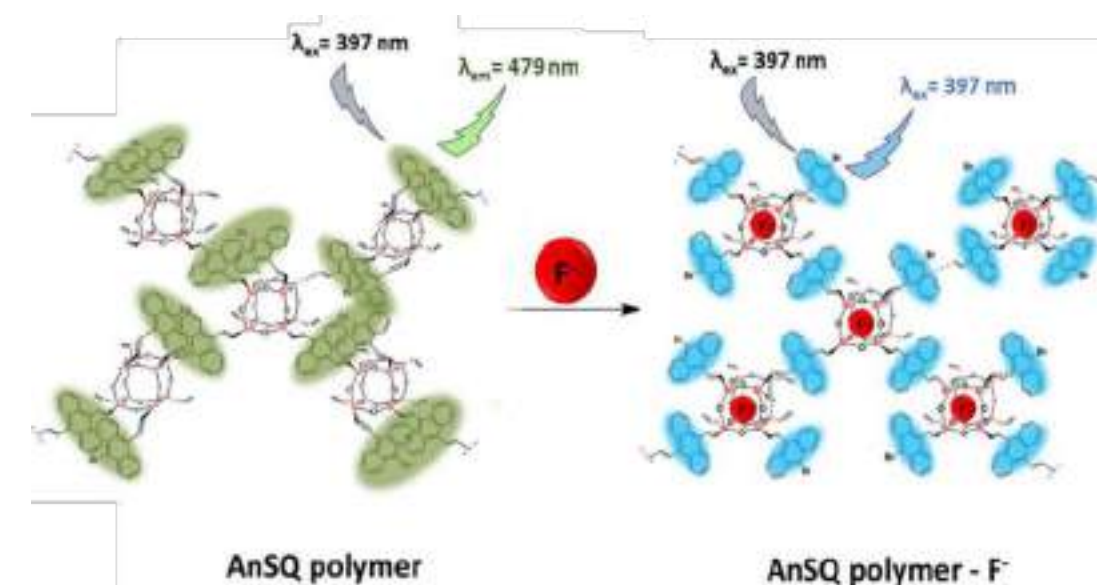


Figure 1. The principle of a "turn-on" fluorescence of AnSQ polymer by fluoride under UV radiation

Macroporous SnO₂ as an electrocatalyst support

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Abstract: SnO₂ is wide bandgap semiconductor which has been investigated in many application fields such as lithium-ion batteries, gas sensors, sensitized solar cells and electrocatalysis [1]. One of the most perspective SnO₂ application is to use it as a support for Pt electrocatalysts in fuel cells because they have a higher stability compared to that of conventional Pt catalysts based on carbon black [2]. To use SnO₂ as a support for a Pt electrocatalyst, it is necessary to obtain a SnO₂ material with high electrical conductivity, stability and a bimodal porous structure that provides the active mass transport of reagents and products. Thus, the aim of this work is to obtain SnO₂ with high conductivity, stability and bimodal porous structure using template technique and to study the influence of synthesis parameters on SnO₂ electric conductivity and electrochemical stability.

Polystyrene (PS) microspheres with average diameter of ~ 250 nm were used as a template for the synthesis of macroporous SnO₂. They were prepared using 4,4'-azobis(4-cyanovaleric acid) as an initiator in accordance with the work [3]. The first series of SnO₂ was synthesized by aging of sols from SnCl₄ in the presence of PS suspension in H₂O-C₂H₅OH solution. The PS was removed from SnO₂ samples by annealing at 450°C. The final powders were yellow. The second series of SnO₂ was synthesized from SnC₂O₄. At first stage, SnCl₂ was precipitated by (NH₄)₂C₂O₄ in the presence of PS suspension while stirring. Then PS was extracted from SnC₂O₄ by toluene at 110°C and then the material was heat treated at 400°C to provide thermal decomposition. The final SnO₂ powders were brown.

The SnO₂ samples were characterized by using low-temperature N₂ adsorption (77 K), Hg porosimetry, the scanning electron microscopy (SEM), X-ray diffraction and CHNS analysis. The SnO₂ stability was studied by using accelerated "Start/Stop cycling" protocol in 1–1.5 V RHE of the potential range in 0.1 M HClO₄. The cyclic voltammograms were recorded in the range of 0.05–1.2 V RHE with a sweep rate of 0.05 V/s before the "Start/Stop cycling" and every 2000 cycles. Electrical conductivity was studied by the impedance spectroscopy in 10⁻¹–10⁵ Hz of the frequency range using home-made cell.

The final SnO₂ samples had the BET surface areas of 31–45 m²/g. The SnO₂ samples had macropores (110–180 nm) and mesopores (6–14 nm) according to SEM and BET, respectively. The increase of sols aging time led to the increase in SnO₂ stability and conductivity due to the larger crystallite size. Using thermal decomposition of SnC₂O₄, SnO₂ with high conductivity up to 0.275 S/cm were synthesized. The increase of the mass ratio of PS to the precursor led to the increase in SnO₂ conductivity and stability. The stability of SnO₂ samples was comparable with that of carbon black Vulcan XC-72.

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Continuous structural gradients in sol-gel derived organic and carbon aerogels

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Abstract: Aerogels are highly porous monolithic sol-gel derived materials. Usually, aerogels are synthesized with a homogeneous structure (particle/pore sizes) over the whole macroscopic sample. However, for some applications, such as thermal insulations for high temperatures or filters, a structurally graded aerogel may be advantageous. In a feasibility study, we investigated the synthesis of an organic aerogel with a continuous gradient in particle and pore size at only moderate density change over the gradient. Hereby a resorcinol-formaldehyde (RF) solution with a gelation time of several hours was prepared and a thin layer of a catalyst solution was added on top. The catalyst was then allowed to diffuse into the solution for several hours to create a continuous gradient in catalyst concentration before the temperature of the sample was raised to initiate gelation and thus freeze the gradient. Since the gel formation (i.e. the rate of particle growth and the rate of cross linking) in RF-solutions is very sensitive to the catalyst concentration, the gradient in catalyst results in a morphology gradient.

The gradient prepared has a width of about 20 mm and covers a range in pore size from 10 µm to about 60 nm at a porosity of about 85% [ref 1.]. Subsequent pyrolysis of the organic precursor leads to equivalent structural gradients in carbon aerogels. Characteristic properties such as the porosity, the pore size and the particle size along the gradient were investigated by scanning electron microscopy (SEM), small angle X-ray scattering (SAXS) and N₂-Adsorption. As expected from Knudsen's relationship, thermal conductivity measurements performed at ambient atmosphere show a strong variation of the gas phase contribution to the overall thermal transport depending on the position and thus on the structural properties in the continuous gradient.

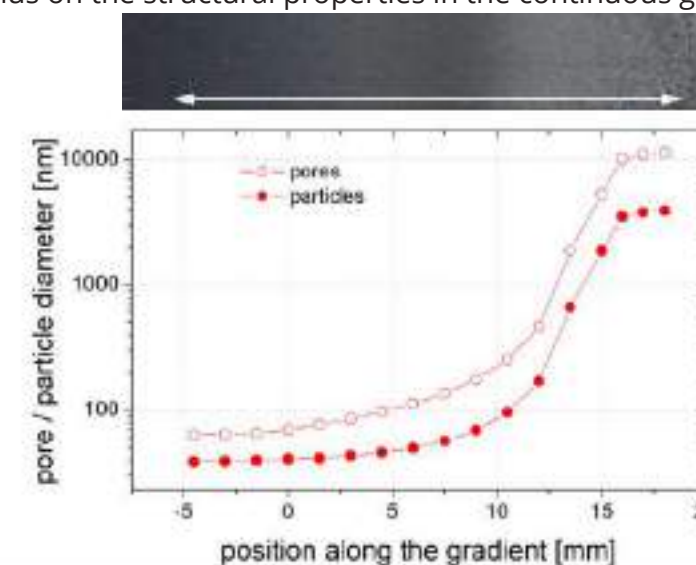


Figure 1. Top: Photo and bottom: particle and pore size along the structural gradient of a sol-gel derived carbon aerogel.

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Characterization of silanol groups in siloxane oligomers

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Abstract: Fine control of molecular structure of siloxane has been desired for achieving highly functional siloxane-based materials. Silanol groups can be used not only to tune physical and chemical properties of siloxane materials but also to introduce new functional groups. In this study, the reactivity and thermal stability of silanol groups in the phenyl-methyl siloxanes were investigated. Phenyl-methyl siloxanes with silanol groups at a high content were prepared via a sol-gel method, and the reactivity of silanol groups was assessed by an acid-base reaction with trimethylchlorosilane

Experimental procedure: Two types of silicon alkoxide ($\text{PhSi}(\text{OMe})_3$, $\text{Me}_2\text{Si}(\text{OMe})_2$) were dissolved in isopropyl alcohol. An acetic acid aqueous solution was added to this mixture, and then refluxed at 100 °C. After completion of the reaction, the solution was subjected to liquid separation three times with water / toluene, and toluene phase was evaporated at 40 °C to remove the solvent to obtain a fluid siloxane oligomer with a large amount of silanol groups. The siloxane oligomer was dissolved in toluene and heat treated at 100 °C to evaluate the thermal stability of silanol groups. Also, the siloxane oligomer was dissolved in a solvent (toluene or THF) and reacted with trimethylchlorosilane (TMCS) to evaluate a reactivity of silanol groups.

Results and discussion: The abundance ratio of Ph-Si and Me_2Si was 1 : 0.9, and the amount of silanol groups was calculated as 6.3 mmol/g from ^{29}Si -NMR and ^1H -NMR. When silanol groups in the siloxane oligomer were heat treated at 100 °C, only the silanol groups in trifunctional T species self-condensed while those in bifunctional D species remained (Fig. 1). This result suggests that two types of silanol groups of different thermal stabilities were present in this oligomer. For the further investigation siloxane oligomer was capped with TMCS and the ratio of silicon species was evaluated. T_2 silanol groups remained even when an amount of TMCS was larger than that of silanol. This result revealed that a part of silanol groups on T units was not able to be used as reaction site (Fig. 2). Also, the reactivity of D_1 unit was decreased when the concentration of siloxane oligomer was high. This result showed a concentration dependence of D_1 silanol groups in siloxane oligomer. To demonstrate selective modification of functional groups, heat-treated siloxane oligomer was capped with TMCS. Almost only D_1 silanol groups reacted with TMCS after self-condensation of T type silanol groups. These results showed that control of the thermal stability and reactivity of silanol groups is important parameters to fine control of molecular structure of siloxane for high functional materials.

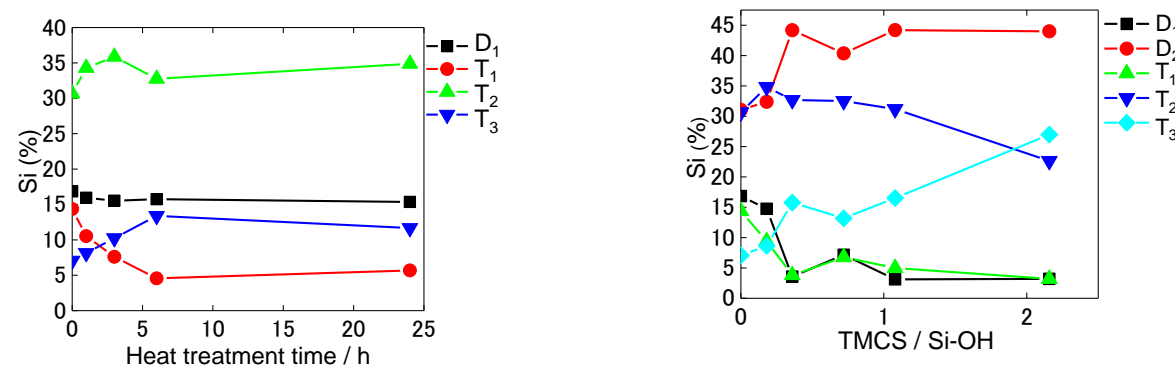


Figure 1. The ratio of silicon species after the heat treatment at 100 °C.

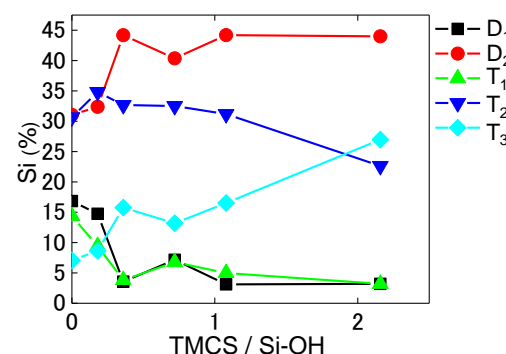


Figure 2. Ratio of silicon species after TMCS capping reaction at various TMCS concentrations.

Template-free seed-assisted synthesis of hierarchical zeolite ZSM-5

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Abstract: Due to the microporosity of zeolites there are diffusion limitations resulting in the rapid deactivation of catalysts in a number of petrochemical processes, such as cracking, isomerization, and alkylation. In the last decade hierarchical zeolites, containing additional system of transport meso / macropores was shown to be more efficient and stable in industrially important reactions than traditional microporous catalysts.

Most known syntheses of hierarchical zeolites are based on the presence of expensive organic templates (usually quaternary ammonium compounds), which is economically unacceptable. That is why template-free seed-assisted synthesis of zeolites was proposed for practical applications. The presence of seed crystals reduces the amount of template used, suppresses the appearance of impurity phases, and also tunes the size and morphology of the zeolite crystals formed.

In the present study, we vary conditions of template-free seed-assisted synthesis such as temperature and time of the hydrothermal synthesis, alkali, aluminum content and amount of seeds to find out the influence of these factors on crystallinity, morphology and texture of hierarchical zeolite ZSM-5. The obtained samples contain phases of ZSM-5 and P zeolite. The presence of meso- and macropores in well-crystallized samples of ZSM-5 has been established by low-temperature nitrogen adsorption, indicating the formation of hierarchical pore structure (Fig. 1).

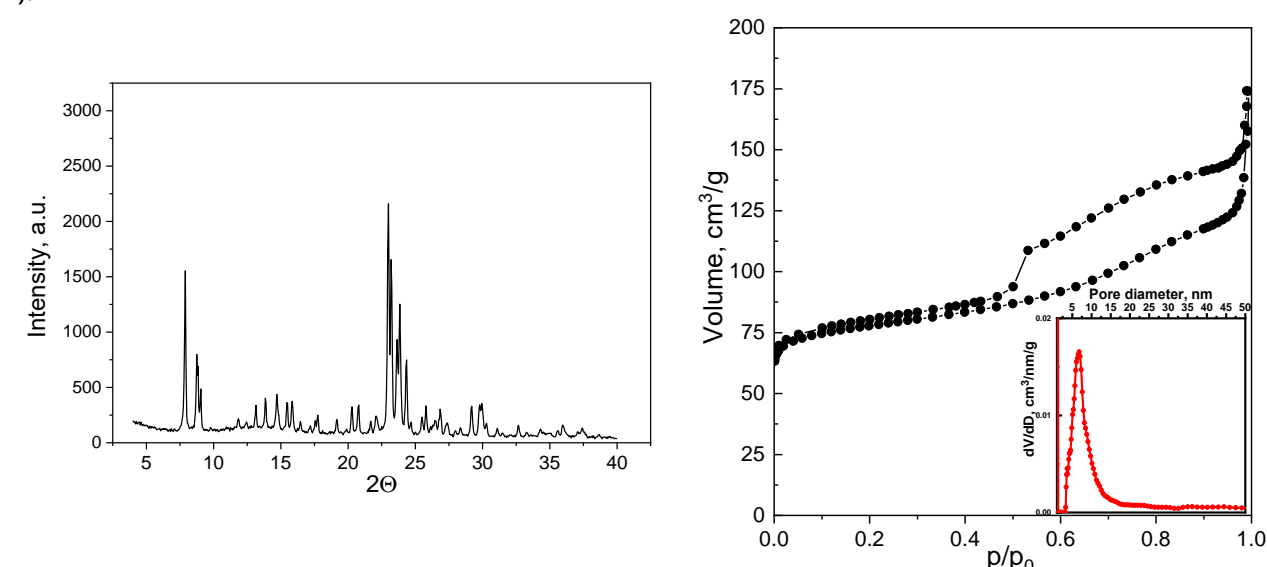


Figure 1. XRD pattern and adsorption-desorption isotherm of hierarchical ZSM-5, obtained by template-free seed-assisted synthesis method. The insert shows mesopore size distribution. The molar ratio of the components: 1.00 SiO₂: y Al₂O₃: x Na₂O: 50 H₂O: 4.74 EtOH, where x = 0.15-0.45, y = 0.01-0.04. Synthesis temperature: 160°C, synthesis time: 24h.

This work was conducted within the framework of State contract with Ministry of Science and Higher Education of the Russian Federation No. 14.604.21.0159 (Unique No RFMEFI60417X0159), the presentation was supported by PJSC Gazprom Neft project.

Structural features and properties of new hybrid solid electrolytes for dye-sensitized solar cells

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Abstract: Dye-sensitized solar cells (DSCs), firstly developed in 1991 [1], have received much attention due to their high energy conversion efficiency and low production cost. Recently, efforts have been made in developing solid electrolytes for use in DSCs [2] to avoid leakage and evaporation associated to liquid electrolytes, initially employed in these devices. Another key point to increase DSCs efficiency is to increase the contact area between the electrolyte and the semiconducting thin film (usually TiO₂ or ZnO) of the system [2]. Sol-gel process is particularly promising for these purpose since allows easy incorporation of a liquid electrolyte in a mesoporous thin film of semiconductor presenting high specific surface area and then gelation of the electrolyte inside the pores. On the other hand the dye responsible for the conversion of visible light into electrons may be incorporated in the pores before or with the electrolyte, which usually contains I⁻ and I₃⁻ species in order to promote the oxidation and reduction reactions for an adequate operating of DSCs [2]. Recent advances in the design of dyes have established that donor-pi-acceptor dyes absorb light much more strongly than commonly employed ruthenium-based dyes, allowing most of the visible spectrum to be adsorbed in thinner films [2]. In this work transparent and flexible hybrid Siloxane-Polyethers electrolytes containing KI and I₂ have been prepared by sol-gel process. The effect, on electrolytes structure and properties, of KI content and of the incorporation of a new donor-pi-acceptor organic dye synthesized in our group has been investigated. Impedance and Raman spectroscopy results show that for both types of polyethers (Polyoxyethylene (PEO) or Polyoxypropylene (PPO)), I⁻ and I₃⁻ species only contribute to ionic conductivity for hybrids containing long polymer chains, while for hybrids containing short chains such species interact with urea groups located at the interface between chains and siloxane nanoparticles. While for Siloxane-PPO hybrids the ionic conductivity of dye-free electrolytes exhibits a maximum around 10⁻⁵ S.cm⁻¹ when [O]/[KI]=15 (the oxygens being of the ether-type), the conductivity increases up to 10⁻⁴ S.cm⁻¹ when [O]/[KI]=4 (the largest ratio used in this work) for Siloxane-PEO hybrids, due to the polar character of PEO which promotes KI dissolution. Furthermore, for both type of hybrids, X-ray diffraction (XRD) and thermogravimetric analysis (TGA) show that dye incorporation promotes complete KI dissolution in the hybrid, which is an extremely promising result for future incorporation of very large amounts of KI and dye in these matrixes, aiming high efficiency of DSCs.

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One-pot Ni@SBA-15 monoliths as efficient catalysts for Methane Dry Reforming

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Abstract: Nickel is more available and cheaper than noble metals, which justifies its use as a catalyst for the Dry Reforming of Methane (DRM). This reaction transforms CO₂ and CH₄ into CO and H₂ (syngas, for the production of sustainable energy) [1]. In order to improve its stability (harsh conditions of the reaction) and increase its dispersion, nickel may be dispersed within the pores of a support thus playing with pore's confinement effect. In our previous work, different Ni/SBA-15 based catalysts were prepared through impregnation of previously prepared supports. However, post-synthesis methods tend to cause a partial or total blockage of pores and/or the agglomeration of nickel species on the surface resulting further in a decreasing catalytic efficiency.

Herein, we present an original protocol where Ni@SBA-15 monoliths are prepared through a single-step sol-gel pathway in order to afford a better dispersion of Nickel NPs (Ni wt. %: 2.5, 5, 7.5) [2]. Here, tetramethylorthosilicate was used as silicon source and as a solvent for P123, then an acidic solution of Nickel (II) was added. Rapid condensation of silica led to the inclusion of nickel in the aerogel. After calcination, the solids exhibited type IV N₂ sorption's isotherms with H1 hysteresis loops typical of mesoporous materials. TPR and XPS results confirmed, on one hand, the presence of nickel oxide and, on the other hand, its strong interaction with the support (high NiO reduction temperature (TPR) and Ni 2p_{3/2} binding energies (XPS)). It was also noteworthy, from XRD and TEM analyses that this preparation method leads to greatly dispersed and tinny nickel oxide particles. Indeed, no NiO peaks could be revealed from XRD and the observation of those particles, by HRTEM, was difficult. Nonetheless, the presence of nickel was confirmed by HAADF/MAPPING observations. After reduction, H₂ chemisorption indicated a Ni⁰ dispersion of 33%, which corresponds to particles size of c.a. 3 nm for the different catalytic performances toward the DRM. Ni_{5%}@SBA-15 monoliths turned out to be much more active, stable (12h on steam at 650°C) and selective than the Ni_{5%}/SBA-15 monolith prepared through impregnation method (Ni dispersion 8%). Ni wt%. This high Ni⁰ dispersion was reflected by superb

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Sol-Gel Materials for Optical Smart Window Applications

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Abstract: Catalytic performances toward the DRM. Ni_{5%}@SBA-15 monoliths turned out to be much more active, stable (12h on steam at 650°C) and selective than the Ni_{5%}/SBA-15 monolith prepared through impregnation method (Ni dispersion 8%).

Smart surfaces with switchable properties by external stimuli have great research and application value. An optical sol-gel thin-film material that exhibits reversible humidity-responsive

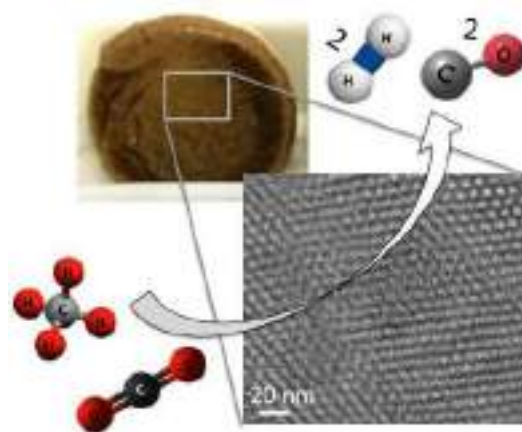
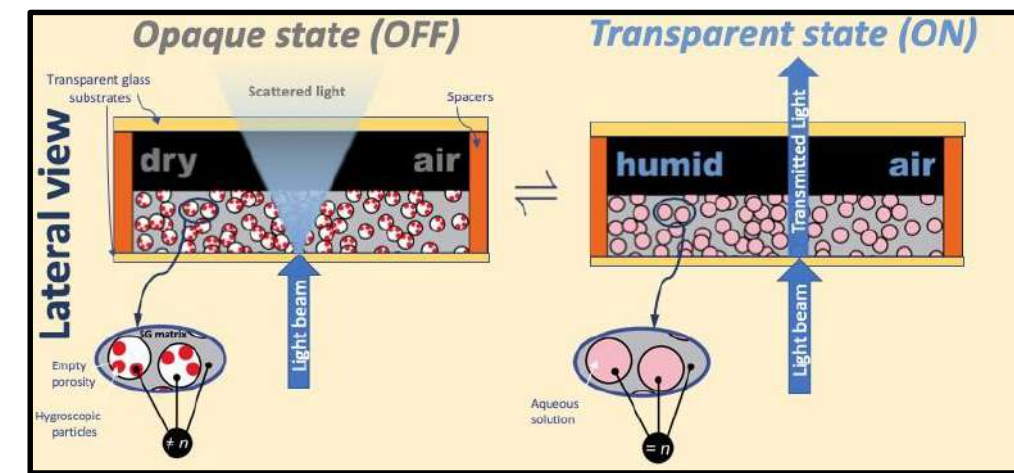


Figure 1. Ni_{5%}@SBA-15 monolith (Test conditions: 10 mg catalysts, GHSV = 960 L.g⁻¹.h⁻¹, flow 1:1 CH₄:CO₂ diluted 10% in Argon).

light-transmittance properties is presented. The reversible humidity-responsive light transmission thin-film material consists on a dispersive porous structure, with embedded hygroscopic and deliquescent compounds, that is able to absorb water molecules from humid air to fill-up the pores and become transparent to the incident light. Upon exposure to dry air, water is released from the structure and the material recovers its original light scattering properties. The developed thin-films can change their transparency when exposed to air with different relative humidity (RH), adjusting the light throughput. However, the transparent and opaque states show several limitations since the refraction index of the sol-gel matrix and the refraction index of the filled pores are not not fully matched. The wide pore size distribution also produces an undesired effect on the switching mechanism. To solve these problems, the chemical formulation has been adapted to match the refraction indices and for a narrow pore size distribution. The results show better EMD switching properties.



Therefore, in comparison to conventional smart windows, this material concept can be used to design new optical windows, having the advantage that they do not require liquid crystal, transparent conductive glass substrates or complex layer-by-layer architectures for operation.

Keywords: smart-window, thin-film, optical coating

Hybrid organic-inorganic silica materials and nanofibers for application in enantioselective catalysis

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Abstract: Periodic mesoporous organosilicas (PMOs) are chemically and mechanically robust materials based on silsesquioxanes, which are obtained by the sol-gel process from organo-bridged alkoxy silanes (figure 1). Due to a tunable size of mesopores and diversity of covalently bound organic fragments in the siloxane framework, PMOs have theoretically unlimited number of applications such as catalysis, drug delivery, gas adsorption or electronics¹. In comparison with other types of organosilica materials, PMOs enable the highest possible loading of active organic molecules with absolutely uniform distribution over the final hybrid material. Here we present syntheses of various novel bis(triethoxysilanes) and subsequent preparations of corresponding hybrid organosilica materials. Alternatively, we used the bis(triethoxysilyl) precursors in the preparation of nanofibers by the electrospinning method. To our best knowledge, it is a first report of electrospun nanofibers made from organo-bridged alkoxy silyl precursors with such a high content of the organic fragments. Finally, we tested the materials and nanofibers in catalysis of e.g. nitroaldol reactions to validate their catalytic activity.

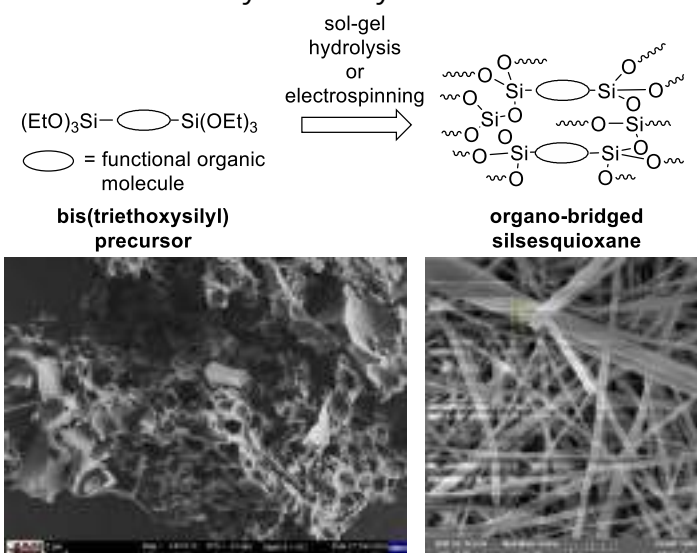


Figure 1. Preparation of PMOs and nanofibres from bis(triethoxysilyl) precursors; examples of SEM images of hybrid material (left) and electrospun nanofibers (right).

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Core@shell nanoparticles: synthesis, properties and catalytic performances

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Abstract: Conventional heterogeneous catalysts containing metallic nanoparticles (NP) supported onto an oxide carrier are usually prepared via synthesis involving interactions between a molecular precursor and the oxide surface sites. However, this approach suffers drawbacks which limit the development of new catalysts and still improvements are expected in order to solve barriers such as deactivation by thermal sintering, coke deposition or surface and bulk poisoning. In that context, the preparation of metal NP coated with mesoporous oxide shell, represents a potential breakthrough in the area of heterogeneous catalysis [1-2]. Indeed, the metal core@oxide shell systems exhibit exciting properties due to the protection effect of the shell which could reduce or inhibit the previous phenomenon. This work highlights the strong oxidation and sintering resistance of two mesoporous core@shell systems: Co@m-SiO₂ and Pd@m-SiO₂ (m for mesoporous) prepared via a modified Stöber or a precipitation method ("trapped" NP). Oxidation resistance of the metallic core has been followed under severe thermal treatments flowing air until 700°C with an in situ XRD analysis. The different core@shell systems or equivalents ("trapped" NP by precipitation) oxidize much more slowly than reference solids obtained by incipient wetness impregnation technique (same NP just deposited onto an oxide carrier, Figure 1a). Shape controlled Pd nanoparticles (cube and octahedron morphologies presenting mostly (100) and (111) facets, respectively) embedded in mesoporous silica (Pd_{cub}@SiO₂ and Pd_{oct}@SiO₂, respectively) were used as catalysts for the CO₂ methanation and compared to a Pd impregnated reference (Pd_{imp}/SiO₂). Comparing the first order rate constants (k, moles of CO₂ converted per mole of exposed Pd atoms) (Figure 1b), Pd_{cub}@SiO₂ and Pd_{imp}/SiO₂ have similar activities and Pd_{oct}@SiO₂ is less active. Interestingly, in terms of stability, the activity of both Pd@SiO₂ catalysts increases, whereas Pd_{imp}/SiO₂ shows a significant deactivation (~35%). This fact might be due to the particle size increase (observed by TEM) and modification of the morphology of impregnated particles: decrease of corners/edges and increase of (111) facets, which seem to have lower intrinsic reactivity considering the Pd_{oct}@SiO₂ result.

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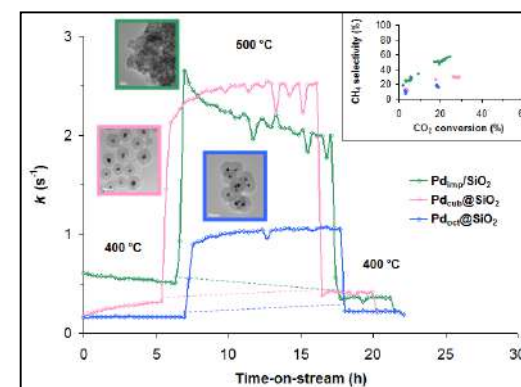
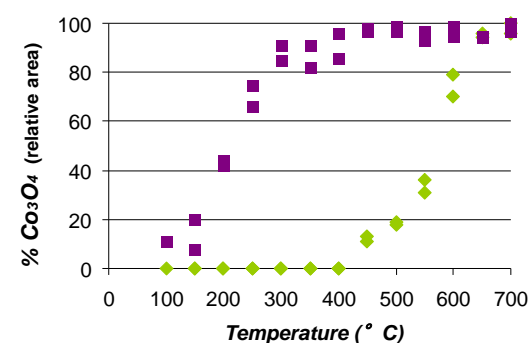


Figure 1: a Co_3O_4 relative particle size versus T for impregnated Co° (green diamond) and embedded $\text{Co}^\circ@m\text{-SiO}_2$ (dark square), b: pseudo order 1 rate constant for CO_2 hydrogenation of $\text{Pd}_{\text{cat}}@m\text{-SiO}_2$, $\text{Pd}_{\text{cat}}/m\text{-SiO}_2$ and $\text{Pd}_{\text{imp}}/m\text{-SiO}_2$

Multi-layered laminated aerogel blankets for various thermal insulation applications

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Abstract: Silica aerogel has been known as one of the most promising materials for high performance thermal insulation. However, the potential applications of this lightweight material are very limited as it is generally highly brittle and fragile due to its ultra-porous nature. Silica aerogel in its most widely applied form is found in fiber-reinforced aerogel blanket, but likely to generate dust when handled. Although silica aerogel particles have been proven to be non-toxic to human body, dust formation remains the major barrier to widespread applications of silica aerogel blankets. In this study a flexible dust-free silica aerogel blanket could be produced by wrapping thin aerogel sheet with a multi-layer laminate material. Making suitable selection of laminating materials it was possible, depending on needs, to control physicochemical properties of the resulting aerogel blanket product. The product may be highly flexible, readily formable, nonflammable, and even waterproof/breathable. A low thermal conductivity less than 10 mW/m-K could be obtained by applying vacuum during laminating. The thermal conductivities of waterproof/breathable resin/fiber laminated aerogel blankets were less than 20 mW/m-K. Here various types of multi-layered laminated aerogel blankets will be introduced.



Figure 1. Vacuum laminated aerogel blankets



Figure 2. Resin/fiber laminated aerogel blankets

This work was supported by the K-DARPA Program (KIST, Demand-based Aim-oriented Research for Public Agenda) of the Korea Institute of Science and Technology.

Anticorrosion Performance of Zinc Phosphate-Polyaniline (ZP-PANI) Composite in Waterborne Epoxy Resin

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Abstract: A zinc phosphate-polyaniline (ZP-PANI) composite designed to improve anticorrosion performance of waterborne epoxy resin (ER) was synthesized via in situ chemical oxidation polymerization of aniline in a flaky ZP suspension, using hydrochloric acid as dopant and ammonium persulfate as oxidant. By dispersing ZP-PANI in waterborne ER, ZP-PANI/ER coatings with different ZP-PANI additions ranging from 2.0 wt.% to 30.7 wt.% were prepared on tinplate. The as-synthesized ZP-PANI powder was characterized by scanning electron microscope, X-ray diffraction, Fourier-transform infrared spectra and thermogravimetric analysis. Using pure ER coating as a reference, the ZP-PANI/ER coatings were examined by bending test and impact resistance test to assess their mechanical properties, and by electrochemical impedance spectroscopy (EIS), potentiodynamic polarization curve and neutral salt spray test to evaluate their corrosion resistance. The results of bending test and impact resistance test showed that all coatings except for 30.7 wt.% ZP-PANI/ER had good adhesion and toughness. The results of electrochemical tests and neutral salt spray test showed that ZP-PANI exhibited superior anticorrosion performance in waterborne ER coating and the higher the addition amount of ZP-PANI, the better the corrosion resistance and passivation effect of the coating. When the addition amount of ZP-PANI rose to 7.0 wt.%, the coating exhibited remarkably improved anticorrosion properties and the coating with the highest ZP-PANI addition amount in the current study, that is 30.7 wt.% ZP-PANI/ER, performed the best in all coatings.

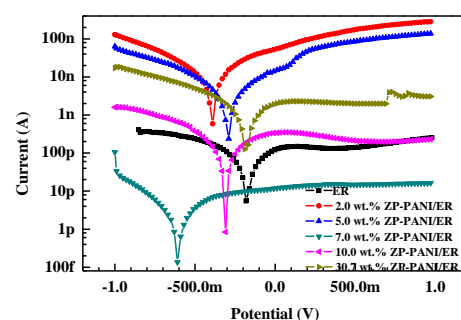


Figure 1. Potentiodynamic polarization curves of pure ER and ZP-PANI/ER coatings (Tafel plots).

Sol-gel synthesis of titanium dioxide and its testing in dehydrogenative cross-coupling of (hetero)arenes for creating new drugs

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Abstract: Nanoscale structures of titanium dioxide (TiO₂) are widely studied for their use in photocatalysis, both for the oxidation of harmful organic substances and for the synthesis of new organic molecules at the visible range of light. Sol-gel synthesis of TiO₂ allows adjusting the structural characteristics of the material by selecting of synthesis conditions. So, the aim of the work was the sol-gel synthesis and study of titanium dioxide as an effective photocatalyst for synthesis bi(hetero)aryls with high yields depending on the annealing temperature of TiO₂ in a hydrogen medium.

Nanoscale TiO₂ were synthesized by sol-gel method from Ti(C₄H₉O)₄, C₂H₅OH and H₂O with a solution of pH=6. The method of preparation is described previously in [1]. Subsequent annealing of TiO₂ powders was carried out in a stream of hydrogen (from device of the generator of pure hydrogen GPH-12A) within 1 h (in furnace MTF-2MP) at temperatures of 200, 400, 600, 800 и 1000 °C.

The X-ray diffraction patterns of the synthesized TiO₂ powder before and after annealing in a hydrogen stream were obtained on a Shimadzu XRD-7000 autodiffractometer. The band gap (E_g) was calculated using the Kubelka-Munk function from the spectra of diffuse optical reflection recorded on an Edinburgh Instruments FS-5 spectrophotometer. The measurement of the specific surface was carried out by the BET method using Gemini VII 2390 analyzer.

It was established that synthesized TiO₂ and annealed at 200 °C have an amorphous structure. The phase transformation from amorphous structure to anatase takes place at annealing at 400 and 600 °C, annealing at 800 and 1000 °C lead to formation of rutile phases. The specific surface area and the band gap decrease with increasing of annealing temperature from 300 to 10 m²/g and from 3.3 to 2.6 eV, respectively. Catalyst testing [1] in oxidative S_N^H cross-coupling of acridine with indole showed an increase in 9-(indole-3-yl)acridine yields until 80% when the TiO₂ annealing temperature rises to 800 °C, but decreases until 60% with a further increase of annealing temperature to 1000 °C.

The results of the product yield using TiO₂ after annealing in a stream of hydrogen (800 °C) exceed the values of industrial Degussa P25 (32%) and Hombifine N (60%), and our earlier sol-gel TiO₂ at annealing in air (until 60 %). Thus, the synthesized titanium dioxide after annealing for 1 h at 800 °C is an effective photocatalyst to obtain 9-(indole-3-yl)acridine with high product yield.

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New procedure for the preparation of metal-oxide mesoporous supported films

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Abstract: We report here an innovative, simple and effective method for the build-up of metal-oxide mesoporous supported films, in this case titanium dioxide on silicon wafer, showing variable thickness, refraction index and porosity. This procedure allows reaching tunable textural characteristics (pore size, shape and distribution of pores) along the film growth by using pre-formed gels at different stages via a simple regulation of the residence time of the precursors deposited on the film support coated with a surfactant (Fig. 1).

The approach reported in the present communication introduces a key modification of the conventional soft templated methods (e.g. Evaporation Induced Self Assembly, "EISA" method), which involves here two consecutive steps. In the first one, it is carried out a coating of the substrates with surfactant species (e.g. Pluronic 123) that will further deserve as a porogen agent after thermal treatment. In the second step, it is deposited the gel precursor on the previous coating, being spontaneously produced a diffusion of species between these two superposed layers. This procedure determines the generation of mesostructures whose nature depends on the dynamics of the reactants at the involved interface, which affect the hydrolysis and polycondensation of the precursors and therefore the final porosity characteristics of the supported film.

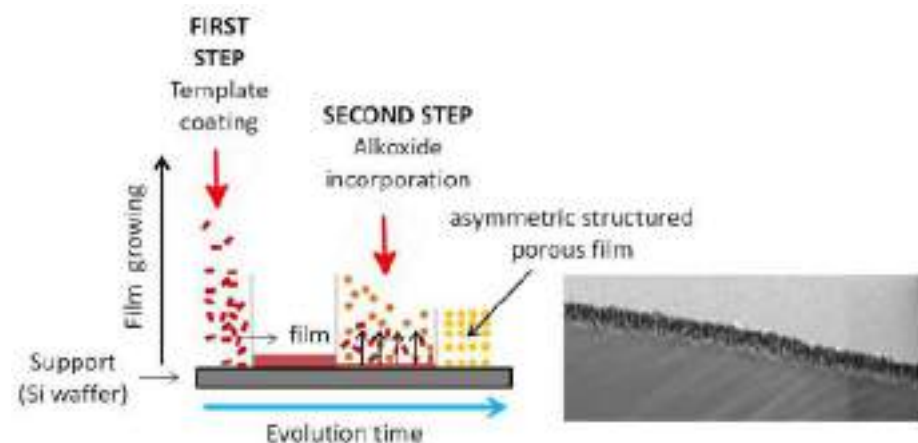


Figure 1. Scheme of the here reported procedure for the supported mesoporous films formation

The main advantage of this method is the possibility to reach the formation of asymmetric pore nanostructures that were not possible to develop using classical EISA procedures. This preliminary contribution opens the way to future developments of a wide variety of nanoporous coatings dealing with diverse potential applications such as photocatalysis, Bragg mirrors, energy generation and storage, including solar cells devices and lithium battery negative electrodes, etc.

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Study of corrosion of AA2024-T3 protected by sol-gel coating with Electrochemical Impedance Spectroscopy and Ellipsometry in liquid cell

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Abstract: Aluminum alloy 2024 T3 is widely used in the aeronautical field thanks to its high weight to strength ratio. However, it is particularly sensitive to corrosion due to its heterogeneous structure. To protect these alloys, the actual strategy is to use a three layer stack doped with Cr^{VI} based corrosion inhibitors. Nevertheless, those substances are highly toxic so their replacement has become a critical issue for the aircraft industry. In this context, sol-gel based coating are good candidate. Indeed, the huge quantity of precursors allows tunable properties and can provide good adhesion on the substrate. Moreover they are easy to deposit and they can incorporate corrosion inhibitors less toxic than chromate¹.

One objective of this PhD is to use sol-gel chemistry to develop new anticorrosion coatings. On one hand, work has been done on hybrid hydrophobic layers to enhance barrier properties. On the other, mesostructured layers, potential matrix for anticorrosion inhibitors has been studied. The final goal is to couple those two material in a multi-layer system in order to optimize anticorrosion properties.

Development and optimization of those system requires particular techniques to analyze in-situ anticorrosion properties as well as coating structural evolution (porosity, swelling, resistance to hydrolysis ...). For this purpose we developed a new analytical approach based on Electrochemical Impedance Spectroscopy² (EIS) coupled with environmental ellipsometry³ that can be used for different coating deposited on the alloy.

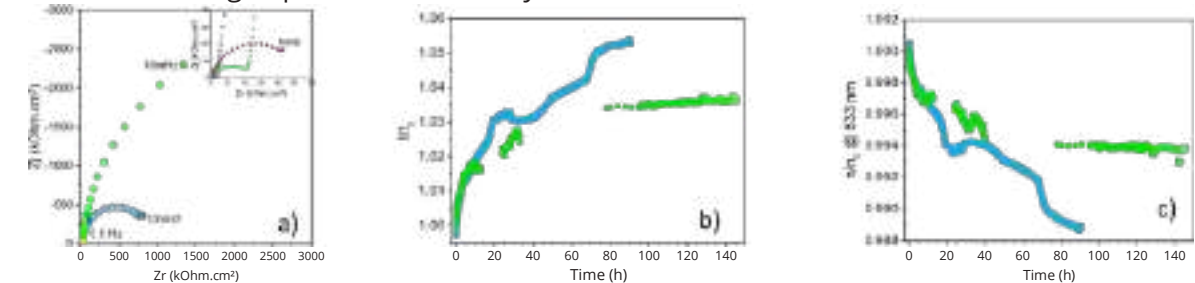


Figure 1. a) Nyquist diagram b) Thickness evolution and c) Refractive index evolution in Na₂SO₄ 0.5 M. In blue for TEOS based coating and in green when methyl groups are added

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Investigating Unusual Organic Functional Groups to Engineer the Surface Chemistry of Mesoporous Silica to Tune CO₂-Surface Interactions

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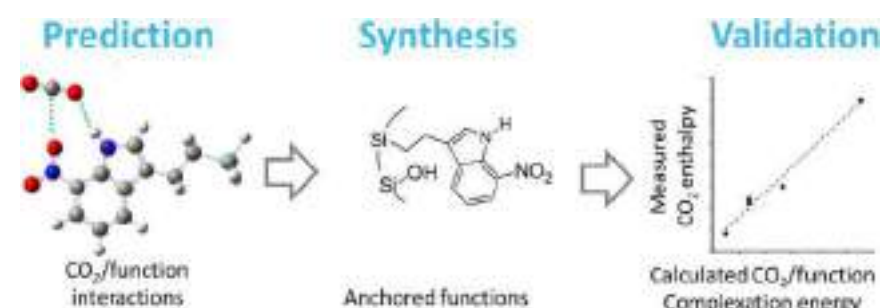
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Abstract: The separation step in any chemical process can represent over 50% of the operational expenditure and separations, in general, represent 10–15% of the world energy use. Adsorption based separation processes, such as Pressure Swing Adsorption, can provide an interesting alternative to other techniques in terms of energy use, environmental impact, simplicity, and overall cost. Indeed, research is active in the use of adsorbents with the search for materials with improved properties in terms of uptake (working capacity) and selectivity for example. Increases in selectivity can be obtained by adjusting the pore size to increase the segregation between molecules of different sizes, known as molecular sieving. One can adapt the shape of the pores to allow for optimal packing and thus induce entropic effects to aid selectivity. One can equally fine-tune the chemistry of the adsorbent surface in order to induce stronger attractions for a target species thus increasing thermodynamic selectivity. In this latter case, there is an infinite range of possibilities to functionalize a material with organic moieties. Then computational methods are extremely useful to screen for the optimal organic functional groups for a given gas.

In this work¹, a strategy is proposed where ab initio calculations are compared and validated by adsorption microcalorimetry experiments for a series of, so far unexplored, functionalized SBA-15 silicas with different spacers (aryl, alkyl) and terminal functions (N₃, NO₂). This validation then permitted to propose the use of a nitro-indole surface functionality. After synthesis of such a material the predictions were confirmed by experiment. This confirms that it is possible to fine-tune CO₂-functional interactions at energies much lower than those observed with amine species.



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Bio-adhesive Gel Based Crosslinked Polymer for Hemostatic and Rapid Wound Healing Process

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Abstract: In this study, we synthesized a bioadhesive gel possessing excellent hemostatic that allowed rapid wound healing process via catechol conjugated poly(dimethylaminoethyl methacrylate-co-*tert*-butyl methacrylate) [poly(DMA-co-*t*-BMA)-CA, C-PDB]. The formation of gel was constituted from crosslinking between C-PDB and chitosan via the Michael addition reaction. Herein, chitosan was utilized as crosslinker due to the reaction between amine group of chitosan and quinone moieties of catechol under mild alkaline condition. As a result, the formulated gel showed a significant adhesive force in lap shear strength test that formed quickly *in vitro*. Furthermore, the gel displayed strong hemostatic behavior *in vivo* test when applied on a bleeding site of rat aorta. The gel also performed rapid wound healing process, observed in Hematoxylin and eosin (H&E), Masson's trichrome, and reticulin staining in histological studies. In conclusion, the prepared glue matrix has shown as a potential candidate for hemostatic and wound tissue healing in biomedical applications.



Figure 1. The synthesized bio-adhesive gel for hemostatic and wound healing applications.

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Structure and Luminescent Properties of Sol-Gel Derived Lanthanide Doped Hybrid Organic-Inorganic Materials

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Abstract: RE³⁺ (Tb³⁺, Sm³⁺, Nd³⁺ and Ce³⁺ or Dy³⁺) doped organic-inorganic hybrid materials prepared by sol-gel method at room temperature and thermally treated at 95°C have been investigated as potential matrices for rare earth luminescence. Tetraethyl orthosilicate (TEOS), ethylene glycol dimethacrylate, ethyl methacrylate, propylene carbonate, organic solvents and inorganic salts (chlorides) of rare earth metals were used in the synthesis of the hybrids. The structure, morphology and luminescence properties were investigated by X-ray Diffraction (XRD), Scanning Electron Microscopy equipped with Energy Dispersive X-ray Spectroscopy (SEM/EDS), Fourier Transform Infrared Spectroscopy (FTIR) and Photoluminescence Spectroscopy (PL). The materials exhibited good transparency. The X-ray diffraction patterns suggest that the hybrids have amorphous structure. IR absorption peaks at about 1440 cm⁻¹ may have been triggered by the formation of coordinate bonds between the oxygen atoms of carboxylic groups and rare-earth ions. Even if photoluminescence efficiency is limited by non-radiative relaxation due to the presence of residual water and hydroxyl groups in the matrices, rare earth photoluminescence is observed in all the samples. Under excitation with UV radiation in a range of 200-350 nm, the luminescence spectra of all the hybrid materials show the relatively intense narrow emission lines corresponding to the RE³⁺ centers introduced into sol-gel matrices.

The luminescence intensity enhancement can be assigned to the co-doping with Ce³⁺ ions and energy transfer from Nd³⁺ and Tb³⁺ ions.

Key words: sol-gel, hybrid materials, Lanthanide doping, photoluminescence

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Extended investigations on multifunctional @SiO₂ nanocomposite for biotechnology and Energy applications

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Abstract: Among the arising nanotechnologies in catalysis, optical or biological, multifunctional nanomaterials with complex or hybrid architectures constitute one of the most promising and studied research fields. For instance, supramolecular materials focusing on gene and drug delivery[1], inorganic luminescent silica nanoparticles for bioimaging[2], superparamagnetic iron oxide nanoparticles as contrast agents for magnetic resonance imaging (MRI) or colloidal mediators for cancer magnetic hyperthermia[3] find numerous applications in the field of nanobiotechnology[4]. During the last decade, we developed sol-gel synthesis in microemulsion environment, which is a versatile, highly reproducible and efficient methods to prepare multifunctional silica nanocomposite particles incorporating magnetic and/or optical nanosized inorganic materials.[5-8] Recently, we focused on metal atom clusters (Mo, Re, Ta) compounds. We demonstrated they could play a significant role for visible-near infra-red (NIR) optical or biological applications. [9-16].

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Springback Effect in Silica-based Aerogels

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Abstract: The springback effect is an interesting phenomenon, because it represents a surprisingly large volume change for a ceramic material. The phenomenon enables drying of sol-gel synthesized aerogels at ambient pressure to achieve porosities similar to those of supercritically dried materials. While drying at ambient pressure (APD), the material might shrink up to half its size. Heat treatment and surface modification may expand the dried gel to almost the original size. Supercritical drying (SCD) bypasses the capillary stresses of the wetgel, because there are no liquid-vapour interfaces, prohibiting the induced stresses leading to shrinkage [1]. On the other hand, silylation of the surface of the gel, which is done by surface modification with i.e. trimethylchlorosilane (TMCS), grants reversibility of this shrinkage by inducing the springback effect, leading to comparable results of APD and SCD derived materials. The phenomenon has to be studied thoroughly for the well-known silica system to predict the behaviour and transfer this knowledge to other systems. Incomplete springback behaviour would lead to higher density materials, prohibits a fit accuracy and might lead to cracking of the material.

We present the influence of different processing parameters (i.e. the used precursors, precursor to water ratio, network modifiers) on the springback effect. Small-angle X-ray scattering (SAXS) is applied to prove the mechanism of the springback effect. The latter is typically attributed to the repelling of the alkyl groups of the dried gels. As the springback effect is observed in gels with a low degree of crosslinking [2], strong and flexible gel networks are required to disengage the silyl groups. As the springback effect influences the geometry, microstructure and stability of the material, its understanding is one of the decisive issues in the ambient pressure drying of aerogels, which is a key step towards continuous aerogel processing.

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Microwave sintering of Alumina-based Sol-Gel abrasives: Direct heating in dynamic mode

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Abstract: One of the major characteristics closely linked to the performance of a polycrystalline abrasive grit is its microstructure, which highly influences its physical and mechanical properties (hardness, fracture toughness, wear resistance under certain conditions...). In addition, one of the main actors in « Abrasive World » being corundum thanks notably to its stability in temperature, corundum-based ceramic composites elaborated by a Sol-Gel process aroused lots of interest for decades [1-2].

Microwave sintering has emerged in recent years as a promising technology for faster, cheaper and more environment-friendly processing of a wide variety of materials, giving it a significant advantage over conventional sintering processes [3]. Moreover, hybrid sintering with the help of a susceptor has been generally developed for their densification by radiative contribution [4].

In this context, a direct Microwave-heating process in dynamic mode has been considered with two project partners: ITACA (UPV) and the manufacturer INNCEINNMAT. A prototype sintering furnace is under development and will be installed at IMERYS research center in Austria.

Thus, the work presently featured focuses on the direct interaction Microwave/Matter by measuring the dielectric properties of alumina-based sol-gel composites using specific equipment developed by ITACA [5]. Some preliminary sintering tests carried out on the lab prototype have already shown promising results with very fine microstructure and hardness up to 25 GPa, for a residence time of less than a minute.

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3D Printing of Hierarchical Porous Silica

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Abstract: We describe a method for the 3D printing of hierarchically organized silica structures that consist of a unique cellular macroporous network comprising cylindrical mesopores on a 2D hexagonal lattice in each strut. The starting sol (ink) contains condensable silanes in the presence of organic porogens and phase separation inducing agents, enabling the formation of an inorganic backbone with at least bimodal porosity. For the printing process we take advantage of the dynamics of the ongoing condensation reactions of the silane precursors, resulting in a viscous, printable ink after a certain time of processing. The printed objects are aged, washed and then dried at ambient conditions. The resulting material combines the features of the hierarchically organized network with meso- and macropores plus an additional hierarchical level arising from the printed superstructure (Figure 1).

We present structural data of these novel morphologies, which have been investigated in detail with comprehensive characterization by electron microscopy, small angle X-ray scattering and N₂ adsorption analysis. In addition, we demonstrate how a variation of selected synthesis parameters influences the printing process as well as the final materials structure.

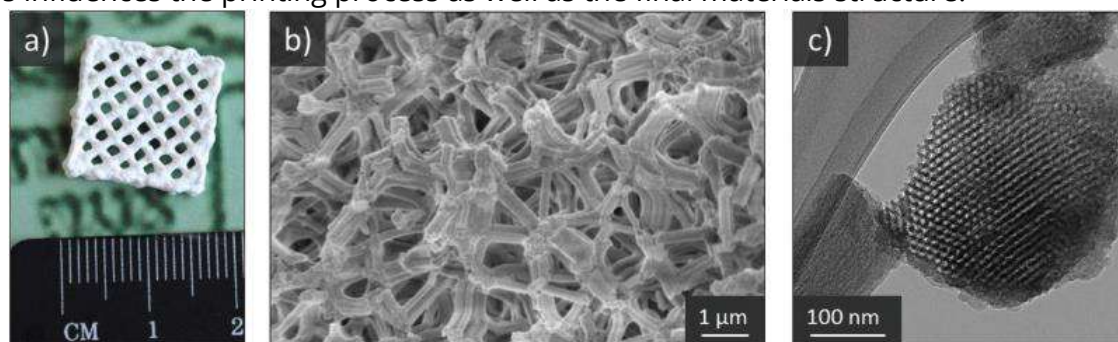


Figure 1. 3D printed silica structures (a, photograph) with a macroporous network of struts (b, SEM image) comprising hexagonally arranged mesopores (c, TEM image). [1]

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Platelet rich plasma loaded injectable hydrogels for cartilage defect repair

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Abstract: Platelet-rich plasma (PRP) is usually used for the repair and regeneration of damaged articular cartilage. However, PRP injection has the shortcoming of unstable biological fixation and burst release of growth factors. Injectable hydrogels have been used to deliver cells and growth factors for an alternative, less invasive treatment of cartilage defect. In this study, hyaluronic acid *hybridized* with gelatin in aqueous solutions were cross-linked with genipin followed by a freezing/thawing treatment to obtain injectable hydrogels. The gelation rate was affected by the concentrations of genipin, hyaluronic acid *and* gelatin, and the pH values. The hydrogels are injectable and strongly adhesive, and have slow enzymatic degradation rate. Hyaluronic acid and the freezing/thawing treatment increased the compressive strength of the hydrogels and facilitated the sustained release of growth factor. The PRP-loaded hydrogel promoted cartilage regeneration in rabbits, which may lead to an advanced PRP therapy for enhancing cartilage repair.

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Aerogels: mechanical and thermal properties measured by Molecular Dynamics

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Abstract: Sol-gel reaction provides some high potential aerogel materials. Among them those made of silica have potential application in high tech application such as aerospace and mass market applications such as packaging, transportation or building retrofitting. Most applications require several functional properties, and the optimal aerogel texture for thermal performance usually do not fit with the optimal texture for mechanical performance. For instance, the low density (smaller than 10% of the bulk density) and the nanostructured porosity of silica aerogels provide extremely low thermal conductivities but also impact their poor mechanical properties.

Atomic scale simulations now offer the opportunity to simulate several properties. For such simulations, the interatomic potential should be carefully chosen to ensure result validity but also reasonable computational times. A modified BKS potential for silica is used here. It allows decreasing the computational time by 3000 compared to a full BKS interatomic potential while predicting correctly mechanical properties. Those simulation were performed on several large volume of aerogel up to 100nm*100nm*100nm. A scaling law was proposed to describe modulus dependence to density. The mechanical behavior was studied in details. The surface stress that silica ligaments experience produces a significant tension-compression asymmetry and an unusual discontinuity in the Poisson ratio. The ductility of highly porous silica aerogels arises from an interplay between surface stress and a significant amount of reorganization in ligaments.

Despite its good performance, this potential still leads to computational times that are too large to predict the thermal conductivity of a representative volume of nanoporous silica. This is due to the low thermal diffusivity of the material. Here, a new method that takes advantage of the amorphous structure of silica and the diffusive nature of phonon heat transfer at the scale is proposed. The time dependent temperature profile in the system obtained from Non-Equilibrium Molecular Dynamics simulations is compared to the classical solution of the thermal diffusion equation and an identification procedure is used to determine the thermal conductivity of silica aerogels.

At an higher scale, the compression of highly porous silica nanospheres is investigated. The ligaments network (3–6 nm) of nano-sized silica sustains the load and nanoparticles deform plastically due to highly localized shear events, at the junctions between ligaments. Dangling ligaments are more numerous as the size of the nanosphere decreases, thus impacting the mechanical response. Based on simulation results, we propose a scaling law that describes the particle size effect on the indentation force when applied to silica aerogel secondary nanoparticles under compression.

Atomic scale simulation might help to simulate properties for a large set of aerogel texture and then only produce by sol-gel the optimized ones. As recent advances in low dose electron microscopy gave 3D image of aerogel texture: pore size distribution, necklace particle, and dead arms: real and simulated aerogel are easily compared.

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Control over Multiscale Pore Size of Hierarchically Porous Carbon Monoliths

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Abstract: A large number of studies in material science have revealed the importance of morphological design in multiple length scales and established several approaches to tailor porous structures, such as hard templating, supramolecular self-organization and phase separation method. Recently, we have developed a facile one-pot sol-gel synthesis of macroporous polymer scaffolds comprising mesoporous nanorods with two-dimensional (2-D) hexagonal ordering by combining the micellar templating in nanometer-scale with the phase separation in micrometer-scale.^{1,2} The subsequent carbonization of the porous resin yields hierarchically porous carbon monoliths.

In this study, we have aimed at tuning mesopore size in wider range while maintaining the well-defined macroporous morphology. The survey on the relationship between sol composition and gel microstructure disclosed that increasing the amount of swelling agent, 1,3,5-trimethylbenzene (TMB), as well as HCl aq. results in the enlargement of mesopore size, which is accompanied by the loss of periodicity and the coarsening of macroporous structure. It was found that the addition of mineral salts, for example KCl, effectively improves the meso- and macroporous morphology, giving rise to the hierarchically porous carbon monoliths with enlarged mesopore size, as shown in Figure 1.

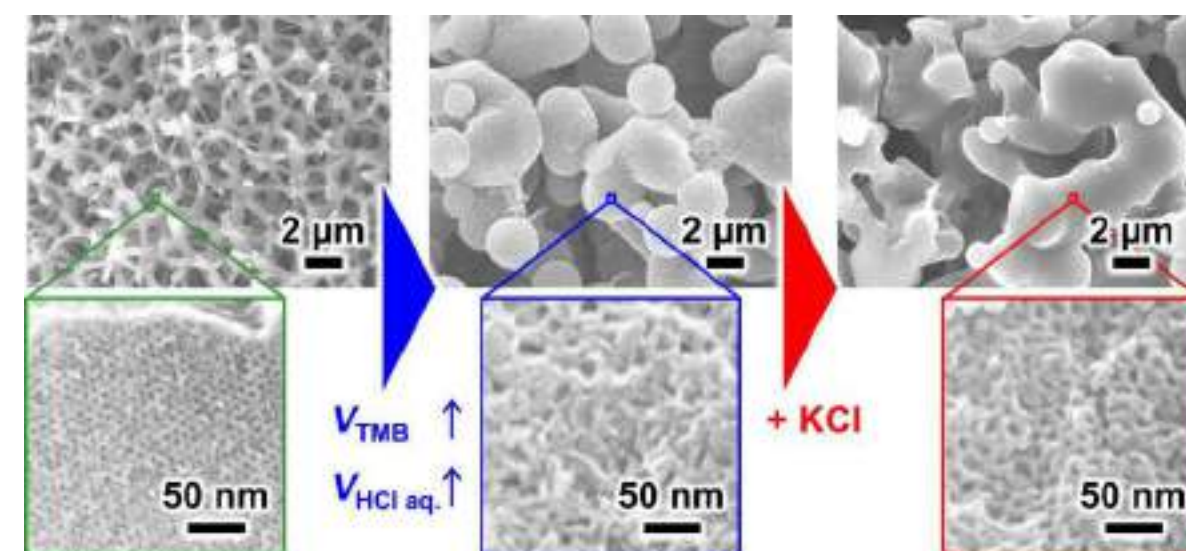


Figure 1. Pore size control of meso- and macropores in the hierarchically porous carbon monoliths.

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Fabrication of Spherical Silica Aerogel Powders via Sol-Gel Technique from Water glass

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Abstract: A silica aerogel is an ultra-porous material containing more than 90 % pores with a highly cross-linked network structure. The silica aerogel has unique properties such as large specific surface area, low thermal conductivity, low dielectric constant, low index of refraction, and so on. Owing to these unique properties, such aerogels have been studied extensively for use as catalysts and thermal insulators, and in applications related to adsorption, and drug delivery systems.

Silica aerogels can be fabricated in the form of a powder, monolith, blanket, and so on. Among these forms, the powder-type silica aerogel is thought to be the most promising because the powder can be applied to a wide field of applications. However, an aerogel powder with a fine particle size is hard to handle since it has a high apparent density and a low flowability. In this regard, much attention has been focused on granule- or bead-type silica aerogels. Until recently, silica aerogel granules or beads from hydrogels or alcogels were mainly synthesized by breaking down the wet gel using a high power mixer or by dropping a silica sol into an aqueous solution containing a gelation catalyst. However, these techniques make it difficult to obtain spherical aerogel granules or beads with a controlled particle size and microstructure.

In this study, a novel synthesis technique was proposed to fabricate spherical silica aerogel powders via one-pot surface modification(SM)/solvent exchange(SE) and the subsequent ambient pressure drying (APD) from water glass. We significantly reduced the total processing time up to 2 to 3 hours, which normally takes 24 h or sometimes several days. The tap densities, particle sizes, and thermal conductivities of the spherical aerogel powders were measured and the processing parameters were discussed in terms of their effect on emulsion polymerization and SM/SE.

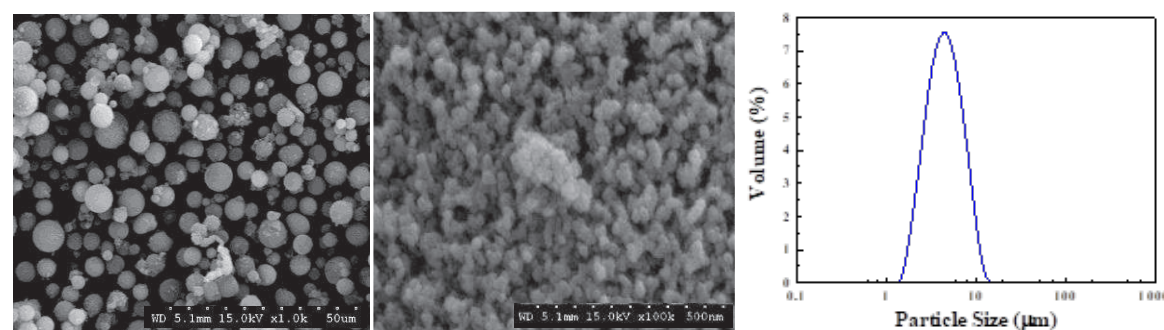


Figure 1. SEM images and particle size analysis of the silica aerogel powder.

Effects of siloxane main-chains in chiralities of single-chain and double-chain polysiloxanes containing binaphthyl groups

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Abstract: Studies on chiral inorganic polymers, such as chiral silica gels, have been reported so far.¹ However, since chiral silica gels are insoluble, it is difficult to apply to various fields compared to the chiral organic polymers. Therefore, the developments of soluble inorganic chiral polymers are important topics for evolution of new chiral inorganic materials. On the other hand, our group have reported the preparation of ammonium-group-containing ladder-like polysilsesquioxane (Am-PSQ)² and linear polysiloxane (Am-PS),³ which have double-main-chain and single-main-chain, respectively.

In this study, we prepared soluble ladder-like polysilsesquioxanes and linear polysiloxanes containing chiral binaphthyl groups in their side-chains (Chiral-PSQs and Chiral-PSs) by reaction of Am-PSQ and Am-PS with binaphthyl derivatives (Scheme 1). Binaphthyl derivatives were prepared by reaction of chiral 1,1'-bi-2-naphthol with 1,1'-carbonyldiimidazole. Based on the ¹H NMR spectra of Chiral-PSQs and Chiral-PSs, it was found that the ammonium groups in the polymers and the functional groups in the binaphthyl derivatives were linked in almost equimolar. From the results of specific rotations, we assume that the main chains of these polysiloxanes have chirality. Since the specific rotations of Chiral-PSQs were higher than those of Chiral-PSs, it is expected that the double-main-chain can stably form a twisted or helical structure.

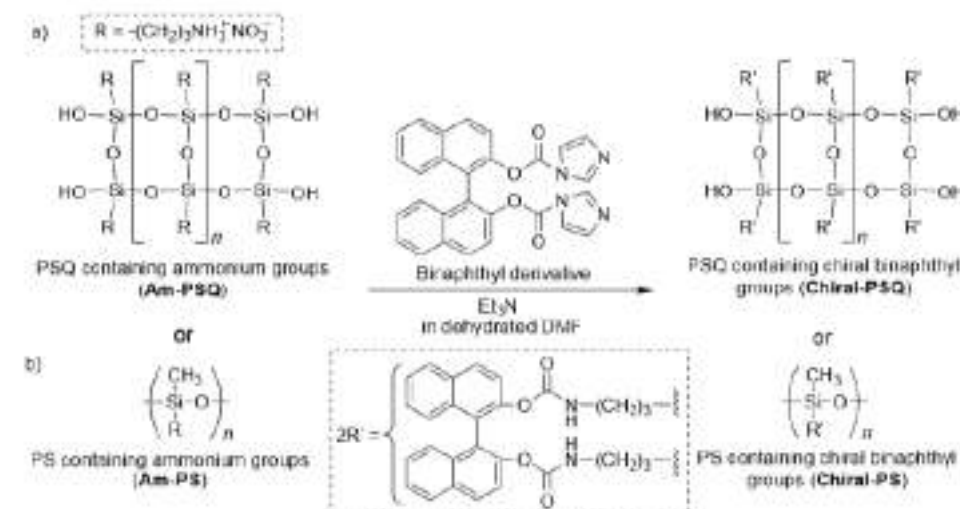


Figure 1. Preparation of a) ladder-like polysilsesquioxane (Chiral-PSQ) and b) linear polysiloxane (ChiralPS) containing binaphthyl groups in their side-chains.

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Hybrid dielectric materials obtained in situ sol-gel reaction

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Abstract: Continuing some previous results, the paper presents some hybrid thin films with improved dielectric properties obtained by modified sol-gel method, using zirconia nanoparticles (NPs) and methylmethacrylate monomer (MMA). Two different ZrO_2 NPs:MMA molar ratio (1:1 and 4:1) sols were used for spin-coating deposition onto n-type doped Silicon substrates. The formation of homogenous hybrid films was promoted by thermal treatment at 160°C and UV irradiation at 256 nm.

The obtained films were investigated by optical microscopy and scanning electron microscopy (SEM) for thickness and morphology. The dielectric properties of the obtained thin films were measured using a Metal-Insulator-Metal (MIM) structure for current-voltage and capacitance-voltage characteristics. Adding ZrO_2 nanoparticles to methylmethacrylate monomer precursor showed higher dielectric permittivity of the resulted thin films with thickness between 100 and 200 nm. The I-V curves of these thin films show dielectric behaviour with leakage current values between 10^{-13} - 10^{-11} A and permittivity values ranging between 3.5 and 7.5 at 1 MHz, depending on the zirconia:MMA molar ratio.

This work was supported by the projects FP7- POINTS (Printable Organic Inorganic Transparent Semiconductor Devices) No. 263042/2011 and CAPACITATI M-III EU 156/2011-POINTS.

Evaporation-driven deposition of WO_3 electrochromic films by low-speed dip-coating technique

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Abstract: We propose a novel coating technique with low-speed dip-coating for preparing metal oxide thin films from aqueous solutions of metal salts. During dip-coating at substrate withdrawal speeds below 10.0 mm min^{-1} , the solvents evaporate from the meniscus, where the deposition of solutes locally progresses. The coating technique accompanied by evaporation-driven deposition would enable a synthetic route for metal oxide films from simple solutions containing only water and metal salts without organic additives, providing a low-cost and resource-saving coating process [1-2]. In this work, we prepared WO_3 film materials from organic-additive-free aqueous solutions by low-speed dip-coating, and evaluated the electrochromic properties.

Coating solutions were obtained by dissolving $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41}$ and SnCl_4 in NH_3 aqueous solutions of pH 11.5 under stirring at 60 °C ($[(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 5\text{H}_2\text{O}] = 6 \text{ mM}$, $[\text{SnCl}_4 \cdot 5\text{H}_2\text{O}] (x) = 0$ or 5 mM). Precursor films were deposited on FTO glass substrates by dip coating at the substrate withdrawal speed of 0.05 cm min^{-1} in a thermostatic oven at 40 °C. WO_3 ($x = 0 \text{ mM}$) and Sn-doped WO_3 ($x = 5 \text{ mM}$) films were obtained by heating the precursor films in air, at 200 °C for 24 h, or 500 °C for 0.5 h.

Precursor films were deposited on FTO glass substrates from the coating solutions of $x = 0$ or 5 mM by low-speed dip coating. Monoclinic WO_3 phase was detected in the XRD patterns for the films heated at 500 °C irrespective of x . On the other hand, the films heated at 200 °C showed no diffraction peaks, which indicates the deposition of WO_3 amorphous layers on the substrates. XPS analysis shows that the amorphous films of $x = 5 \text{ mM}$ contained Sn^{4+} ions and the Sn : W mole ratio was 1 : 0.14. The electrochromic properties of WO_3 and Sn-doped WO_3 films heated at 200 °C were evaluated. Both films showed electrochromic response (Fig. 1), where the electrochromic properties was improved by doping with Sn^{4+} ions. The Sn-doped WO_3 films exhibited the fast coloration and bleaching.

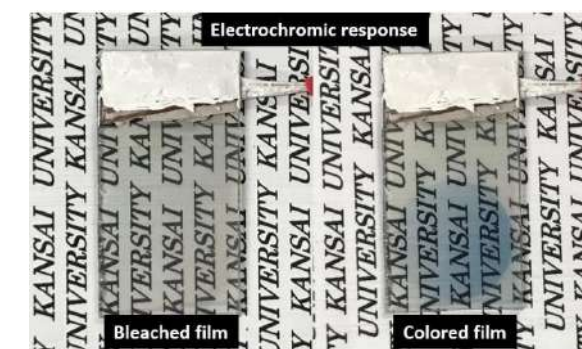


Figure 1. Appearance of Sn-doped WO_3 films after coloration and bleaching.

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Fabrication of Topological SERS Sensing Film by One-Push Wrinkle Processing

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Abstract: Mother nature provides the ultimate inspiration for various topologically ordered patterns, structures, and flexible motion from one-dimensional (1D) linear structures such as actin filaments and muscle fibers, two-dimensional (2D) arrayed compound eyes of insects, Morpho butterfly wings composed of three-dimensional (3D) hierarchical complex structures, etc. With self-assembly and self-organization, which are the driving principles in the formation of these natural structures, a number of biologically inspired artificial materials have been prepared. Surface wrinkling is an inventive and unconventional technique that is also fast and inexpensive for various types of surface patterning involving sinusoids (ripples), herringbones, labyrinthine designs, etc. It is especially suited for large-area surfaces of poly(dimethylsiloxane) (PDMS) elastomers based on mechanical (buckling) instability. This self-organization buckling phenomenon is widely observed in natural systems such as humanskin, brain cortex, fruits, and plants. Owing to the periodic structure and dynamically tunable wrinkles, it has been used in many applications. Previously, we have succeeded in fabricating ultrasmall attoliter-sized (10^{-18} L) 1D metallic nanocup arrays embedded in PDMS films by colloidal soft-lithography and wrinkle processing.¹⁾ Moreover, we described the fabrication of various topological 1D colloidal arrays, including single, helical, zigzag, triple-line, and random arrays integrated in sinusoidal wrinkle grooves, through simple spin-coating.²⁾ Moreover, the particles in these arrays can be connected using plasma etching, forming beaded, robust, and long (>100 μm) colloidal chains. In this study, we succeeded in the fabrication of a large-area ultra-water-repellent film on which water drops can be flexibly controlled by utilizing original 3D-stretching method. It found that surfaces with different properties— an ultra-water-repellent and high-adsorption area and an ultra-water-repellent area—can be generated on the basis of two different pattern structures by applying water-repellent coating to the wrinkle film. Moreover, we succeeded fabrication of film with highly adhesive superhydrophobic surface and SERS activity. The results of this study will not only contribute to resolving issues of conventional top-down lithography techniques but will also be applicable to environmental, water-saving, medical and many other fields.

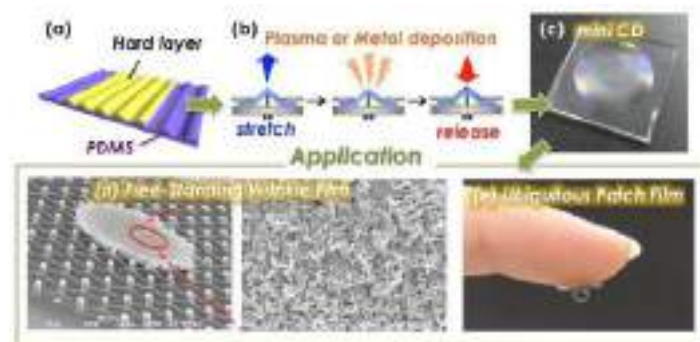


Figure 1. (a) Schematic illustration of wrinkle structure. (b) Schematic illustration of 3D-axial stretching method. (c) Photograph of wrinkle film prepared by 3D-method. (d) SEM image of free-standing wrinkle film with SERS activity. (e) Photograph of ubiquitous film with highly adhesive superhydrophobicity.

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Facile preparation and white-light-emitting properties of Flexible nano-sized POSS-based hybrid materials

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Abstract: Organic white light emitting devices (OWLEDs) have attracted great interest in the flexible displays and solid state lighting devices. Here we report a kind of novel POSS-based white-light-emitting single molecular nanohybrid (POSS-WLED), which was precisely controllably prepared via click chemistry by simple controlling the feed ratio of blue (B) and yellow (Y) emitting units. It was found that the self-absorption of emitting component and the intramolecular energy transfer was well adjusted based on theoretical simulation and molecular design. The incorporation of nanosized inorganic POSS effectively restrained intramolecular rotation (RIR) and shows significantly decoupling effect of emitter and AIE (aggregation induced enhancement) effect, which provided an important contribution to high emission efficiency of hybrid molecules. The resultant nanometer organic-inorganic hybrid (W62) exhibited very well flexible film formability and significantly enhanced emission in the solid film ($\Phi_{\text{film}}=95\%$) because of particular gel property with significantly AIE effect, which is attributed to the incorporation of nano-sized POSS moiety. Simultaneously, the resultant hybrids also exhibited high thermal stability. Herein, this work will provide a novel strategy for design and preparation of highly efficiency white-light-emitting molecules with high emission efficiency, thermal stability, and well film formability.

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Decellularized Plant Extracellular Matrices as a Scaffold for Tissue Engineering

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Abstract: Although the artificial porous biomaterials scaffold has been widely used in tissue engineering, the highly ordered structure and porous morphology in the organism is difficult to imitate. Therefore, the allogeneic or xenogeneic animal tissue decellularization is one of the actively developed technologies in recent years. In animal tissue decellularization, the highly complex morphology brings a higher difficulty in decellularization lead to influence further its application development. In contrast, plant tissue homogeneity is much higher than animal tissue. In our study, we collected as starting materials includes roots, stems, leaves, fruits and flowers firstly. Find out plants extracellular matrix is major composed of cellulose. Then, analysis decellularized plants physical properties and cell viability. In practically, plant sample was placed in 1% sodium dodecyl sulphate solution and shaken for 48 hrs. To clean the plant scaffold, they were washed with 1X PBS. After decellularization with different detergents and lyophilization, the morphology, pore size, mechanical property of decellularized plant tissue were performed by scanning electron microscope, porosimeter, universal strength tester, respectively. Plant scaffold was histological analysis stained with hematoxylin and eosin (H&E stain). In order to verify its biocompatibility, NIH3T3 were cultivated on decellularized scaffold and further cell attachment and cell proliferation were measured by MTT assay. In the results, the difference in decellularized plant scaffolds surface microstructure was presented in Fig. 1, respectively. The decellularized Spanish with feasible leaf vein and can be used to recellularization verify its biocompatibility was demonstrated in Fig.2. The difference between plant scaffold mechanical property could be applicable in different tissue. The mechanical property of apple, Iris japonica, and Iris virginica is 90 Pascal, 0.3 MPa, and 0.2 MPa, respectively (data are not shown). Apple scaffold with high porosity and low Young's modulus has a high potential as soft tissue or epidermal tissue. Iris japonica and Iris virginica with parallel leaf veins perform highly tropism structure could be modified as tendon related scaffold. Spinach radial leaf vein is similar to blood vessels and gland duct might have the ability to be a related scaffold. Now, we have selected an appropriate decellularized spinach to graft polyglutamic acid on the surface for the elevation of physiological activity as a salivary gland substitute for autologous tissue reconstruction.



Figure 1. SEM micrographs of various decellularized plant scaffold. (A) Apple (B) Aloe Vera (C) Celery (D) Iris japonica (E) Iris virginica (F) Spinach



Figure 2. Micrographs of CT scanned (A) and rhodamine perfused (B) decellularized spinach leaf vein pattern, and it were recellularized by NIH3T3 via vein perfusion and cultured for 2 days. 40X (C) 200X (D). HE staining of Celery implanted into rabbit Achilles tendon for 3 weeks. 40X (E) 200X (F).

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Hierarchically Targetable Polysaccharide/Lipid Hybrid Nanoparticles for Oral Chemo/Thermotherapy against Colon Cancer

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Abstract: This study aims to develop functionalized solid lipid nanoparticles (SLNs) as an oral drug delivery system for the local treatment of colon cancers featured with highly selective delivery to cancer cells and minimized systemic drug absorption. Folate-modified D- α -Tocopherol polyethylene glycol 1000 succinate (FA-TPGS) was synthesized and incorporated into the SLN formulation to endow the cancer-targeting ability of nanoparticles (FSLNs). Chemodrug, doxorubicin (DOX), and magnetothermal agent, superparamagnetic iron oxide nanoparticle (SPION), were simultaneously loaded into SLNs to achieve chemo/thermal combination therapy. The dextran coating can not only shield the folate targeting ligand but also give SLNs selective accumulation to colon via enzymatic degradation occurring exclusively in colon. The in vitro results demonstrated that SLNs incorporated with dextran coating and FA-TPGS (DFSLNs) promoted the cellular uptake and cytotoxicity by folate-receptor-mediated endocytosis after DFSLNs pre-treated with dextranase. The in vivo experiment showed that orthotopic CT26 tumor-bearing mice orally administrated with DFSLNs exhibited the best colorectal drug accumulation by virtue of the active tumor targeting of folate ligands following the extensive enzymatic degradation of dextran shells in large intestine. Moreover, the growth and abdominal metastasis of CT26 colon tumor were also inhibited by the chemo/thermal combination therapy of DFSLNs. These results showed that the developed DFSLNs are potential as an oral drug delivery system for local colon cancer therapy.

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Single-injecting, bioinspired nanocomposite hydrogel that can recruit host immune cells in situ to elicit potent and long-lasting humoral immune responses

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Abstract: Vaccination is an effective medical intervention for preventing disease. However, without an adjuvant, most subunit vaccines are poorly immunogenic. This work develops a bioinspired nanocomposite hyaluronic acid hydrogel system that incorporates N-trimethyl chitosan nanoparticles (TMC/NPs) that carry a model subunit vaccine ovalbumin (OVA) that can elicit a potent and prolonged antigen-specific humoral response. Experimental results indicate that the nanocomposite hydrogel system (NPs-Gel) can retain a large proportion of its TMC/NPs that are bonded by covalent/electrostatic interactions and extend the release of the encapsulated OVA, enabling their localization at the site of hydrogel injection. The positively charged TMC/NPs can be effectively internalized by dendritic cells, significantly augmenting their maturation, suggesting that TMC can function as an adjuvant-based OVA delivery system. Upon subcutaneous implantation in mice, the NPs-Gel acts as an in situ depot that recruits and concentrates immune cells. The TMC/NPs that do not have any specific interactions with the hydrogel network are released rapidly and internalized by the neighboring immune cells, providing a priming dose, while those retained inside the NPs-Gel are ingested by the recruited and concentrated immune cells over time, acting as a booster dose, eliciting high titers of OVA-specific antibody responses. These experimental results suggest particulate vaccines that are integrated in such a bioinspired hydrogel system may be used as single-injection prime-boost vaccines, enabling effective and persistent humoral immune responses.

Silver nanowire conductive film for flexible electrodes and devices

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Abstract: Flexible and wearable electronic devices have attracted an increasing amount of attention in recent years for their wide potential applications in some cutting-edge areas, such as flexible display, E-skin, and biosensors. Flexible electrode is the essential component for these flexible and wearable devices. Indium tin oxide (ITO) films are widely used as transparent conductive films (TCFs), but it has its intrinsic limitations in moderate conductivity and mechanical flexibility due to the inorganic oxide nature of the ITO film. Therefore, there is increasing demand to seek replacement of ITO. Silver nanowires (AgNW) TCF is one promising alternative due to its high transmittance, excellent conductivity and capability of mass production. In this work, long AgNWs with high aspect ratio have been synthesized by modified polyol method. Conductive inks with AgNWs were formulated. AgNW TCFs have been fabricated on polyethylene terephthalate (PET) film substrate by roll-to-roll slot die coating process. The flexible TCFs show low sheet resistance of 9-70 Ω/sq and high total optical transmittance of 80-88%. The effects of loading density of AgNWs on the sheet resistance and optical transmittance of the TCFs were comparatively studied. Theoretical model was proposed to estimate the optical and electronic properties of AgNW TCFs. The trade-off between sheet resistance and optical transmittance of AgNW TCFs was simulated through adjusting the diameter, length and surface coverage of AgNWs. Flexible heater and Electroluminescent (EL) lighting display have been fabricated with AgNW electrodes by roll-to-roll printing. In addition, flexible carbon-based electrodes were also fabricated, and flexible energy storage devices were fabricated.

Sol-gel based buffer layers and their roles in growth of optoelectronic films

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Abstract: As an important component of optoelectronic devices, optically functional coatings such as nonlinear optical films and ferroelectric films are often required to epitaxy grow, or at least preferential orientation grow, on single crystal substrates. However, there is always a lattice mismatch between the film and the substrate, direct heteroepitaxy will result in many structural defects in the film, which lead to degradation of film performances. Inserting a buffer layer is an effective way to relief the mismatch, give rise to the relieves of dislocation density, surface roughness, as well as strians. Sol-gel process provides the advantages such as easy composition adjustment, convenient handling and compatibility of silicon fabrication process, the sol-gel based buffer layer is therefore one of the highly effective strategies and solutions to the high quality silicon-based crystal film growth. In this talk, we will show our recent progress of three kinds of buffer layers fabricated with the sol-gel process, they are potassium-substituted SBN, MgO, and TiN layer, respectively, and they are proved to be the qualified templates for the growth of ferroelectric strontium barium niobate (SBN) and barium strontium titanate (BST) films on silicon substrate.

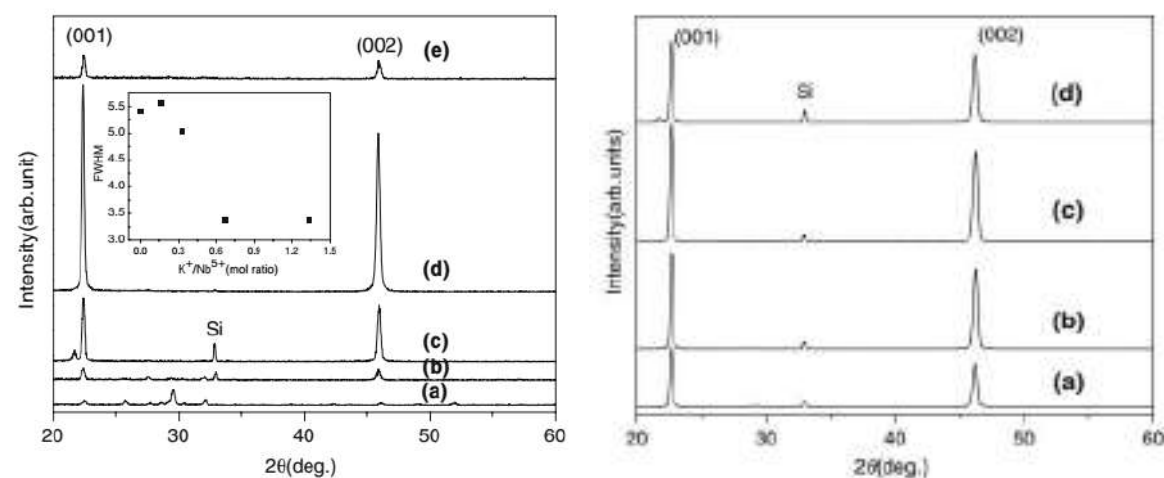


Figure1. (Left) XRD patterns of potassium-substituted SBN buffer layers on Si(100) with the K^+/Nb^{5+} molar ratio of (a) 0:3, (b) 1:6, (c) 1:3, (d) 2:3, (e) 4:3. (Right) XRD patterns of SBN films on K-SBN buffer layer with the buffer thickness of (a) 25 nm, (b) 50 nm, (c) 75 nm, and (d) 100 nm, respectively

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Micro mechanical studies of urethane-linked siloxane hybrid materials for flexible display

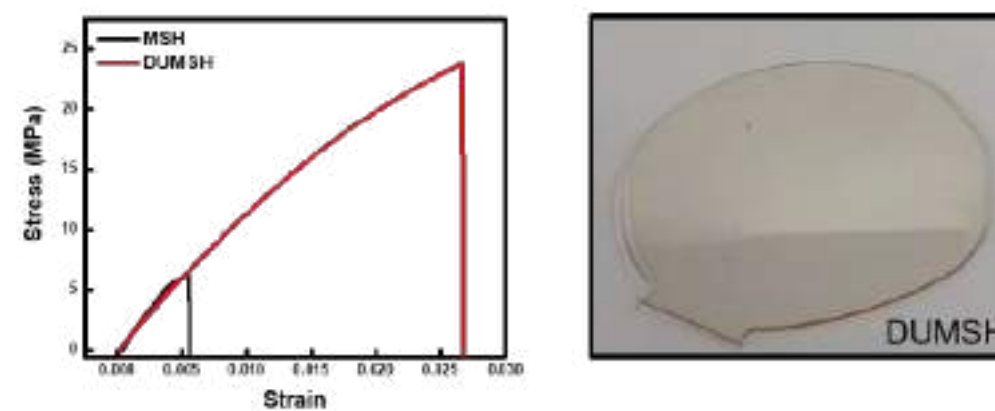
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Abstract: Flexible display occupies the largest portion of the upcoming display market. One of the main challenge to commercialize the flexible display is fabrication of flexible cover window while maintaining its protective properties from the external environment. Therefore, it should be sufficiently hard enough to protect the inner part and flexible enough to give a device flexibility. In other words, the cover window must be sufficiently rigid and flexible at the same time. Additionally, as it is used to optical devices, it should be highly transparent.

Previously, transparent urethane-siloxane hybrid materials for flexible display are reported in our laboratory. These urethane-siloxane materials are formed by cross-linking between urethane monomer and oligo-siloxane resin by radical polymerization. Since urethane monomer is in the solid phase at room temperature it should be agitated over 60°C. Due to the solid phase of urethane monomer, additional agitation process to make a homogenous resin is necessary. Herein, we use the silane which already contains urethane bond and hydroxyl group as an end group in organic chain to make a double urethane bonds. Since urethane bonds are formed in the organic chain of silane, additional urethane monomer does not need, rather double urethane bonds are formed in the precursor state. Then, we fabricate double urethane-methacrylate oligo-siloxane (DUMOS) resin by sol-gel reaction with methacrylate silane. DUMOS resin are analyzed by FT-IR and ²⁹Si-NMR analysis.

Furthermore, double urethane contained siloxane hybrid films (DUMSH) are fabricated through UV radical polymerization process. It is analyzed by tensile test and 3-point bending test to confirm the improved elastic and flexural properties. Its elastic modulus is 1.35 GPa, and it is similar to methacrylate oligo-siloxane hybrid materials (MSH) without urethane bond. However, it has a strain about 2.6%, which is four times higher than that of the conventional MSH. And it exhibits 2 GPa of flexural modulus and it is comparable to MSH which has 2.9 GPa. However, DUMSH shows 3.1 % of flexural strain that is 4 times larger than that of MSH.



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Aqueous citrate sol-gel synthesis towards the double $A_2Ni(Te, W)O_6$ and triple $A_3(Fe, Co)_2(Te, W)O_9$ perovskites

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Abstract: Specific structure of perovskite compounds provides them with various interesting properties which vary from magnetic and electric properties to magnetic frustration and half-metallicity. Double $A_2Ni(Te, W)O_6$ and triple $A_3(Fe, Co)_2(W/Te)O_9$ ($A=Sr, Ba$) perovskites have been prepared in nanocrystalline form using a modified aqueous sol-gel citrate route. Solution chemistry synthesis mechanism and synthesized compounds itself have been studied by electrochemical measurements. Structural investigation has been conducted by ambient and in situ X-ray powder diffraction (PXRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), selected area electron diffraction (SAED), thermogravimetric analysis (TGA) and unpolarized Raman spectroscopy, while their magnetic properties have been determined using SQUID measurements. Similar research has already been conducted with tellurium- [1] and tungsten- [2] based perovskites. In this research the advances of solution chemistry methods (bottom up approach), namely sol-gel citrate route, over the solid-state routes towards the synthesis of complex perovskite structures will be presented. The obtained compounds have been structurally characterized using above mentioned state-of-the-art techniques and, in addition, magnetic ground state has been determined.

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Preparation of Photocatalytic Titania on Organic Support via Sol-Gel Method for Water Clarification

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Abstract: The water is an important resource for life which should be recycled. The recycling of water is getting more difficult with the industrialization and release of versatile pollutants in big quantities. There are research activities to create new methodology for clarification of resistant pollutants, which are hard to remove. An alternative method is to oxidize these pollutants via photocatalytic oxidation. Titania (TiO_2) has photocatalytic activity that it may be used for the clarification purpose. The previous research reported that the titania has a higher catalytic efficiency with decreasing particulate size. Using sol-gel method is promising to have submicron titania particulates with high photocatalytic activity. The crystal morphology of titania was also reported to be effective on its photocatalytic activity. The anatase phase and/or mixture anatase & rutile phases were reported to have higher catalytic activity. The sol-gel method enables preparation of titania with controlled crystal morphology that will enable preparation of photocatalytic titania with relatively higher efficiency. The efficiency of photocatalytic activity of titania was also tried to be enhanced via decreasing its energy band gap for excitation, which will make it sensitive to radiations with relatively lower energy (i.e. higher wave length). For this purpose different elements (e.g. Fe, Ni, Au, S, N, C, etc.) were doped in titania, or some dyes were used to make it photocatalytically active under visible light (instead of ultraviolet (UV) light which has higher energy but is with limited ratio in sunlight). In present work sol-gel method was used to prepare nano/submicron-titania on organic supports using titanium isopropoxide. The organic supports were ground nut shell powder (e.g. walnut) which are waste/side products. The photocatalytic activity of organic supported submicron titania catalyst was determined via oxidation of dyes (e.g. methylene blue) under excitation via UV and/or visible light and it was compared with activity of commercial nano titania powder. Higher efficiencies were obtained by using the prepared organic supported titania catalyst which may have relatively lower cost than the commercial nano titania powder. The particle size distribution (PSD) analysis was performed via laser light scattering technique and average particle sizes of a few nanometers were measured for the sols prepared. The prepared catalyst using the sols and the fine (ground) powder of nut shells was characterized via SEM (scanning electron microscope) and XRD (X-ray diffraction). Research continues on possible enhancements for photocatalytic activity of the prepared catalyst, which already has promising efficiency for clarification of water. The utilization of prepared organic supported titania catalyst may also be possible for some other applications.

A mixed thermosensitive hydrogel system for sustained delivery of tacrolimus in skin allotransplantation

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Abstract: Tacrolimus is an immunosuppressive agent for allotransplantation to treat acute rejection. However, low aqueous solubility makes it difficult to formulate as an injection dosage form. Polypeptide thermosensitive hydrogels as a drug delivery depot have several advantages, such as excellent biocompatibility and biodegradability and in situ gelation at low concentrations. The hydrogel was synthesized by polymerizing poloxamer and poly(alanine) together with lysine segments at both ends to form PLX-poly(alanine-lysine) (P-Lys-Ala-PLX) copolymers. The copolymers had low gelling concentration of 3 to 7 wt%. Adding Pluronic F-127 to the formulation enhanced drug encapsulation efficiency and release rate. The mixed hydrogel system showed stable in vitro release rate more than 100 days. Preliminary in vivo data also showed effectual anti-rejection results over extended period of time.

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Production of aerogels in form of microparticles: new techniques allowing the transfer from lab to pilot scale

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Abstract: Aerogels are low-density (typically < 0.2 g/cm³), highly porous (> 90% v/v) nanostructured solids. Nowadays aerogels are routinely prepared at lab scale using so called low temperature supercritical drying (sc-drying). For this, wet gel is prepared and then the solvent filling the gel pores is extracted by supercritical carbon dioxide (sc-CO₂) eliminating the capillary forces that would collapse the nanostructure. Subsequently, sc-CO₂ is vented out leaving behind the solid material, aerogel. In case, the pore filling solvent is not miscible with sc-CO₂ (for example water in biopolymer hydrogels) it has to be exchanged with another, less polar solvent, e.g. ethanol. This step is unavoidable and contributes considerably to the processing time and costs.

Aerogels have been for a long time seen as a curious material existing mainly in the lab. Significant progress in the supercritical drying and advances in sol-gel chemistry over the last decades has been achieved, aerogels are already commercially available and no longer limited to small charges for academic purposes. However, mostly aerogels are available in form of monoliths or small irregularly shaped particles. At the same time for many applications, including adsorption, personal care and food, aerogels in form of spherical particles of defined size are required.

In frame of the EU project Nanohybrids, which main results will be presented in this paper, the existing technology of organic aerogel monoliths (panels) was extended to the production of organic and hybrid aerogels in form of (micro)particles with targeted particle and pore size distribution at the pilot scale. Further, the properties of organic and hybrid were tuned by specifically adjusting their matrix, hybrid systems based on different polymers were firstly developed.

Significant acceleration of both the supercritical drying and solvent exchange of gel particles were achieved, and it was firstly demonstrated that these processes can be completed within minutes, instead of hours usually reported in the literature. The experimental findings are supported by the detailed modelling of supercritical drying and solvent exchange steps including mass transfer phenomena and especially the solvent spillage out of the gel matrix. Based on this, novel technological solutions allow the time- and cost-effective production of aerogels in form of microparticles in the range between 10 µm to several millimeters. The technology was realized in a pilot scale, firstly allowing the production of over 100 liters of polysaccharide aerogels (Fig.1).

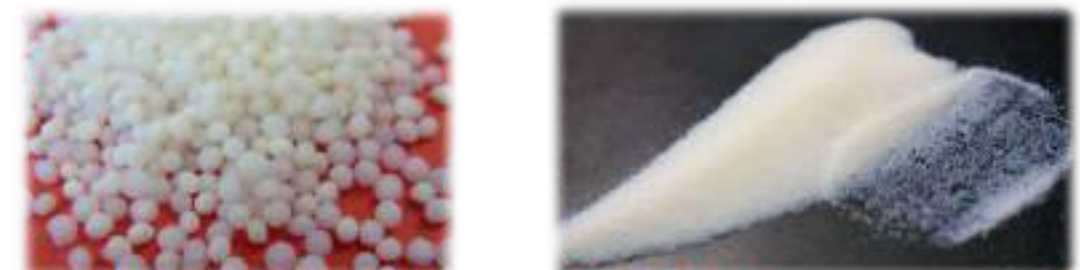


Figure 1. Organic aerogel particles of different size

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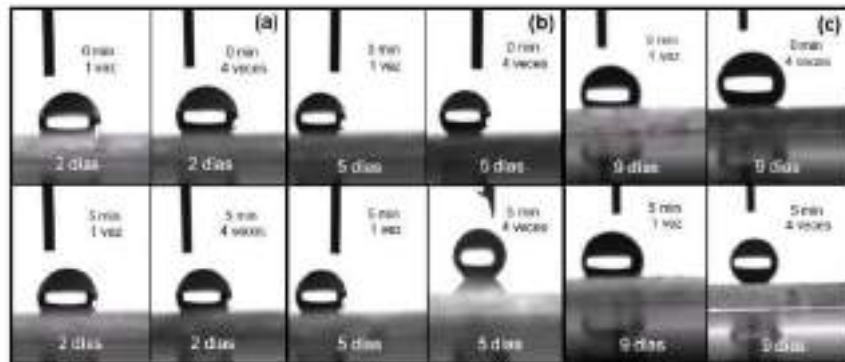
Superhydrophobic sol-gel coatings with high temperature resistance

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Abstract: Superhydrophobicity, is known as having a high-water contact angle (WCA>150°) where the water droplets easily roll off the surface with a sliding angle less than 10° to wash away the contaminants from the surface, phenomenon known as the “Lotus Effect”. For the achievement of these properties’ sol-gel technique have been applied using Stöber methodology for the fabrication of superhydrophobic and self-cleaning coating. For the development of the coating, TEOS was dissolved in ethanol. Separately, ammonia, water and ethanol were mixed combining then both solutions heating it at 60°C under stirring for 90 min. Finally, a solution of MTES and EtOH was added to the sol stirring it for 19h at 60°C with a condensation reflux device. The prepared white silica sol was kept for 2, 5 and 9 days under room temperature producing monodisperse silica sphere around 1micron size. The experiments were prepared with one or multilayer coating by dip coating technic with different deposition time. The silica films were later heat treated first at 150 °C for 30 minutes and second at 400°C for 2 hours. The silica films were characterized measuring contact angles and temperature resistance (400°C), noticing in a wetting behaviour enhancement observed in a range between 108 to 149°.



Keywords: Superhydrofobic, Sol gel, Stober method, High temperature.

Hybrid Organic-Inorganic photoresists, a promising class of materials for Optofluidic integration

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Abstract: Optofluidics refer to a wide range of applications in which optics and fluidics are integrated on the same device and used synergistically to synthesize creative, novel and highly versatile functionalities, in which light is used to manipulate fluids or vice versa.

Through the efforts to fuse planar optics and microfluidics in order to produce dye lasers, biosensors, trapping and cell sorting device, we can notice the rising interest in optofluidics since early and mid 2000's. In addition, the growing capability to use Hybrid Organic-Inorganic materials for the fabrication of integrated optics components and microfluidic channels makes this class of material an ideal candidate for the fabrication of Optofluidic Lab on Chip devices.

Mass production of such devices heavily relies on fast and easy processing of Polydimethoxysilane (PDMS). PDMS gained an added value because of its elasticity, hydrophobicity and permeability to gaz, however these specifications aren't convenient for all types of applications.

As an alternative, E. Mechref et al. developed an organic-inorganic chemically amplified positive photoresist based on Polyamic acid (PAA) and suitable for microfluidic channels fabrication using single step (deposition, insulation, and engraving) sol-gel processing. Integrated optical layers were as well fabricated using a mixture of [3- (trimethoxysilyl)propylmethacrylate] (MAPTMS) and Zirconate propoxide (ZPO) chelated by methacrylic acid (MAA), as well as [2-(3,4epoxycyclohexylethyltrimethoxysilane)] (EETMOS).

This work aims to integrate, on the same chip, an optical and a microfluidic layer. The interest in this vertical integration arises from the need to manipulate the fluid in the microchannels using evanescent field optical pressure which acts on particles in a way that pushes them along the wave propagation direction. As a proof of concept we implemented an optofluidic mixer using the configuration of the figure below.

It is important to note that the 5x5µm single mode waveguides shown below were written due to selective photo-induced increase of refractive index in a hybrid organic-inorganic negative type photoresist, composed of MAPTMS and ZPO and showing an index step of around 0.004 in the visible. The smooth core-cladding interface, resulting from the fabrication process that needs no harsh revelation step, is expected to show very low attenuation to conserve the energy needed for the actuation of the liquid.

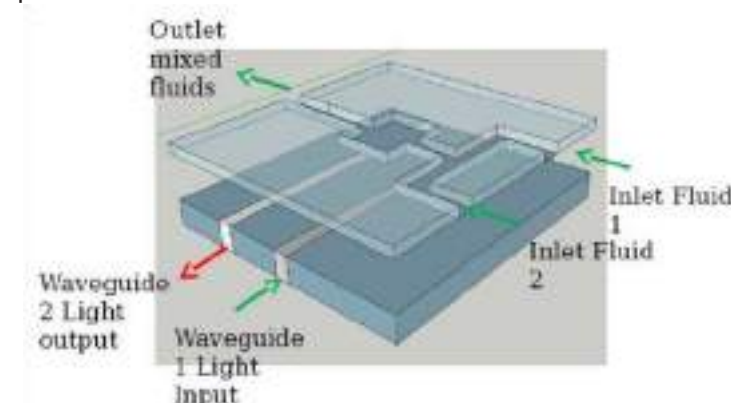


Figure 1. Initial design for an optofluidic mixer

Characterization of pore interconnectivity in mesoporous thin films by ellipsometry porosimetry : an experimental study

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Abstract: Thin films with ordered mesoporosity and defined pore size can be elaborated on small and large surfaces through sol-gel process combined with evaporation-induced self-assembly (EISA) of templating agents. The assessment of this porosity is necessary to understand their interaction with their environment in many applications such as microelectronics, sensors or optics. While inert gas physisorption techniques are often used to characterize bulk nanoporous materials, they lack the sensitivity required to investigate thin films. SEM and TEM are also used to image nanoporous materials but the samples preparation requires a considerable amount of time and often involve milling steps that will damage the porous structure.

Ellipsometry is a non-destructive spectroscopic characterization in which a polarized beam of light is reflected on the sample and recovered in a polarization sensitive analyzer which allows the determination of the refractive index, extinction coefficient, thickness and porosity of thin layers by fitting with theoretical models. Ellipsometry can be combined with an environmental cell to observe in situ the adsorption of solvents, for instance water or alcohols. This technique, called ellipsometry porosimetry, can be used to determine the pore size distribution, give critical insights on surface chemistry, pore organization and interconnections which are not easily accessible by other techniques. Assessing pore interconnectivities

In this poster, experimental work is presented where mesoporous silica thin films with one or two defined pore size are elaborated by self-assembly of multiple templating agents. The coatings are investigated by ellipsometry porosimetry and a new technique, desorption scanning, is employed to get additional information on the pore connectivities. Additionally, the adsorption-induced deformations of the thin films are exploited to determine their elastic properties and calculate their pore load modulus.

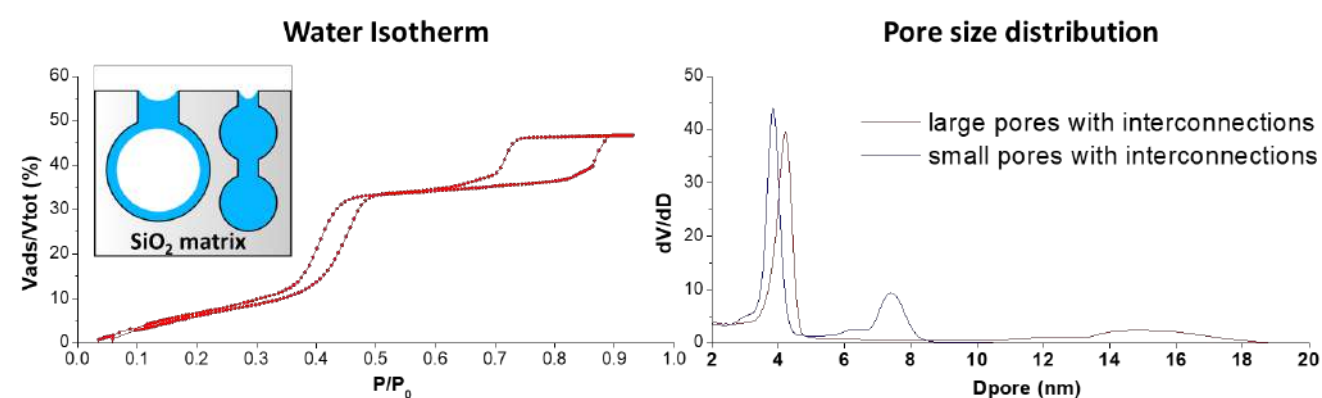


Figure 4 . Pore size distribution of a bimodal mesoporous silica thin film

High conductive carbon aerogels for battery applications

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Abstract: Carbon aerogels are well known open porous solid materials first introduced by Richard Pekala in 1989 [1]. Usually carbon aerogels are derived by pyrolysis of organic precursors such as resorcinol-formaldehyde, melamine-formaldehyde [2], and other organic precursors. Due to their high inner surface area of about 2000 to 2500 m²/g, high pore volume of about 3 to 5 cm³/g [3] carbon aerogels have a broad field of applications. Caused by their electrical conductivity of up to 10² S/m [4], the field of electrical applications extends from super-capacitors to rechargeable lithium based batteries.

High electrical conductivity of carbon aerogels is necessary for battery applications. In order to improve the electrical conductivity, additives such as different graphite powder can be homogeneously embedded to carbon aerogels. Due to low viscosity and long time gelation, it is difficult to produce such composites by simply mixing additives into the resorcinol-formaldehyde sol.

In our study, we compare two synthetic routines, first based on resorcinol-formaldehyde (RF) and the second on resorcinol-melamine-formaldehyde (RMF), for synthesis of carbon aerogel composites. Due to adjustable viscosity of RMF-sol, composites with homogeneously distributed additives could be successfully synthesized. Various additives with different amounts have been tested. The received composites were characterized in terms of skeletal density, specific surface area, micropore and mesopore volume and size distribution and most important electrical conductivity as these are critical parameters for the use in electrochemical applications.

Within the presentation we will report on the actual research and development of carbon aerogel composite materials and will focus on its benefit on new concepts in batteries applications.

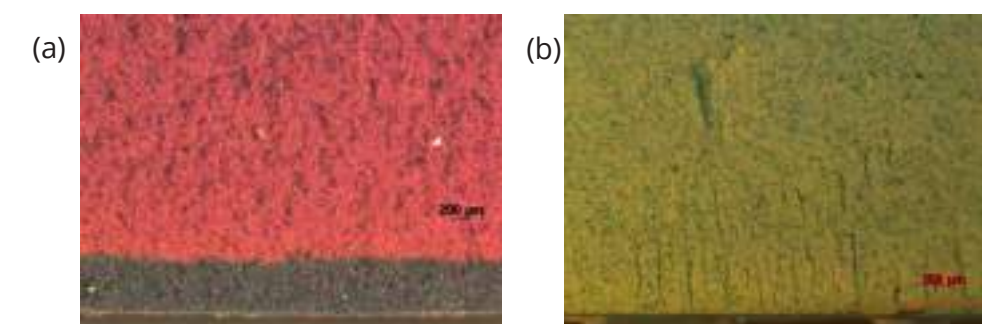


Figure 1: Microscopical images of (a) resorcinol-formaldehyde aerogel with sedimented graphite powder, (b) resorcinol-melamine-formaldehyde aerogel with homogeneously distributed graphite powder.

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SnO₂/V₂O₅ core/shell composite film with multicolor electrochromism for adaptive camouflage

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Abstract: Nowadays, electrochromic (EC) materials are applied in many fields due to their special optical modulation functions, such as smart windows, eyeglasses, energy efficient information displays, and adaptive camouflage. Specifically, adaptive camouflage in the visible region requires materials to adjust their colors according to the color change of background, to achieve the purpose of merging with the background, and realize perfect concealment of visual detection. Organic EC materials are often used in camouflage filed, owing to their multicolor, fast switching time and flexibility. However, complex synthetic route, harsh reaction conditions, low yield, and poor stability in the natural environment limit their practical applications. Therefore, exploring inorganic EC materials is of great means because of their good chemical stability, simple preparation process, and ease to realize all solid state of the device. Herein, we synthesize a SnO₂/V₂O₅ core/shell composite electrochromic film by combining sol-gel and electrodeposition methods on fluorine-doped tin oxide (FTO)-coated glass. It is gratifying that the composite film exhibits high coloration efficiency (118 cm² C⁻¹) and admirable optical cycling stability with 85% retention of the optical transmittance modulation after 2000 cycles. The core/shell structure plays a pivotal role in the enhanced performances due to the large reactive area and good adhesion to substrate. Impressively, the EC film can be reversibly changed between yellow, green and blue colors when different voltages are applied, which has great application prospects in adaptive camouflage for conditions of desert, oasis and ocean.

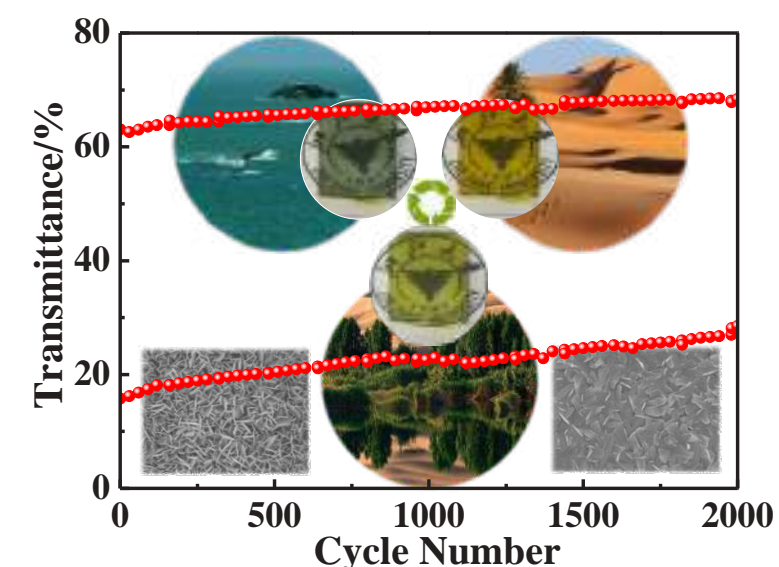


Figure 1. SEM images, in-situ transmittance and durability tests of SnO₂/V₂O₅ EC film at 450 nm

Sol-gel derived alumina glass : NMR elucidation of molecular mechanism

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Abstract: Single-component Al_2O_3 glass cannot be obtained as a bulk by conventional glass forming methodology¹. Previously, far from equilibrium conditions were employed to obtain amorphous Al_2O_3 , which limit their dimensions to thin film or nanoparticles. Therefore there is much interest in understanding the mechanistic details of a facile aqueous sol-gel process based on aluminum lactate precursor which leads to homogeneous Al_2O_3 glass². Similar observations are reported here also for aluminum citrate, which indicates that the Al-chelating approach to alumina glass is general. Detailed ^{27}Al NMR analysis supported by several other analytical methods, indicate that the formation of a metal coordination network based on aluminum cations-lactate (citrate) ligand interactions occurs during the sol-gel transition. This water soluble metal coordination network demonstrated a facile reversible sol-gel-sol transition based on concentration-driven formation and breaking of the intramolecular non-covalent interactions between the monomers. Subsequent annealing of the xerogel by gradual heating to 500-700 °C promotes the formation of the interconnecting Al-O-Al bonds, concomitant with the removal of the lactate or citrate ligands upon heating, resulting in pure alumina glass as the final product. The current research also provides the mechanistic study of a model system for aqueous metal ion-chelate complexes precursors.

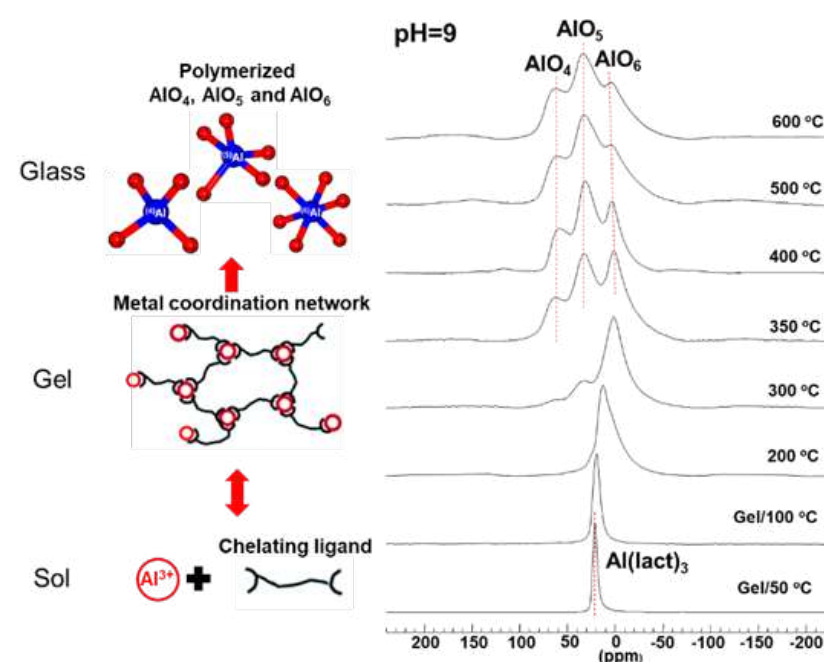


Figure 1. The scheme (left) and ^{27}Al MAS NMR (right) of the sol-gel-glass transition

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Synthesis of silica aerogels via APD methods and their applications beyond

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Abstract: Aerogels have received considerable attentions in recent years, and the excellent properties and great potential applications of the silica aerogels in thermal insulation have been recognized by the industrial community. One of the great challenges for the wide application of silica aerogels is the safe, scale-up, and economically production of high-quality silica aerogels. In the present work, various ambient pressure drying (APD) methods to synthesis of silica aerogels are introduced.¹⁻³ The approaches may scale-up production of silica aerogels and reduce the costs. Beyond the application of aerogels in the field of thermal insulation, we developed plenty of unconventional applications of silica aerogels, namely superhydrophobization of living creatures³ (Figure 1), functionalization of hydrogels for solar steam generation⁴ (Figure 2), and even gave birth to aerohydrogels that possessed tri-continuous phases and multiple interfaces. We believe that the present work will gives brand-new perspectives to the field of silica aerogels.



Figure 1. The application of silica aerogels in superhydrophobization of living bodies.

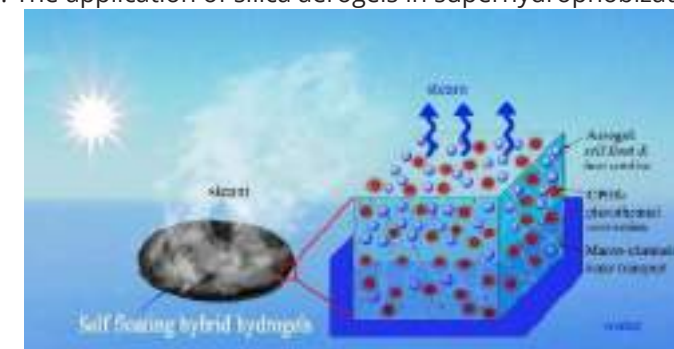


Figure 2. Self-floating hydrogels functionalized by aerogels for solar steam generation.

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Defect Chemistry of Er³⁺-Doped TiO₂ and its Photocatalytic Activity in Gas Phase

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Abstract: A series of Er-doped TiO₂ photocatalysts, using Er(NO₃)₃•6H₂O precursor ranging from 0.5 to 2mol%, were synthesized via sol-gel method with TIP solution as reactants. The structure and properties of as-prepared samples were characterized by SEM, TEM, XRD, UV-vis, XPS, FT-IR, TG, PL, EIS and photocurrent. The as-synthesized Er-doped TiO₂ nanoparticles demonstrated improved photocatalytic activities for the photodegradation of selected volatile organic compounds (VOCs), including acetaldehyde, o-xylene, and ethylene. Additionally, a high photodegradation of acetaldehyde was recorded in the visible region ($\lambda > 420$ nm). XPS analysis revealed that a handful of Er in anatase TiO₂ was presented in the form of Er₂O₃, which benefited to increase the specific surface area ranging from 59.28 to 110.34 m²/g and consequently enhance the adsorption capacity for acetaldehyde, o-xylene and ethylene by 3.3, 3.7, and 3.8 times, respectively, in contrast to the undoped TiO₂. ESR results showed that Er doping caused production of oxygen vacancies (Vo) and Ti³⁺, which promoted the photocatalytic activity of the catalyst. The TiO₂ samples containing 0.5~1.5% Er content exhibited higher photoactivity in comparison with other samples. The highest removal efficiency of acetaldehyde and o-xylene within 100 min was 99.2% and 84.6%, respectively, and ethylene degradation efficiency reached 22.4% within 180 min. Furthermore, the visible light elimination efficiency of acetaldehyde was 25.5%. Finally, the results suggested that Er doping predominantly inhibited the catalyst poisoning in the degradation of o-xylene..

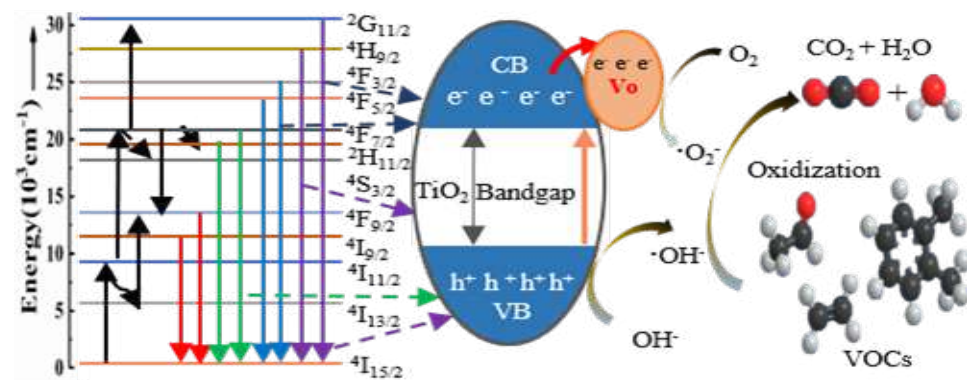


Figure 1. Schematic diagram of the mechanism of intra-4f electron structure of Er³⁺ and Vo promoting electron-to-electron transfer enhancement and up-conversion enhanced light energy utilization.

Long-chain ionic liquids assisted sol-gel synthesis of ZnO and their antibacterial properties

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Abstract: A series of ZnO nanoparticles were synthesized via sol-gel method in the presence and absence of long-chain room temperature ionic liquids (RTILs) including 1-tetradecyl-3-methylimidazolium chloride ([C₁₄MimCl]), 1-tetradecyl-3-methylimidazolium tetrafluoroborate ([C₁₄MimBF₄]) and 1-tetradecyl-3-methylimidazolium hexafluorophosphate ([C₁₄MimPF₆]). The as-prepared samples were characterized by x-ray diffraction pattern (XRD), x-ray photoelectron spectroscopy (XPS), photoluminescence (PL) spectroscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM), respectively. Results showed that RTIL can restrict crystalline growth in [002] direction and cause more oxygen defects of ZnO. Meanwhile, the type of RTIL anion had a significant influence in the structure and oxygen defects generation for the samples. The antibacterial properties of the as-prepared ZnO nanoparticles were investigated by colony counting method against the bacterium of Escherichia coli (Gram negative) and Staphylococcus aureus (Gram positive). ZnO synthesized in the presence of RTILs showed better antibacterial performance in comparison with that without RTIL, and the antibacterial ability of all samples was positively related to the oxygen defects.

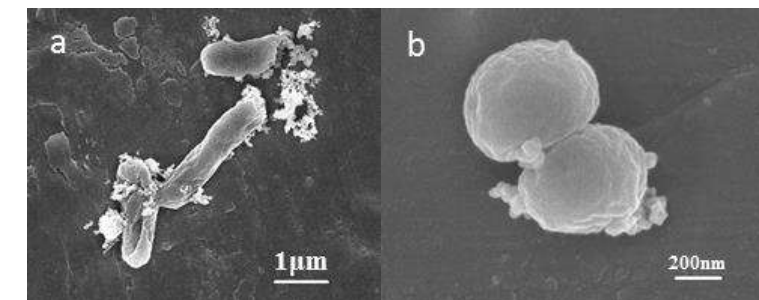


Figure 1. SEM micrographs of ZnO nanoparticles interact with E.coli cells (a) and S.aureus cells (b)

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Sol-gel-derived mesoporous metal-oxide granules for VOC adsorption

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Abstract: Volatile organic compounds (VOCs) have become one of the major precursors for ozone and secondary organic aerosols (SOAs), which are harmful to both human health and the environment. Toluene, the most commonly encountered VOC, is one of the largest contributors to both ozone and SOA formation. Since the presence of toluene in the atmosphere can cause a variety of severe health problems, many VOC removal methods have been developed, including adsorption, condensation, incineration, and biological degradation. Among these methods, adsorption has been considered one of the most favorable method to control VOCs due to ease of application and high efficiency.

In this work, various mesoporous metal-oxide granules (Al₂O₃, SiO₂, and TiO₂) were prepared by combining sol-gel method and spray pyrolysis technique. First, stable boehmite, silica, and titania sols were prepared by sol-gel methods. Then, the sols were mixed with CTAB, nebulized and pyrolyzed in the tubular furnace, producing the metal oxide granules. The porosity of the product granules were controlled using the CTAB concentration. The product granules were characterized by FE-SEM, BET, XRD, and TGA. A toluene breakthrough test was carried out using a glass bed under atmospheric pressure. For each run, 0.25 g of metal oxide adsorbent was loaded in the bed, and 1000 ppm of toluene gas was used as feed gas. Among the examined metal oxides, SiO₂ showed the highest toluene adsorption capacity of 111.3 mg/g.

This work was supported by the Technology Development Program to Solve Climate Changes (NRF-2017M1A2A2086815, 2017M1A2A2086647) through the National Research Foundation (NRF) funded by the Ministry of Science and ICT, Republic of Korea.

Aluminophosphate and -phosphonate Xerogels by Non-Hydrolytic Sol-Gel Reactions

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Abstract: We have investigated the preparation of high-surface area mesoporous aluminophosphates and aluminophosphonates by non-hydrolytic sol-gel reactions. The first synthetic method is based on reactions of EtAlCl₂ with trialkylesters of phosphoric acid (OP(OR)₃, R = Me, Et, ⁱPr, ⁿBu, in dry organic solvents. The condensations proceed by alkylchloride elimination. Various reaction and calcination conditions were examined. Porosity is obtained after calcination by removal of organic residual groups. This thermal processing at 300 °C of as-synthesized precursor gels leads to amorphous aluminophosphate xerogels with surface areas of 400–500 m² g⁻¹ provided by small mesopores (2–8 nm). Changes in coordination environment of aluminium from six- to four-coordinate are evidenced by shift of ²⁷Al MAS NMR resonances. The second method involves reaction of Al(NMe₂)₃ with trimethylsilylated phosphate, phosphonate, and bis-phosphonate esters in dry toluene. The reactions proceed by silylamine elimination and provide organic-inorganic hybrid xerogels with properties influenced by organic substituents and the Al:P ratio of the precursors. Dried xerogels exhibit large surface areas (up to 1000 m² g⁻¹) and Al–O–P networks stay stable under medium high thermal conditions. ²⁷Al, ¹³C, and ²⁹Si MAS NMR was employed to characterize aluminum coordination and residual amido and trimethylsilyl groups. The amount of residual groups was determined by gravimetric measurements and by thermal TG-DSC analysis. These unreacted groups have the potential to be used in post-synthetic grafting of catalytically active metal centers.

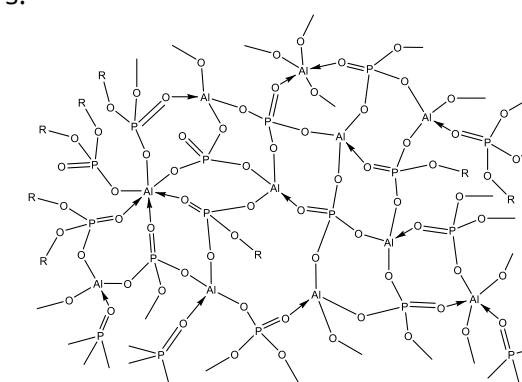


Figure 1. Model of network structure of aluminophosphate gels.

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Influence of solvents on corrosion mitigation property of the organic-inorganic sol-gel coating

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Abstract: Metallic materials are widely used engineering materials. Steels and alloys, such as alloys of alumina, copper and titanium, working in various environments, often very aggressive and demanding, are exposed to destruction processes, including corrosion. According to data provided by the National Association of Corrosion Engineers (NACE), the global effects of corrosion account for about 2.5 trillion dollars, which is close to 3.4% of global GDP.

Sol-gel oxide materials constitute one of the possibilities of enhancement the corrosion mitigation, which can be an alternative to Cr⁶⁺ [1,2]. Sol-gel organic-inorganic hybrids combine properties of inorganic components eg. high scratch resistance and hardness, with properties of organic ones, which enhance the flexibility and crack resistance of the sol-gel network. The choice of reaction medium is highly important to obtain the sol-gel materials with corrosion mitigation properties. In this regard, the choice of solvent and catalyst has significant influence on matrix structure and in consequence on barrier - anticorrosion properties of the final materials [2,3].

The present paper presents changes of electrochemical properties of the sol-gel (based on (3-Aminopropyl)trimethoxysilane and (3-Glycidyloxypropyl)trimethoxysilane) coated steel surfaces, depending on used solvent. Experiments were conducted in the 3% NaCl environment. Tools as scanning electron microscopy (SEM), Raman spectroscopy, electrochemical potentiodynamic measurements and impedance spectroscopy have been used to demonstrate the changes in the corrosion resistance of coated steel substrates.

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Fluorescent pH sensors based on a sol-gel matrix for acidic and neutral pH ranges in a microtiter plate

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Abstract: In this study, two typical pH-sensitive dyes, fluorescein amine (FA) and 8-hydroxypyrene-1,3,6-trisulfonic acid trisodium salt (HPTS), were doped into two types of silica particles. The dye-doped silica particles were entrapped in a mixture of 3-glycidyloxypropyltrimethoxysilane (GPTMS) and 3-aminopropyltrimethoxysilane (APTMS) sol-gel matrix (GA) and a polyurethane hydrogel (PU) to prepare stable pH-sensitive membranes in a microtiter plate. Four pH-sensing membranes prepared at the bottom of wells in 24-well microtiter plates showed high sensitivity, fast recoverability, and good photostability. Supporting materials with fast ion transport properties were used to produce a pH-sensing membrane with rapid response time. The membranes entrapped with FA-doped silica particles had a linear detection range from pH 2 to pH 6, while the membranes entrapped with HPTS-doped silica particles had a linear detection range from pH 5 to pH 8. Dye-leaching from the pH-sensing membranes did not occur due to tight binding between functional groups in the dyes (FA and HPTS) and the GA matrix, the capture of dyes in the silica particles, and the addition of an anti-fading agent (DABCO). Four pH-sensing membranes were used to measure the pH of wastewater. The measured results were consistent with standard pH values.

Keywords: FA, fluorescent pH sensors, HPTS, microtiter plate, sol-gel GA

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Hybrid sol-gel multilayered coatings nanodoped for corrosion protection of Magnesium AZ31B substrates

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Abstract: Nowadays corrosion is a big concern in terms of economics and engineering. One of the most spread techniques to prevent corrosion is the use of coatings as a physical barrier to isolate the metallic substrates from the aggressive environment.

Following this strategy, SiO₂ ceramic multilayer coatings doped with nano-charges have been used in this research to protect the metallic substrates against corrosion.

Different hybrid multilayered coatings have been generated by the sol-gel technique, from two silica alkoxide precursors: Tetraethoxysilane (TEOS) and Methyl-triethoxysilane (MTES). Some of the coatings have been doped with carbon nanotubes or with graphene nanoplatelets using 0,005 wt% proportion.

Once obtained, these hybrid-doped-sols have been deposited on Magnesium (Mg) AZ31B alloy substrates by the dip-coating method to obtain multilayer, homogeneous and thickness-controlled coatings.

The behavior against corrosion has been tested in 3,5%NaCl solution and simulated body fluid media (Hank's solution) by electrochemical tests, hydrogen evolution and mass loss.

Corroded samples have been characterized by scanning electron microscopy to find out the corrosion mechanisms that took place.

Final results confirm that sol-gel is a feasible, eco-friendly and low energy method to generate ceramic coatings that behave effectively as a protective barrier against corrosion in aggressive media.

Development of innovative coatings using sol-gel process for high power laser applications

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Abstract: The Megajoule Laser (LMJ) plays a vital role in simulation program of CEA, as it is used to validate the numerical codes and certify the skills of French physicists. In the nominal configuration of the Laser Megajoule, 176 beams are assembled together delivering energy which will be amplified in the infrared (1053 nanometers - nm - wavelength) to be converted into ultraviolet light (351 nm wavelength) and focused on the target in the center of the experience chamber. The optics are major components of the laser chain positioned all along the pathway traveled by the beams.

To minimize the parasite light reflection and to maximize the energy on the target, all the large-sized optical components (400 x 400 mm) working in transmission are coated with an antireflective thin film. This surface treatment is manufactured via a sol-gel process, associated with a liquid phase coating technique to prepare thin film made of metal oxides. This work presents initially how this expertise, which combines chemistry and process was implemented. High-homogeneity coatings with physical thickness from 50 to 200 nm have been prepared onto different large-sized optical substrates using meniscus coating and dip-coating technics. These antireflective coatings have been developed using catalytic curing in gas atmosphere (ammonia curing) conferring to the initially fragile coating, good abrasive resistance, hydrophobic property due to apolar species grafted onto silica nanoparticles and low sensibility to organic molecular absorption (low-sensitivity to polluting agents). We will describe how work on the chemistry and the coating process can optimize performance regarding industrial LMJ operating costs and can increase productivity. For this goal, different strategies of sol-gel synthesis and new deposition process have been developed. For example, spray coating method is under development for industrial application onto large optics. Using this method, we could save on sol-gel solution amounts, on time process and handling equipment. To optimize optical quality with such process, work on the solution and process parameters is needed to control film formation before complete evaporation of solvent.

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Physicochemical evolution of siloxane-peo-pla hybrids matrixes during long-term delivery of penicillin G

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Abstract: Kidney fever is a pediatric cardiac disease whose treatment consists of a painful intramuscular monthly administration of Penicillin G until 21 years old [1]. High serum concentrations of this drug are achieved rapidly but its half-life is approximately 30 min and its bioavailability lower than 30%. Penicillin G has also a low physicochemical stability and presents low resistance to temperature, light and pH. The development of biocompatible materials able to preserve the chemical structure and therapeutic properties of Penicillin G during long periods of delivery is a great challenge. In this work, Siloxane-Poly(ether/ester)-hybrid materials, in which siloxane nanoparticles are interconnected by hydrophilic polyoxyethylene (PEO) and hydrophobic Polylactic acid (PLA) chains of molar mass 1900 g/mol and 1500 g/mol, respectively, have been synthesized by Sol-Gel process. These biocompatible, flexible and chemically stable matrices have been loaded with 30% wt of Penicillin G. Three different [PLA]/[PEO] ratios (0.25, 1 and 4) were employed, in order to investigate how the more hydrophilic or the more hydrophobic character of the hybrids affect their structural and physicochemical features before and after drug release. For this purpose, X-ray diffraction (XRD), Infrared Spectroscopy (FTIR), Small-Angle X-ray Scattering (SAXS), Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) have been used. Figure 1 shows the Raman spectrum of the hybrid prepared with [PLA]/[PEO]=1, with a peak located around 1000 cm⁻¹, characteristic of b-lactam absorbance mode. This evidences that chemical structure of Penicillin G has been preserved. Small-Angle X-ray Scattering (SAXS) pattern of the same sample before drug release shows an interference peak located around 1.6 nm⁻¹ (attributed to the spatial correlation between siloxane nanoparticles) and another peak located around 3nm⁻¹ (attributed to the long period between PLA lamellas in PLA crystalline phase). The resulting interparticle distance d and long period L can be determined by the position of the peaks maximum and are 3.9 nm and 2.1nm, respectively. This result shows that homogenous hybrids presenting interpenetration at nanometer scale between PEO, PLA and siloxane nanoparticles have been obtained, which diminishes degradation of PLA with time. After drug release, a shift of both peaks towards lower q-values is observed, associated to the increase of d and L up to 7 nm and 2.6 nm, respectively. This illustrates the swelling of the hybrid matrixes during drug release and the presence of confined water after the process. This also evidences that crystalline PLA still exists before and after release, despite of XRD measurements showing that PLA crystallization has been strongly reduced in the hybrids networks by comparing with pure PLA, which is a promising result aiming to avoid fast PLA degradation. The excellent dispersion of Penicillin in all materials revealed by XRD led to a prolonged drug release of several months, initially governed by PEO surface swelling and then by diffusion mechanisms.

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High refractive index nanocomposite polymers for encapsulation of solar cells

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Abstract: Solar power is one of the main sources of sustainable energy. Conventional consumer grade solar panels have efficiencies of approximately 20%. One of the main challenges for the solar cell industry is to increase the efficiency of the solar panels. In order to reach higher efficiencies, the refractive index of the polymer encapsulant (located in between the PV cell and the glass layer) can be increased by the addition of nanoparticles with a high refractive index (Figure 1). This will lower the reflectance of light and increases the efficiency of solar cells. Titanium dioxide nanoparticles possess a high refractive index and are, after modification, suitable for incorporation polymer matrices. Since the properties of these nanoparticles are dependent on their size, shape and chemical composition, precise control of the synthesis is necessary for tailoring the properties of the resulting products, on laboratory, pilot and production scale. A scalable and controlled production of nanoparticles is thus needed, for which continuous flow reactors were employed. This way, titanium dioxide particles (diameter of 50 – 200 nm) were successfully synthesized, surface modified and incorporated into polymer foils to enhance the efficiency of solar cells.

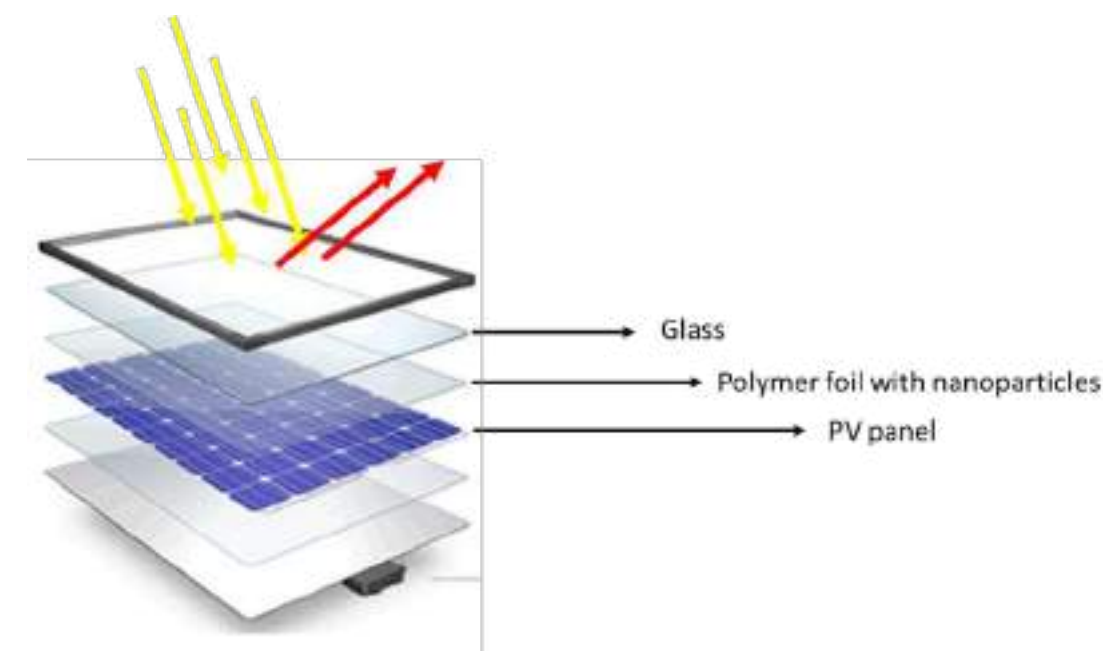


Figure 1: Integration of titanium dioxide nanoparticles into the polymer foil leads to less reflectance of light and thus more efficient solar panels.

Annealing temperature dependence of structural and optical properties of sol-gel derived copper gallium oxide films

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Abstract: Copper gallium oxides have attracted interest as semiconductor materials for fundamental science and device applications. Delafossite CuGaO₂ is p-type conductivity and the wide bandgap energy of 3.6 eV, and it has been widely studied for p-type transparent conducting films¹. Wurtzite CuGaO₂ is a p-type narrow bandgap material of 1.47 eV, and the application to solar cells was expected². Spinel CuGa₂O₄ has promoted the n-type material to gas sensor and photocatalysts³. Thus it is necessary to clarify the phase transition of copper gallium oxide films. In this work, we study the sol-gel processing of spinel-CuGa₂O₄, wurtzite- and delafossite-CuGaO₂ films.

The precursor solution was prepared by dissolving copper (II) acetate monohydrate and tris(acetylacetonato) gallium (III) in 2-propanol. The molar concentration of Cu and Ga was 0.2 mol/L, respectively. 1.0 mol/L of monoethanolamine was added as the stabilizer, they were stirred at 50 °C for 1-2 h. The coating on the glass substrates was prepared with dropping or spin coating methods. After the coated films were pre-baked at 100 °C for 5 min, they were crystallized by the annealing at 200-800 °C. The structural and optical properties of the samples were characterized by X-ray diffraction and UV-visible absorption measurements, respectively.

As shown in Figure 1, the optical bandgap energy of the samples changed discretely for the annealing temperature. Although the films were amorphous by the annealing at 200 °C, spinel CuGa₂O₄ (001) films were formed at 220-300 °C. Single-phase CuGa₂O₄ film without mixing of Cu₂O was prepared by the annealing at 280 °C for 1 h, and the optical bandgap was 1.46 eV. At 300-350 °C, phase transition occurred in wurtzite CuGaO₂. The mixture of CuGa₂O₄ and Cu₂O into the films were observed at 300 °C for 1 h, but wurtzite CuGaO₂ were formed by the annealing more than 6 h and the optical bandgap was estimated to be 1.73 eV. The large blue shift of absorption edge was observed above 350 °C, delafossite CuGaO₂ of 3.6 eV was prepared. These results suggest that copper gallium oxide films of spinel-CuGa₂O₄, wurtzite- and delafossite-CuGaO₂ structure were successfully fabricated by the anneal temperature control of sol-gel processes.

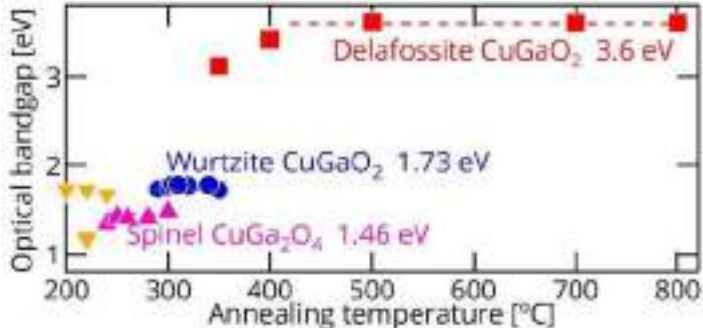


Figure 1. Annealing temperature dependence of optical bandgap of the samples.

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Preparation and properties of oligo(cyclohexylsilsesquioxane)/PMMA composite film

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Abstract: To improve thermal and mechanical properties of polymers, silsesquioxane (RSiO_{1.5})-based materials with cage or random structure has been extensively studied. For example, Bizet and coworkers¹⁾ reported that chemical and physical properties of poly(methyl methacrylate) (PMMA) could be improved by incorporating cage silsesquioxane into polymer sidechain. However, cage silsesquioxanes are generally high cost due to its low synthetic yields. In this study, we used cyclohexyltrimethoxysilane (CHTMS) and prepared OCHS/PMMA composite films via simple process.

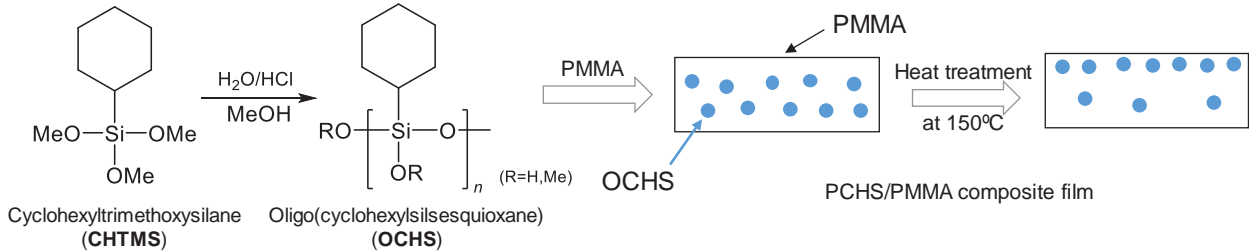


Figure 1. Sol-gel reaction of CHTMS and preparation of OCHS/PMMA composites.

The CHTMS monomer was polymerized by the sol-gel reaction with water in methanol using HCl as a catalyst at 70°C under nitrogen flow. The obtained sols were characterized as summarized in Table 1. With increasing water amount, degree of crosslinking was increased and the state was changed from viscous liquid to solid. IR analysis showed that the OCHS contains Si-O-Si bond and Si-OH group.

Table 1 Prepetition of oligo(cyclohexylsilsesquioxane)								
run	Molar ratio H ₂ O/Si	Yield ^{a)}	Reaction ratio ^{b)}	State	Peak area ratio by ²⁹ SiNMR (%) ^{c)}			DC (%) ^{d)}
		(g)	(%)		T ¹	T ²	T ³	
1	1.5	1.60	75.7	Viscous liquid	62	38	0	46
2	2.5	1.50	91.4	Solid	46	43	11	55
3	8.0	1.59	94.4	Solid	0	81	19	73

a) Scale in operation: CHTMS 2.04 g(0.01 mol). b) Calculated by ¹H NMR. c) T¹: CySi(OSi)(OMe)₂, T²: CySi(OSi)₂(OMe), T³: CySi(OSi)₃. d) Degree of condensation of siloxane bonding, calculated by the rate of T¹ unit.

The OCHS/PMMA composite film was also prepared by mixing the sol and PMMA followed by casting process. Interestingly, the resulting film contains OCHS after heating at 150 °C locally distributed on the top layer, which were analyzed by ATR-IR. The pencil hardness test using spin-coated film on silicon wafer showed increasing hardness index compared to the pristine PMMA film.

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Plasmon Enhanced Photoluminescence in Ag NPs – Carbon Dots Nanocomposite Films with Organosilica Functionalization

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Abstract: Carbon dots (C-dots) are of great interest as they show the unique photoluminescence properties in aqueous solution in spite of carbon-based nanomaterials. In the meantime, C-dots based solid-state emitting device has not yet been well-designed to achieve an efficient emission due to the difficulties in dispersion and in preventing reabsorption by surrounding substances. Here, silver nanoparticles (Ag NPs) – C-dots nanocomposite films in a functionalized organosilica matrix have been designed and prepared, to enhance the photoluminescence in solid-state using surface plasmon resonance (SPR) between Ag NPs and C-dots. Ag NPs^[1] and C-dots^[2] are prepared by well-established methods. To prevent the aggregation in the solid matrix, C-dots are functionalized by organoalkoxysilane (GPTMS), and the functionalized sol is used to be a part of the organosilica matrix through sol-gel process.^[3] Surface functionalization of C-dots by the organoalkoxysilane enables to prevent the quenching of C-dots due to aggregation. Furthermore the functionalization induces a large blue-shifted emission (525 → 425 nm) of C-dots due to the surface structural changes. The shifted emission range, overlapping with the Ag NPs plasmonic extinction, is suitable for the plasmon enhanced photoluminescence in this Ag NPs – C-dots nanocomposite system. The photoluminescence intensity of the designed films increases depending on the Ag NPs concentration, suggesting the plasmon enhanced photoluminescence, as shown in Figure 1. On the other hand, the non-functionalized C-dots films using the same manner, show the quenching with the Ag NPs concentration due to the contact between Ag NPs and C-dots. Therefore, the functionalization of C-dots and further sol-gel process enable to keep the dispersibility of C-dots and Ag NPs in organosilica matrix. In a certain concentration, the nanocomposite film is efficient for plasmon enhanced photoluminescence. This system can be one of the promising strategies to expand the application fields of C-dots especially for solid-state emitting devices.

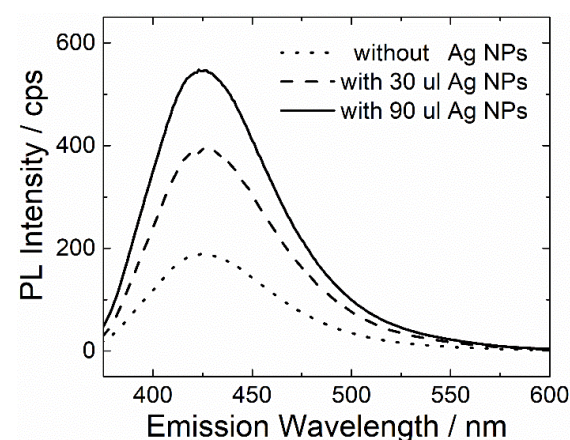


Figure 1. PL intensity of Ag NPs – C-dots nanocomposite films with organosilica functionalization depending on Ag NPs concentration.

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Polysiloxane-based organic-inorganic hybrid aerogels via ambient pressure drying

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Abstract: Porous materials with controlled porosity and microstructure are essential both for efficient production and high-performance applications. To open the way for commercial applications of monolithic transparent aerogels with superinsulating performance, we are studying polysiloxane-based organic-inorganic hybrid aerogels prepared via modified sol-gel processes and ambient pressure drying. Polymethylsilsesquioxane (PMSQ, $\text{CH}_3\text{SiO}_{3/2}$) aerogels with drastically improved mechanical strength and spring-back behavior against compression have been prepared and are currently under development for the scale-up production for insulating applications (Figure 1). Modifications of the synthetic parameters lead to optimized structure of pore skeletons and ensure even higher flexibility both against compression and bending. In addition, composites with nanofibrous materials such as cellulose nanofiber result in higher flexibility, while keeping the transparency is still challenging.

Other polyorganosilsesquioxane aerogels with ethyl, vinyl, chloromethyl have been developed to investigate the effect of organic substituents and impart functionality to aerogels. Polyvinylsilsesquioxane ($\text{CH}_2=\text{CHSiO}_{3/2}$) offers an opportunity for improving strength and flexibility through post-gelation vulcanization of the vinyl groups, and functionalization via the thiol-ene reaction. Polychloromethylsilsesquioxane ($\text{ClCH}_2\text{SiO}_{3/2}$) gives reactivity and anchoring sites for nucleophiles. Fluorescent aerogels embedded with carbon dots have been prepared.

Another way for improving mechanical flexibility relies on an introduction of organic bridging moiety within the polysiloxane networks. Organo-bridged polysiloxanes from, for example, 1,2-bis(methyldiethoxysilyl)ethane provide possibility of even higher strength and flexibility. Due to the combination of the organic bridges and hydrophobic polymethylsiloxane network, viscoelastic behavior of the resultant aerogels has been observed. Further, polysiloxanes with polymerized organic bridges have been prepared via a successive radical polymerization and hydrolysis-polycondensation from vinyl- or allyl-substituted alkoxy silanes such as vinylmethyldimethoxysilane. The resultant double crosslinked networks allow large deformations of the aerogels.



Figure 1. Examples of PMSQ aerogel-based insulating materials.

Hydrolysis of Methoxylated Layered Metal Hydroxides for Facile Preparation of Metal Hydroxide Nanosheets

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Abstract: Recently, we have reported that direct synthesis of interlayer-modified metal hydroxides with tripodal ligands (eg. tris(hydroxymethyl)aminomethane) through tridentate alkoxy bondings¹ and that the stability of immobilized ligands depends on the number of bondings per a molecule.² Such organically modified metal hydroxides would show unusual hydrolysis and condensation behavior because they are regarded as two-dimensional alkoxide. In fact, the structure of solid-state metal alkoxides largely affects the morphology of hydrolyzed products.³ In this study, methanol was used for the surface modification of layered metal hydroxides and we have found ultrathin metal hydroxide nanosheets were formed through hydrolysis of methoxylated layered metal hydroxides (Figure 1. (a)).

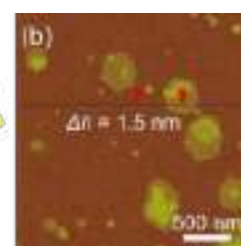
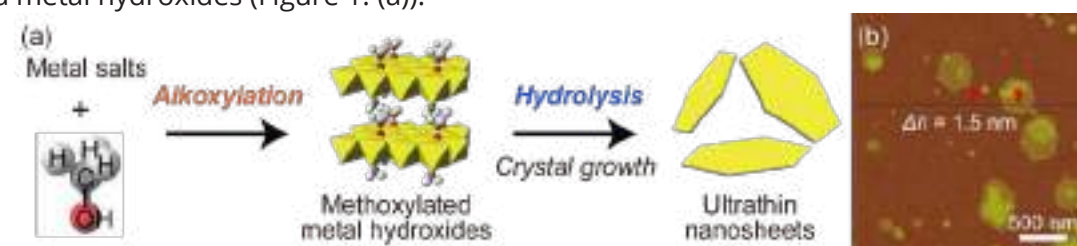


Figure 1. (a) Illustration of the preparation of metal hydroxide nanosheets through hydrolysis of methoxylated layered metal hydroxides and (b) AFM image of hydrolyzed product of methoxylated nickel hydroxide.

When a nickel salt was precipitated with sodium hydroxide in methanol, methoxylated nickel hydroxide (Ni-OMe) was obtained as a powder. The XRD pattern and FTIR spectrum indicated that Ni-OMe was a layered compound consisting of aggregated small nickel hydroxide sheets modified with methanol. When Ni-OMe was hydrolyzed in water, colloidal dispersion with a Tyndall effect was obtained after centrifugation. The AFM image of the spin-coated dispersion (Figure 1. (b)) showed the hexagonal shaped particles with several tens to several hundred nanometers in lateral size and about 1.5 nm in thickness. The nanosheets showed electron diffraction spots corresponding to in-plane structure of nickel hydroxide, which indicated that the obtained nanosheets were crystalline nickel hydroxides. Because nanoparticles composed of aggregates of Ni-OMe were initially obtained, the crystal growth of nickel hydroxide nanosheets occurred during the treatment with water. Therefore, hydrolysis of two-dimensional alkoxide is not a part of simple sol-gel reaction, accompanied with the process of topochemical reaction forming nanosheets. This paper has opened a new avenue for facile preparation of metal hydroxide nanosheets by hydrolysis of methoxylated layered metal hydroxides because exfoliation of layered metal hydroxides is generally difficult due to the absence of inherent layer charge effective for intercalation and subsequent exfoliation.

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Heteroepitaxial growth of covalent organic framework (COF) on copper hydroxide nanobelts

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Abstract: Thin films of porous materials have showed great potentials for various applications such as separation, photonics and electronics. Controlling a crystallographic orientation of such materials on a substrate (centimeter scale) allows for sophisticated functionalities required for realistic devices. We have recently succeeded in the fabrication of metal-organic framework (MOF) thin films with crystallographic orientations along all three axes [1]. The methodology is based on the heteroepitaxial growth of MOF on metal hydroxides. The achievement motivated us to expand for other systems. Covalent organic frameworks (COFs) were chosen as target porous materials because oriented COFs thin films had been also demanded for organic electronic devices and host-materials of functional molecules due to their π -electron systems and 1D pores [2]. In the present work, oriented COF-1 ($(C_3H_2BO)_6 \cdot (C_9H_{12})$) thin film was successfully fabricated on copper hydroxides nanobelts. Detailed XRD investigations indicated a crystallographic alignment of the COF-1 crystals (Figure 1a), in which boronic ester linkages in COF-1 were found to be parallel to the a-axis of copper hydroxides (Figure 1b). At the interface of copper hydroxide and COF-1, the boronic acid is considered to be bonded to hydroxyl groups of copper hydroxides with B-O bonds parallel to a-axis of copper hydroxides.

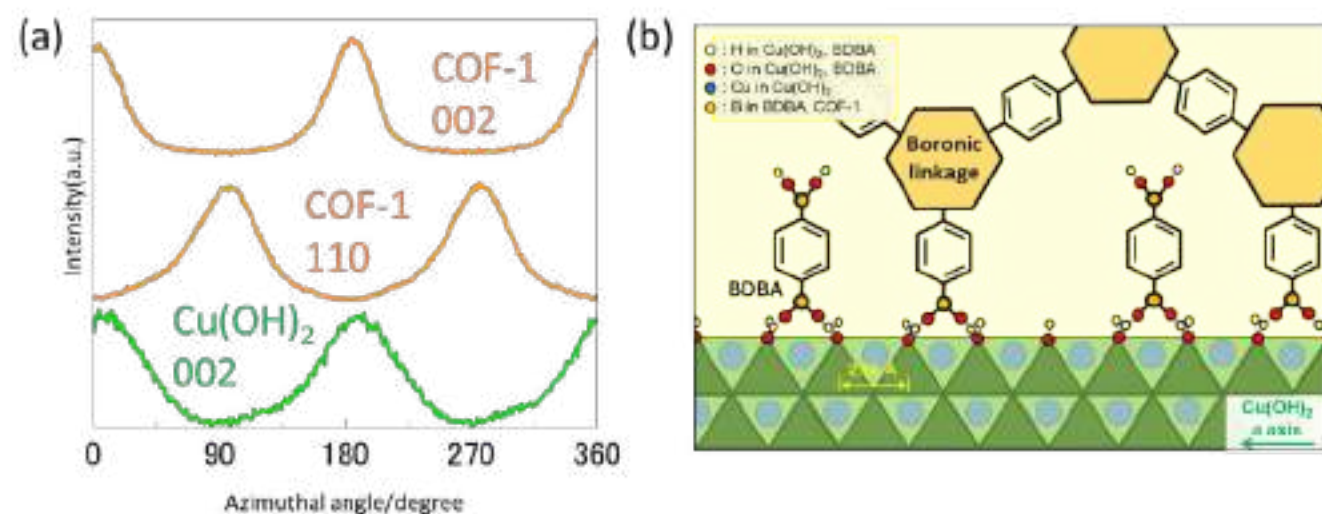


Figure 1. (a) Azimuthal angle dependence of intensity profiles X-ray diffractions of COF-1 grown on $Cu(OH)_2$ nanobelts substrate, indicating the formation of oriented COF-1 crystals on copper hydroxides. (b) A proposed interface structure of COF-1 on $Cu(OH)_2$.

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Thermo-responsive wettability in hydrophobic regime on polymer-coated titanate nanorod brushes

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Abstract: Surfaces with stimuli-responsive wettability are of importance for various applications including micro-fluidic control, drug delivery, and interfacial applications [1]. Wettability of materials is closely related to the surface chemistry and roughness (nanostructures). Thus, a control of surface chemistry or roughness is considered as two strategies to fabricate materials with responsive wettability. Surfaces with stimuli-responsive wettability have been achieved using stimuli-responsive polymers or organics of which surface functional groups are switchable by external-stimuli. Although this strategy is well-established and many types of responsive surfaces have been developed thanks to a variety of stimuli-responsive polymers available so far, the changes of surface functional groups may affect components in liquid in some applications like micro-fluidic control and drug delivery. Herein, we report the fabrication of surfaces with stimuli-responsive wettability on which only surface roughness is changed by thermal stimulus while the surface functional groups remain unchanged. The surfaces are fabricated as follows. At first, vertically-oriented titanate nanorods (TNR brush) were prepared on Ti plates by a reported method [2]. The surface of TNR brush was modified with (octyl)trimethoxysilane (OTMS) (OTMS-TNR brush). Then, paraffin dissolved in isooctane was spin-coated on the OTMS-TNR brush (Paraffin-coated OTMS-TNR brush). The paraffin was homogeneously coated on the OTMS-TNR brush as shown in Figure (a). The paraffin shows around 10 % thermal expansion over 40 °C. The thermal expansion of paraffin on OTMS-TNR brush resulted in a decrease of surface roughness (Figure (b)), which makes the surface less hydrophobic (Contact angles: from 147° to 112°) at higher temperature than 40 °C (Figure (c)). The detailed methods and mechanism will be discussed in the presentation.

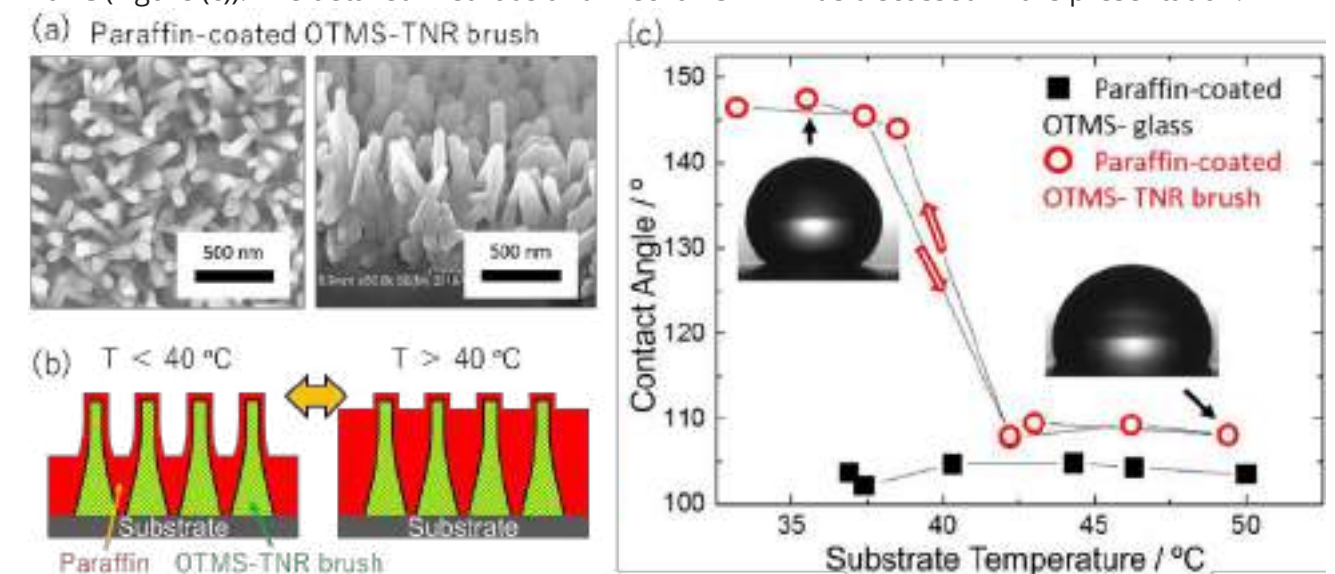


Figure. (a) SEM images (top view and cross-section) of Paraffin-coated OTMS-TNR brush. (b) Expected structures of Paraffin-coated OTMS-TNR brush at lower and higher temperatures than 40 °C. (c) Contact angles on Paraffin-coated OTMS-TNR brush and Paraffin-coated OTMS-glass at different temperatures.

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Adhesive properties of water-soluble polysilsesquioxanes containing ammonium, mercapto, and vinyl groups in side-chains

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Abstract: The adhesives are mainly classified into drying adhesive, chemical adhesive, and hot-melt adhesive by solidification methods. Although many adhesives have been developed, most adhesives consist of the organic polymers, which can be applied to all types of adhesives described above. Conversely, cement and water glass are practically used as inorganic adhesive, and have properties of excellent heat resistance, durability, and adhesion between inorganic materials. However, because general inorganic materials are poor solubility, "drying adhesive" with excellent storage stability are limited.

So far, we have successfully prepared water-soluble silsesquioxane copolymer containing ammonium and mercapto side-chain groups (PSQ-AM), which act as adhesives for inorganic materials such as stainless steels and glasses, by the hydrolytic polycondensation of a mixture of 3-aminopropyltrimethoxysilane (APTMS) and 3-mercaptopropyltrimethoxysilane (MPTMS) using HCl in water/methanol (1:19 v/v) mixed solvent.¹ However, this copolymer could not maintain adhesiveness at 150 °C. It is presumed that PSQ-AM could not endure the strain derived from the temperature change in the adherends with different thermal expansion coefficients, i.e., a stainless steel and a glass, because this copolymer has a rigid structure.

Therefore, in this study, slightly flexible structure and loose cross-linked structure were introduced into the aforementioned PSQ to develop inorganic drying adhesives maintaining adhesiveness even at high temperature. To prepare such PSQ, instead of APTMS used in PSQ-AM preparation, 3-(2-aminoethylamino)propyltrimethoxysilane (AEAPTMS) as an organotrialkoxysilane containing longer alkyl chain was used. In addition, vinyltrimethoxysilane (VTMS) was also included as a starting material. The hydrolytic polycondensation of a mixture of AEAPTMS, MPTMS, and VTMS was performed using aqueous phosphoric acid (Scheme 1). The resulting terpolymer (PSQ-2AMV) was soluble in water. The stainless steel plate and the glass plate adhered using aqueous PSQ-2AMV solution were not peeled off even at 200 °C. Moreover, copolymers (PSQ-2AM and PSQ-2AV) were prepared from AEAPTMS-MPTMS and AEAPTMS-VTMS mixtures, respectively. The stainless steel plate and the glass plate adhered using an aqueous solution of a PSQ-2AMPSQ-2AV mixture were also not peeled off at 200 °C.

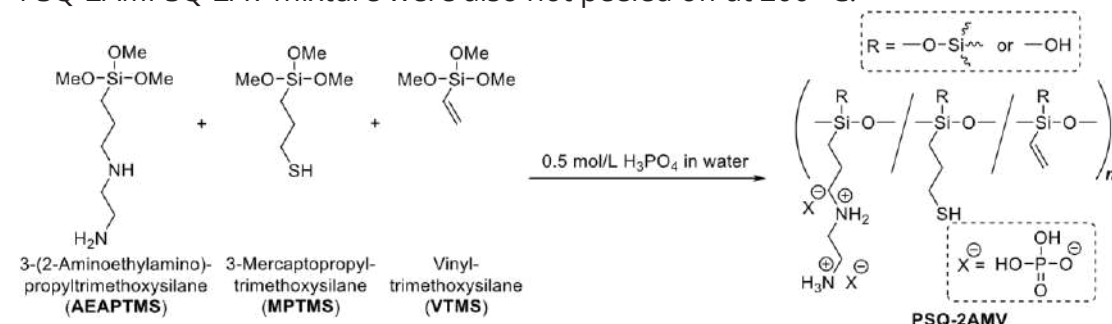


Figure 1. Preparation of water-soluble PSQ adhesive containing ammonium, mercapto, and vinyl groups in side-chains (PSQ-2AMV).

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Alumina-based aerogels modified by luminescent complex tris(8-hydroxyquinolino)aluminum

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Abstract: Aerogels are sol-gel derived solid materials with porosities from about 80% to 99.8 %. Since the first synthesis of an aerogel, by Kistler in 1931, aerogels of various types, based both on inorganic compounds and organic polymers, have been studied in detail. In recent years, extensive studies on hybrid aerogels have been conducted. Another line of research which is of considerable interest nowadays concerns synthesis of aerogels modified with metal coordination compounds which provide them with additional functionality. These aerogels can be used as catalysts, gas sensors, Cherenkov detectors and scintillators. The metal complexes immobilized in the aerogel matrix combine the advantages of both homogeneous and heterogeneous catalysts. Unfortunately, data on potential synthetic approaches to coordination aerogels are still quite scarce, and reported methods are typically complex, multi-stage and require the use of expensive reagents.

In the present work a facile procedure was developed for the production of Al₂O₃ aerogels modified with tris(8-hydroxyquinolino)aluminum complex (AlQ₃). It was demonstrated that the incorporation of 8-hydroxyquinoline into the alumina sol leads to a significant increase in the duration of epoxide-initiated gelation, and markedly affects the microstructure of the produced aerogels. The translucent monolithic aerogels were obtained by supercritical drying of lyogels in CO₂. The composition and properties of aerogels were analyzed using low-temperature nitrogen adsorption, helium pycnometry, IR spectroscopy, UV-visible spectroscopy, luminescence spectroscopy, powder X-ray diffraction, scanning and transmission electron microscopy, and thermal analysis combined with mass spectrometry of evolved gases. The obtained aerogels had low density (0.15–0.18 g cm⁻³), high specific surface area (480–550 m²/g), high porosity (90–95%), and showed bright luminescence upon excitation in the UV range. Thus, the possibility of a one-step preparation of metal oxide aerogels, surface-modified with metal complexes and, therefore, possessing a bright luminescence, was demonstrated.



Figure 1. The general synthetic scheme for Al₂O₃ aerogels, modified by AlQ₃.

The work was supported by RFBR 17-53-150007

Anti-fogging coatings by a sol-gel process using alkoxysilanes containing polyglycerin structure

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Abstract: Functional coatings, such as flexible hard coating, self-healing coating, anti-reflection coating, anti-fogging coating, and so on, are one of most attractive applications of industrial fields. In particular, anti-fogging coating has an important function of the improving visual properties, which is applied for optical films, glasses, lenses, etc. The achievement of this function has been done by the preparation of hydrophilic surface. In order to prepare such surface, surfactants have been commonly coated on the glass substrates. However, there are some disadvantages from this procedure. As surfactants are not bonded chemically onto the glass surface, the water-soluble surfactants are easily detached from the glass substrate and the durability of anti-fogging properties is quite low. Therefore, new concept of anti-fogging is motivated, which is (1) hygroscopic network compounds, (2) nonionic surfactant network compounds, and (3) chemical bonding to glass surface. In this work, we have been investigating the hygroscopic sol-gel network for new type anti-fogging coatings.

EO (ethylene oxide) modified polyglycerin is a good candidate for hygroscopic and nonionic compounds. In the case of glycerin tetramer, six terminated hydroxyl groups could be reacted by some EOs, which EO extension could be carried out. As next step, trialkoxysilane groups could be successfully introduced into the terminal hydroxyl groups via two reactions. The chemical structure of novel multifunctional silane coupling agent is described in Figure 1. The crosslinked coating on glass plate and PET film substrate was prepared by a sol-gel process using this silane coupling agent with formic acid catalysis. The sol-gel coating (ca. 25μm thickness) was prepared and the anti-fogging property was demonstrated as shown Figure 2. After 60 sec exposing to the steam from 50°C hot water, the coated part was not clouded at all. It could be confirmed that this coating has the good anti-fogging property. However, as the contact angle is 47°, it was recognized that hydrophilicity is not high. Therefore, it seems that this anti-fogging property resulted from hygroscopic characteristics caused by EO-extended polyglycerin embedded in the network coating. And also, it was found that absorbent water and dehydrated properties are existed. This is an interesting characteristic of active moisture transportation. Furthermore, the Mandrel-bend test of these coatings on PET film indicated the result of <2mm, and good flexibility was confirmed in spite of the cross-linked structure. The anti-fogging hybrid coatings with methyl silicate are also in progress.

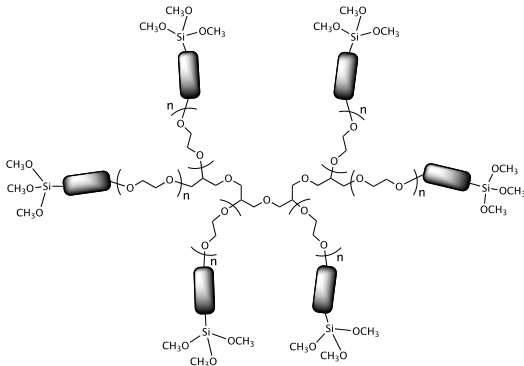


Figure 1. Chemical structure of novel silane coupling agent.



Figure 2. Anti-fogging property of sol-gel coating from silane coupling agent containing EO-extended polyglycerin.

Facile and Fast Synthesis of Flexible and Superhydrophobic Aerogel-like Silica Monolith

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Abstract: A fast and simple approach for preparing flexible aerogel was obtained via a sol-gel process. The ultralow density silica material in Fig. 1 has excellent porosity and exhibit superhydrophobic properties. The flexible network gave the material good mechanical properties and durability as shown in Fig. 1a. It can recover its size and shape following 80% compressive strain. The material can quickly absorb oil as shown in Fig. 1c-e and the oil can recovered by a simple mechanical squeezing instead of the traditional heating desorption method. It is also capable of breaking emulsion and would be particularly useful in treating oil and solvent contaminated water.

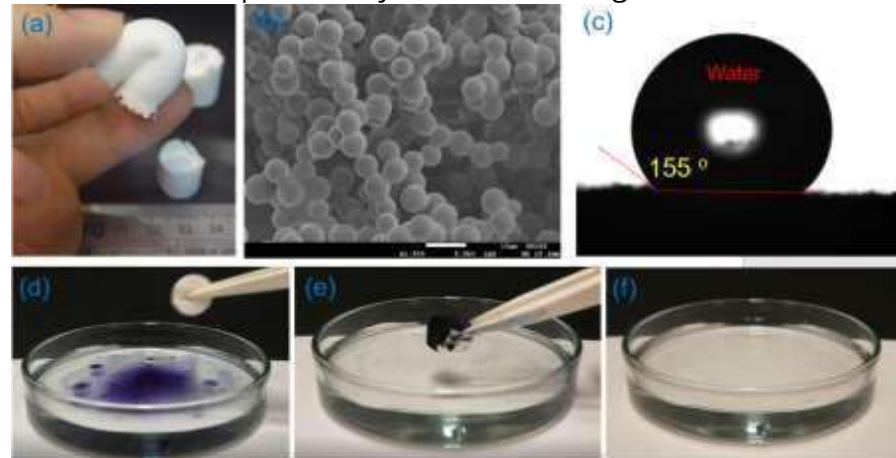


Figure 1. Flexible (a), porous (b), and hydrophobic (c) aerogel-like monolithic silica shows oil excellent sorption ability (d) to (f). (The oil phase is toluene colored with sudan black)

Metal-Organic-Framework (MOF) Aerogels with Hierarchical Pore Structures

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Abstract: Metal-organic-framework (MOF) materials are known for their large surface area and ordered pore structure. These properties make MOFs interesting materials for many applications. This work describe a method for creating ultralow density MOF aerogels with hierarchical pores that allows rapid internal transport for potential applications in flue gas treatment. Two presentative MOFs, ZIF-8 and MOF-5, were selected and prepared using a new synthetic approach. The MOF crystallization and network formation were monitored by X-ray diffraction and electron microscopy. A crystallization model was developed from the XRD data, while the pore network created through the network formation was visualized in Fig. 1. The 3D reconstructed images were obtained by focused ion beam-scanning electron microscopy. It reveal a complex interconnected solids made of macro- and mesopores that provide access to the MOF micropores.

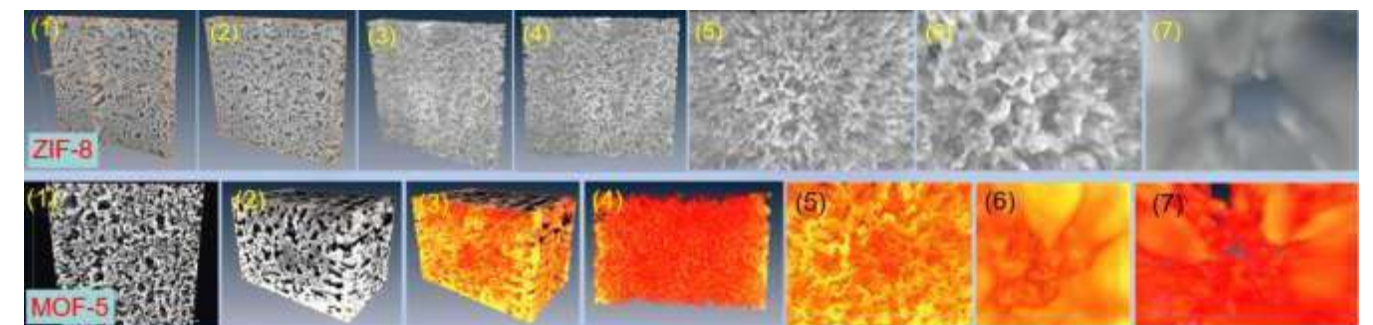


Figure 4. Focus ion beam-scanning electron microscopy (FIB-SEM) analysis of the MOF-5 aerogel prepared from zinc precursor aerogel. The images (1)-(8) are 3D reconstruction images (from FIB-SEM) of the aerogels ZIF-8 (Up) and MOF-5 (Bottom).

Preparation of transition metal nitride and oxynitride thin films by nitridation of sol-gel derived oxide thin films with urea

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Abstract: Transition metal nitride and oxynitride thin films have received much attention for the application to such as electrodes, photo-anodes and hard-coatings. Metal nitride and metal oxynitride thin films have been prepared by physical vapor processes such as RF magnetron sputtering, Pulse Laser Deposition or Molecular Beam Epitaxy process and chemical vapor deposition processes. However, preparation of nitride and oxynitride thin films using solution-based process should be important for the composition and morphology control of the thin films.

In the present study, thin films of Cu_3N or TaON were prepared by nitridation of sol-gel derived precursor oxide thin films using urea as a nitrogen source. First, CuO or Ta_2O_5 thin films were prepared by a solution process. Then precursor oxide thin films and urea were placed downstream and upstream side in a tube furnace, respectively, and heated under a nitrogen flow.

X-ray diffraction patterns and UV-visible light absorption spectra showed that Cu_3N thin films were formed with a heat-treatment at 400°C for 12 h under the nitrogen flow. FT-IR and Raman spectra suggested that Cu_3N was produced by the reaction of CuO and decomposition products of urea. Formation of TaON thin films was also confirmed with a heat-treatment at 1000°C .

The present study was supported by JSPS KAKENHI Grant Number 17H04950 and 17H03382.

Structural influence of silica-based ionogels on their performance as electrolytes for all-solid-state Lithium-ion microbatteries

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Abstract: The emerging market of the Internet of Things, smart objects and others increase the demand for micro energy sources. Rechargeable Li-ion batteries are a well-known technology for energy storage. However, safety issues and high production costs constrain progress. Research on solid electrolytes, such as LiPON, was performed to evade leakage. But LiPON suffers from low ionic conductivity and a cost and time intensive production process. Another approach is the substitution of volatile and flammable organic electrolyte solvents with ionic liquids (IL), which display negligible vapor pressure and wide chemical, electrochemical, and thermal stability. Electrolyte solution based on ILs can be confined into inorganic porous networks forming so-called ionogels (IG), which are investigated as solid electrolyte materials. IGs combine low hazard and good ionic conductivity [1].

Silica-based IGs compatible with Li/LiCoO_2 systems were prepared in a one-pot sol-gel process. The composition of the IG precursor solution and the influence of trifluoroacetic acid as catalyst were studied to obtain a fast condensation. Homogeneous and transparent IGs were obtained with a gelation time of less than 4 h. The physical properties of the host matrix were characterized by N_2 sorption, Hg porosimetry and SEM. The silica host matrices were 3D networks predominantly built from 3-fold condensed silicon centres.

The influence of its structural changes on the electrochemical behaviour was studied by varying the catalyst amount and by increasing the IL amount in the gel. The electrochemical performances of the IG were measured with complex impedance spectroscopy and galvanostatic cycling. Results show that IGs with IL amounts $n_{\text{IL}}/n_{\text{SiO}_2} \sim 3$ may be successfully used as solid electrolyte in Li/LiCoO_2 cells. Batteries were prepared, which cycle more than 100 cycles at a rate of C/2 with no evidence of dendritic growth. Impedance characterization reveals the high internal resistivity of these batteries due to the dense structure of the silica matrix.

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Preparation of PDA/TiO₂ Composite Film on PTFE and Its Cellular Responses

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Abstract: Polytetrafluoroethylene (PTFE) is reported to have good physical and chemical properties, as well as good biocompatibility. It has wide biomedical applications as ???. However, some drawbacks, such as low surface energy and poor hydrophilicity, directly affect its further biomedical application. In this work, polydopamine/Titanium dioxide (PDA/TiO₂) composite film was prepared on the surface of PTFE substrate, so that the hydrophilicity and cytocompatibility of PTFE surface could be improved. A mixed colloidal-sol of dopamine chloride and TiO₂ nanoparticles was prepared and then used for film preparation. Dopamine could self-polymerized into PDA and TiO₂ nanoparticles were embedded during this process. As a result, a PDA/TiO₂ composite film was obtained. The surface of the film was uniform in morphology and firmly bonded to the substrate, the shear strength reached 23.5 MPa. The energy dispersive spectrum indicated the presence of Ti element on the surface, and the water contact angle test showed that the water contact angle of the modified substrate reduced from 118° to 65°. That further confirmed the presence of TiO₂ on the surface. Fibroblasts and osteoblasts were seeded on the surface of the modified substrate. It was found that adhesion and spreading of the cells improved significantly in comparison with film-free PTFE substrate. Also, the one-day cell adhesion experiment and three-day cell proliferation experiments showed improved adhesion and proliferation of the cells. It is suggested that such PDA/TiO₂ films could effectively improve the surface cytocompatibility of PTFE substrate.

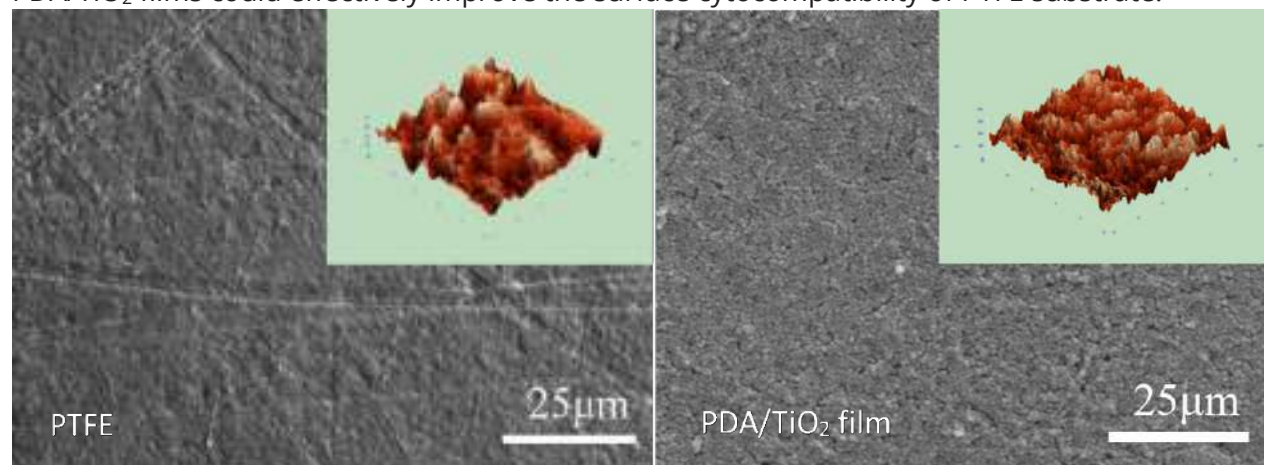


Figure 1. Surface morphology of the substrate and film.

Surface-tension gradient on Sol-Gel coatings for liquid droplet handling

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Abstract: Surface tension phenomena between a liquid droplet and a solid surface act in various applications (inkjet printing, superhydrophobic textile, anti-fog windows, ...). Recently, the ability to control the position and motion of a liquid droplet, along a defined path, further expands the application field and finds an even greater interest in microfluidics (« lab-on-chip ») or for biological tissues obtained by 3D printing.

A solution to control droplet motion is to prepare an anisotropic surface presenting a surface tension gradient [1]. Therefore, favored direction is defined from the hydrophobic to the most hydrophilic area. Spontaneous movement can be observed for high surface-tension gradients [2]. Nonetheless, following experimental conditions, mostly surface-tension gradient are limited to around one centimeter length.

Usually, chemical gradient surfaces are obtained through Self Assembled Monolayer (SAM) by modulating hydrophobic groups density absorbed on the top surface. However, this solution suffers from some problematic issues such as weak homogeneity, mechanical damage and UV light sensitivity. Otherwise, few studies are devoted to Sol-Gel coatings showing a hydrophobic surface gradient. Hybrid Sol-Gel coatings are known to take the advantage of specific organic groups and the strength of the inorganic network. In addition, Sol-Gel coatings are completely covering with a thickness from the nanometric to the micrometric scale. These benefits promote the lifetime of the chemical gradient properties.

This is why, we synthesis Sol-Gel coatings with a pluri-centimetric surface-tension gradient (figure 1.). Coating has to be smooth enough in order to neglect topography influence on the wetting. Hydrophobic gradient could be produced directly by balancing the polar/apolar groups ratio in the sol composition. An other non-standard method studied is to control the radical oxidation of apolar groups on a hydrophobic Sol-Gel layer by an atmospheric plasma gun. According to the Cassie and Baxter's equation, the resulting contact angle, at a given position, is defined following the contributions of hydrophilic and hydrophobic ratios.

Hydrophobicity and surface energy characterizations are carried out by sessile drop technique. Microstructure, topology and roughness of the coatings are characterized by SEM, AFM or profilometer. The physico-chemical analyses are performed by EDS, IR-Raman or XPS.



Figure 1. Example of a Sol-Gel coating showing a wettability gradient.

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Electrochemically assisted deposition of sol-gel films: manipulation and applications

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Abstract: Electrochemically assisted deposition has been developed as an important approach for preparing sol-gel films since it was clearly proposed by Mandler *et al.* in 1999^[1]. It is based on the electrochemical generation of OH⁻ ions, which serve as catalyst for the sol-gel film formation on the electrode (Figure 1). Since the OH⁻ generation occurs only near the cathode, the pH of the bulk sol is not affected, allowing deposition to be carried out from a stable sol precursor. Like in other electrodeposition systems, the deposition process can be controlled by potential and time. These advantages have been well supported by experimental results^[2, 3]. However, the kinetics of the electrochemically assisted deposition of sol-gel films is still unclear. Obviously, since the driving force of deposition is not directly the electron transfer, the classical rules for electrodeposition such as Faraday's Law do not apply. In this presentation, I will briefly introduce my experimental work since 2003, which covers the manipulation of deposition and applications in corrosion protection, composite film formation, *etc.* Moreover, I will mainly discuss my recent attempts on developing quantitative kinetic models for the electrochemically assisted deposition process^[4], including unpublished results. The aim is to provide deeper understanding of the process for better manipulation, paving the way towards scale-up applications of the technique in the future.

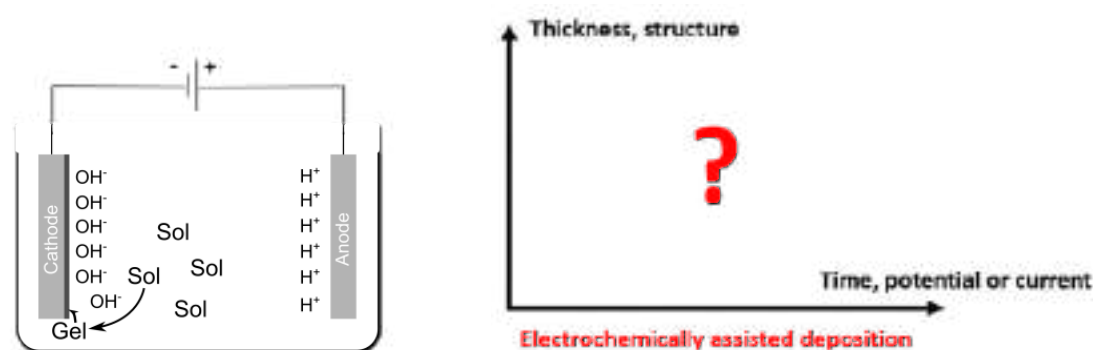


Figure 1. Scheme of cathodic electrochemically assisted deposition of sol-gel films^[2].

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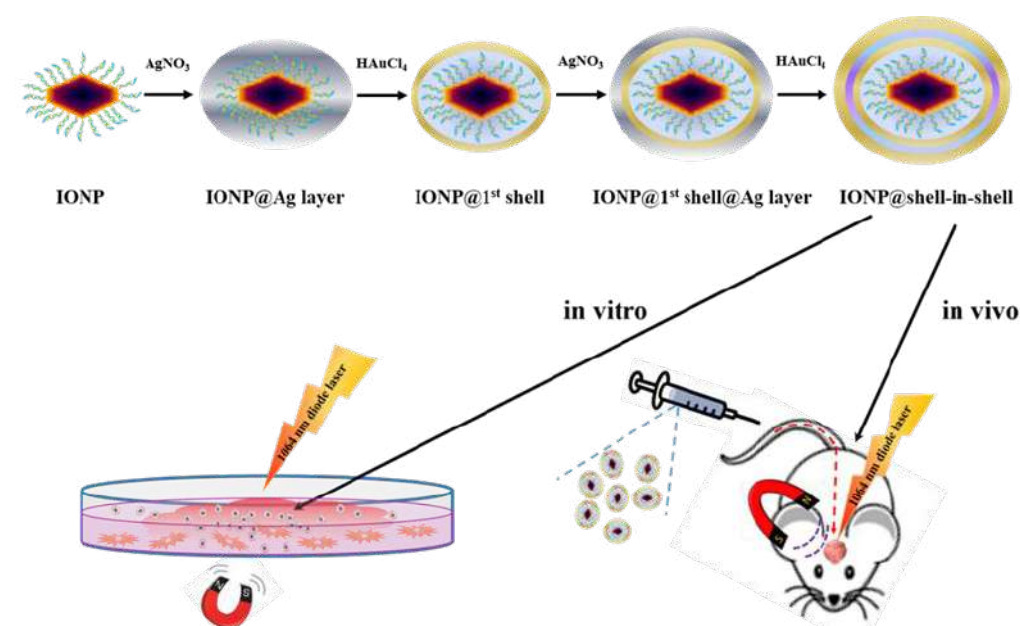
The author gratefully acknowledges all the co-workers since 2003, from Prof. Jiming Hu's group in Zhejiang University (China), Prof. William J. van Ooij's group in University of Cincinnati (USA), Prof. Daniel Mandler's group in The Hebrew University of Jerusalem (Israel) and my current colleagues in ELAN group of LCPME (France) led by Dr. Alain Walcarius. The author also acknowledges CNRS-MOMENTUM program over the 2018 - 2020 period.

IONPs@ Au/Ag Core-Shell Constructs for Magnetically-Targeted Photothermal Therapy

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Abstract: Construction of multifunctional nanoparticles (NPs) with near-infrared (NIR) plasmonic responses is considered a versatile and multifaceted platform for several biomedical applications. Herein, a double layer of Au/Ag alloy on the surface of truncated octahedral iron oxide NPs (IONPs) was prepared and the distance between the layers was controlled to exhibit broad and strong NIR absorption. The rattle-shaped IONP@shell-in-shell nanostructure showed light-response to the NIR biological window from 650 to 1300 nm for photothermal therapy (PTT) and magnetic guidance for hyperthermia and magnetic resonance imaging (MRI) diagnosis. Exposing the aqueous solution of IONP@shell-in-shell to a 1064 nm diode laser, its heat conversion efficiency was ~28.3 %. The in vitro cell viability at a gold concentration of 100 ppm was ~85 %, and decreased to ~16 % when the cells were treated with the NIR irradiation and magnetic attraction. T2-weighted MRI images showed a clear accumulation of IONP@shell-in-shell at the tumor site with magnetic attraction. In vivo luminescence tumor images explained that the IONP@shell-in-shell could reduce the U87MG-luc2 cancer cell proliferation in mice with the NIR irradiation and magnetic attraction. These results indicate the IONP@shell-in-shell as a promising nanomedicine for PTT, magnetic targeting, and magnetic resonance imaging (MRI).



Development and Application about Aerogels from Natural Polymers

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Abstract: In the past decade, a series of aerogel products based on natural polymers, such as alginate based aerogel^[1,2], cellulose based aerogel^[3-7], SiO₂/cellulose composite aerogel^[8] and chitosan based aerogel^[3,4,9], were prepared by sol-gel and freeze-drying techniques in our group. The application properties of materials, including in as heavy metal ion adsorbents, organic adsorbents and intelligent responsive drug carriers have been extensively studied. These natural polymer aerogels have good thermal insulation performance, adsorption properties (oil, water, organic matter, heavy metal ions, etc.), oil and water selectivity, as well as good elasticity and reusable performance. The smart alginate based aerogels possess both temperature and pH sensitivity, and is good for drug control-release. At the same time, the cold plasma surface modification technology has been developed to achieve non-destructive hydrophobic modification. After modification, the contact angle of the aerogels can reach as high as 150°^[1,3,6,8]. These works have expanded broad space for the functionalization and application of natural polymer aerogels.

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Development and Characterization of Swellable and Bioadhesive Composite Materials Composed of Polyelectrolyte Hydrogel of Chitosan with ring-opened Polyvinyl Pyrrolidone

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Abstract: A novel GRDDF (Gastroretentive Drug Dosage Form) system could not only sustain release of drug but also increase the residence time of the drug in stomach by three retentive mechanisms of swelling, floating and bioadhesion. Alendronate preferably absorbed from upper gastrointestinal tract was selected as the model drug. The aim of this study was to prepare and characterize a swellable and bioadhesive gastroretentive drug dosage form (sbGRDDF) based on the complex hydrogel formed between chitosan (CS) and ring-opened polyvinyl pyrrolidone (roPVP) via charge interaction. The complex hydrogel of CS/roPVP was produced by blending CS (cation) with roPVP (anion) obtained by basic treatment. The influence of heating time and NaOH concentration for preparing roPVP, different MW of CS, and different ratio of CS/roPVP on the swelling ability of resultant complex hydrogel was characterized and optimized. Results demonstrated that roPVP in 0.5M sodium hydroxide solution with a 4h-heating at 50°C had the optimal property for preparing complex hydrogel with CS. However, there showed an insignificant influence of different Mw of CS, different ratio and different tableting pressure on the swelling ratio. Among all, the rheological properties (amplitude sweep, frequency sweep, creep compliance and viscosity) of hydrogels were characterized and compared as revealed in Fig.1. The complex hydrogel formed with roPVP and high Mw chitosan at 20:1 weight ratio possessed the optimal swelling ability. In vitro dissolution test showed optimized formulation reveals that the drug released slowly and constantly and drug release data is related to swelling behavior. In vivo pharmacokinetics study demonstrated that the oral bioavailability of alendronate was enhanced three folds and the mucosa irritation was reduced.

In conclusion, sbGRDDF composed of CS/roPVP complex hydrogel was successfully developed and is potentially applicable to improve clinical efficacy of bisphosphonates with minimization of side effects.

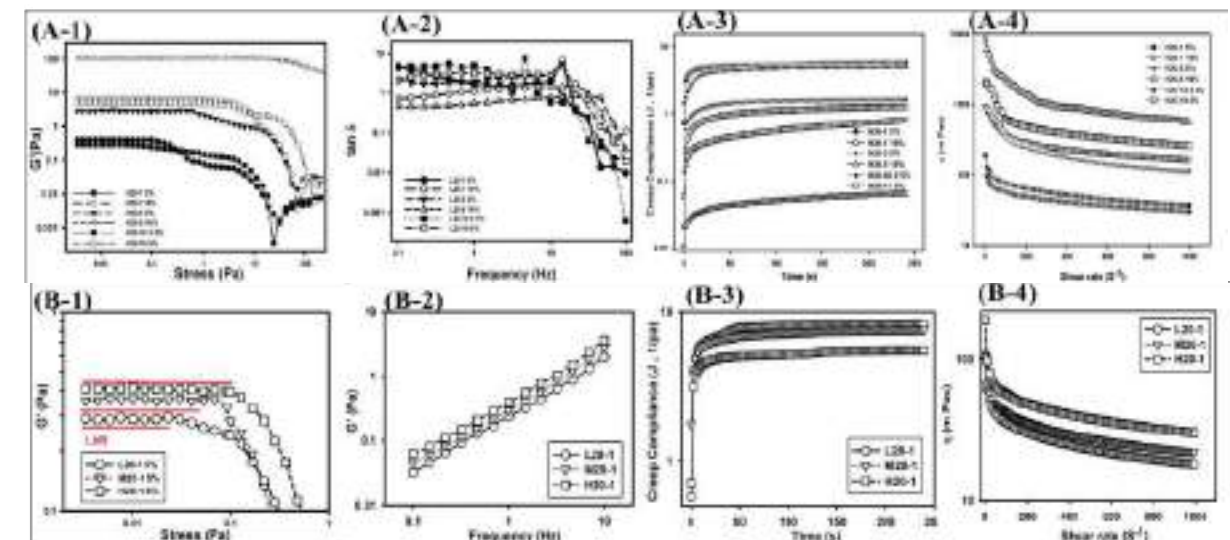


Figure 1. Comparison of amplitude sweep(A-1), frequency sweep(A-2), creep compliance (A-3) and viscosity (A-4) of roPVP/CS hydrogels composed of roPVP with high MW chitosan at three roPVP:CS ratios of 20:1, 20:5, 20:10.

Comparison of amplitude sweep (B-1), frequency sweep (B-2), creep compliance (B-3) and viscosity (B-4) of roPVP/CS hydrogels composed of roPVP with either, low, medium or high MW chitosan at roPVP:CS ratios of 20:1.

Hollowsphere Nanoheterojunction of g-C₃N₄@TiO₂ with High Visible Light Photocatalytic Property

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Abstract: g-C₃N₄@TiO₂ nanostructures with hollow sphere morphology, small grain size, high crystalline quality and high surface area is successfully synthesized by anneal method using melamine and hollowsphere precursor, which could be a universal method to synthesis hollow sphere nanoheterojunction. Excellent photocatalytic property was observed from the as-prepared g-C₃N₄@TiO₂ nanostructure with 466.43 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ hydrogen generation rate under visible light irradiation(>420nm) which was 5.5 times as much as the control couple, nanoparticle nanoheterojunction g-C₃N₄@TiO₂. No apparent deactivation was found during the follow-up cycle performance test. The special morphology and the heterojunction construction do contribution to both visible light absorption and photo-generated electron-hole pairs separation efficiency and final the photocatalytic property. The content of g-C₃N₄ was proved to be an important parameter for the promotion of photocatalytic property. Overlarge content may lead to lower photo-generated electron-hole pairs separation efficiency.

Composite coatings based on sol-gel MgO or TiO₂ oxide nanopowders for buildings and monuments protection

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Abstract: Coating formulations for the protection of buildings and monuments have been intensively researched lately. Such formulations are based on multifunctional composite coatings incorporating metal oxides. The metal oxides obtained by sol-gel method have photocatalytic and antimicrobial proprieties contributing to reducing the effect of environmental pollutants and biodegradation.

The present research aims to combine the hydrophobic properties of sodium polyacrylate (NaPAC16) with the safe-to use antimicrobial effectiveness and good compatibility of MgO (a low cost and environmental friendly material, with interesting antimicrobial activity even in the absence of light) and TiO₂ (antibacterial and antifungal properties), in order to develop antifungal coatings for stone materials protection.

Phase-pure MgO (periclase form) and TiO₂ (anatase form) nanopowders were obtained by sol-gel synthesis starting from magnesium nitrate and titanium alkoxides respectively followed by thermal treatment.

The oxide nanopowders were characterized by: Thermogravimetric and Differential Thermal Analysis (TG/DTA), Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), Fourier-Transform Infrared spectroscopy (FT-IR), BET specific surface area and porosity, UV-VIS Spectroscopy for band gap determination and Zeta-potential measurements. An aqueous dispersion of modified polyacrylate polymer and oxide nanopowders was deposited on different substrates (glass slides, red bricks, gypsum mortars). Coating hydrophobicity was verified by contact angle measurements. The color parameters were evaluated. Photocatalytic and antimicrobial activity of the powders and composite coatings were tested.

The results confirmed the possibility of applying thin coatings/ composite materials – with hydrophobic, antimicrobial and photocatalytic properties- by simple methods (dipping, brushing, spraying) on various supports (shape, size, composition, structure) with the possibility of controlling the thickness by multilayer deposition without altering the aesthetic properties of the substrates.

This work was supported by a grant of the Romanian Ministry of Research and Innovation, CCCDI-UEFISCDI, project number PN-III-P1-1.2-PCCDI-2017-0476/51PCCDI/2018, within PNCDI III.

A novel method for polyimide aerogels production

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Abstract: Aerogels are ultralight materials with high porosity, very low density, large surface area and low values of thermal conductivity. As a consequence of their properties, they can be used in many industrial applications. Among them, organic aerogels have attracted much attention due to their improved mechanical properties and lower cost in comparison with inorganic aerogels. However, organic aerogels present low stability at high temperatures so they could not be used in applications that require high thermal stability. Thus, the necessity of organic aerogels with high temperature resistant is increasing. In this regard, polyimide aerogels have received much attention because of their extremely high stability at high temperatures that allows them to use in fields with high benefit such as aerospace industry.

In this work, different types of polyimide aerogels (linear and crosslinked) have been synthesized by means of a simple, novel and eco-friendly freeze-drying process. Furthermore, they were characterized to analyse in detail their physical, mechanical and thermal properties. Polyimide aerogels showed many layers tangled together and they presented a porous structure with a monomodal pore size distribution. Furthermore, polyimide aerogels are hydrophobic with high values of water contact angle (Figure 1). On the other hand, linear polyimide aerogels showed lower mechanical resistance (compression) in comparison with the crosslinked ones. Otherwise, the thermogravimetric analysis demonstrated the high thermal stability of polyimide aerogels up to 550 °C.

The synthesized polyimide aerogels were evaluated as sorbent materials for oil spill, resulting in a retained oil amount of 14 times higher than its dry weight. Besides, polyimide aerogels were analysed as thermal insulation materials with enhanced sound absorption properties. Results showed very low values of thermal conductivities ($0.038\text{--}0.045 \pm 0.006 \text{ W/m}\cdot\text{K}$) and extremely good values of sound absorption coefficient (0.91). Summarizing, linear and crosslinked polyimide aerogels synthesized by means of freeze-drying process, present excellent behavior as thermal insulation material (with high moisture resistance, sound absorption properties and excellent thermal stability) and as sorbent material in oil spill.

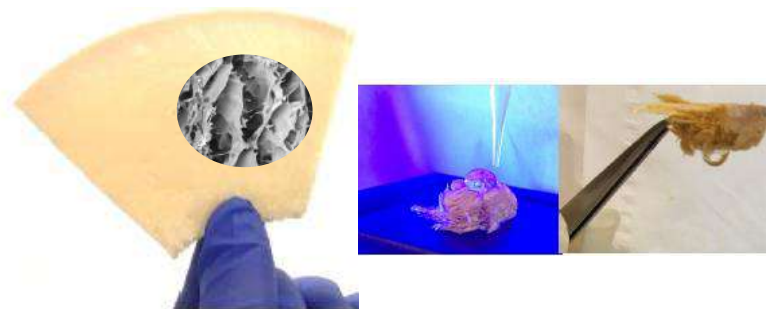


Figure 1. Polyimide aerogels.

Polymer-based aerogels doped with nanoclays

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Abstract: Organic polymer aerogels present better mechanical properties than inorganic aerogels. However, polymers are known for their relatively high flammability due to their chemical composition. Moreover, most of them are accompanied by toxic gasses during the combustion. Thus, it is interesting to improve the flame-retardant properties associated to the polymeric aerogels in order to expand the application field of this interesting materials. In this regard, nanoclays are considered a good alternative to improve the flame-retardant properties of polymeric aerogels. Nanoclays can improve barrier properties which effectively impede mass and heat transfer and promote the formation of chars. On the other hand, the combination of water-soluble polymer solution into a clay dispersion improves the mechanical properties of both polymer and clay-based aerogels.

In this work, polymer aerogels doped with different types of nanoclays were synthesized at pilot plant scale by means of an environmentally friendly and low-cost freeze-drying process. Furthermore, it was analysed the influence of the nanoclay addition on the physical, mechanical and thermal properties of the synthesized aerogels. The nanoclay incorporation into the polymeric matrix resulted in a lower porosity and compact structures with small pore size as a consequence of the agglomeration of the particles. Moreover, nanoclay addition (up to 3 wt.%) resulted in improvements in the mechanical properties of the aerogels. In addition, nanoclay incorporation into the polymeric matrix improved the thermal stability of the aerogels.

On the other hand, the flame retardancy performance of the synthesized aerogels were evaluated by means of the ignition of the samples. After the measurements, it was concluded that the nanoclay incorporation into the polymeric matrix increased the flame retardancy of the resulting aerogels. Summarizing, the synthesized polymer aerogels doped with nanoclays present good mechanical and morphological properties, as well as appropriate thermal stability. Furthermore, these aerogels are nontoxic materials with flame retardant properties.

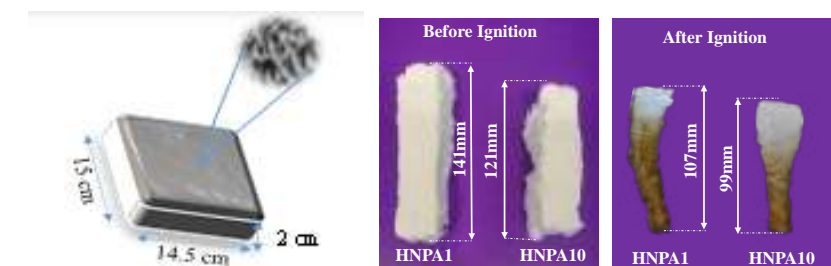


Figure 1. Polymer aerogels doped with nanoclays.

Synthesis, thermal evolution and photoluminescence of Nd³⁺-doped TiO₂ xerogels

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Abstract: Nd³⁺-doped TiO₂ compounds are bifunctional materials that, when excited, exhibit simultaneous photocatalytic activity (PCA) and near-infrared (NIR) photoluminescent emission. Nd³⁺-TiO₂ could then be potentially used in environmental remediation, smart materials, and display technologies, to name a few applications. In this study, we have prepared undoped and Nd³⁺-doped xerogels (0.5, 1, 2, 3, 5, and 10 mol%) by drying at 80°C colloidal sols prepared by a “green sol-gel route” in aqueous media

One of the objectives of this work is to investigate the effect of Nd³⁺ doping on the thermal stability of TiO₂ using a combination of both ex-situ and in-situ characterization techniques (i.e., X-ray diffractometry (XRD), X-ray thermo-diffractometry (XRTD), high-resolution electron microscopy (HREM), and Raman spectroscopy (RS)). The other is to investigate the effect of Nd³⁺ doping on the photoluminescence (PL) behaviour of TiO₂ with both anatase and rutile crystal structure, as well as their critical comparison.

Photocatalytic self-cleaning TiO₂-WO₃-rGO composite thin films

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Abstract: Surface fouling can impact materials used in the built environment, leading to their advanced deterioration. On building windows, it can prevent light transmittance which can lead to an increase in electricity consumption. On photovoltaic (PV) cells it can lead to a decrease of up to 10% in the power output due to light blocking by dust, water droplets, ice, organic pollutants, etc.. While commercial PV glazing includes self-cleaning thin films, these can suffer damage over years of being exposed to rough weather. One solution can be the (re)application of a multifunctional thin film with controlled optical properties (high transmittance, low reflectance in the visible (VIS) range), controlled wetting properties (contact angle below 10°) and high photocatalytic efficiency to degrade organic pollutants adsorbed to the surface.

The present work focuses on the deposition, characterization and testing of composite thin films based on TiO₂, WO₃ and reduced graphene oxide (rGO) as self-cleaning thin films with controlled optical properties for deposition on PV glazing. Sol-gel composite powders of TiO₂:rGO (mass ratio 100:1) were obtained in water-ethanol mixtures using titanium tetraisopropoxide, acetylacetone and sodium dodecylsulfate, which were aged for 24 h and annealed at 100°C for 1 h. Similarly, WO₃:rGO powders were obtained from WCl₆ and H₂WO₄, while maintaining all other conditions. The powders were then dispersed in water-ethanol with different anionic, cationic and polymeric stabilizers and the most stable dispersions were then sprayed on PV glazing in a layer-by-layer fashion to obtain composite thin films. The number of layers was varied between 4 and 10, as was the layer order. Alternatively, a composite sol-gel powder of TiO₂:WO₃:rGO (mass ratio 50:50:1) was dispersed and sprayed under similar conditions to obtain the one-batch composite thin film.

All films proved highly crystalline, but substantially different from a morphological point of view. The importance of the layer order on surface roughness and interface match was evidenced through scanning electron microscopy and atomic force microscopy. The WO₃:rGO layers exhibit a more rounded morphology, whereas the TiO₂:rGO layers are more coarse. When used as an upper layer, WO₃:rGO induces good superhydrophilicity (~6°) to the composite, but VIS reflectance is above 15%. The photocatalytic efficiency of methylene blue degradation under low irradiance (35 W/m²) UV+VIS radiation was above 30% for all investigated samples. It is clear that rGO plays an important role both in charge separation, as well as in extending the activation domain of TiO₂ and WO₃ to the VIS range.

The stability of the thin films was investigated through accelerated aging tests up to 120 h under the controlled variation of: irradiance (300..1000 W/m²), temperature (-20..40°C) and humidity (10..90%) in a climatic chamber. The thicker films (10 layers) proved more stable, showing the least change in optical properties and photocatalytic efficiency. However, some deterioration was observable in all cases, which suggests the need for improved adhesion of the thin film to the substrate.

This work was supported by the grant of Ministry of Research and Innovation, CNCS-UEFISCDI, project number PN-III-P1-1.1.-PD-2016-0289, within PNCDI III, Contract no. 78/2018.

Sol-Gel-derived Luminescent Di-Urethanesil Electrolytes for Electrochromic Devices

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Abstract: Smart windows are a promising technology enabling control of the sunlight transmittance (visible radiation) and solar heat (near-infrared (NIR) radiation). In this context, an attractive solution is to prepare electrochromic devices (ECDs) including conducting electrodes transparent in the visible/NIR [1] and electrolytes doped with lanthanide (Ln^{3+}) complexes able to harvest ultraviolet radiation and provide an aesthetic appearance to the window. Herein, sol-gel-derived electrolytes based on a poly(oxyethylene)/silica di-urethanesil [2,3] host matrix doped with lanthanide complexes were produced, characterized and tested in ECDs.

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Vanadium and Manganese doped ZnO thin films obtained by sol-gel method

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Abstract: Zinc oxide is a versatile n-type semiconductor material which has been intensely investigated by researchers in pure and doped form. Doping it with different metal ions influences the structural, electrical, optical, and magnetic properties, therefore making them suitable in various applications, like TCOs, sensors, microelectromechanical systems and piezoelectric devices. Both Vanadium and Manganese are promising elements in improving the electrical conductivity and the piezoelectric properties of ZnO.

This paper reports the synthesis and properties of 2% V-doped and 2% Mn doped ZnO thin films obtained by sol-gel method. The resulted films were characterized by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Spectroellipsometry and X-Ray Photoelectron Spectroscopy (XPS). The investigation revealed that the oxidation state of the dopants influences the thickness and the properties of the films.

Effect of modified Zinc Oxide Nanoparticles on mechanical properties of cement mortar using advanced design of experiment method

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Abstract: Adding zinc oxide nanoparticles is known to have a strong effect on the properties of hardened cement paste, as well as the rheology and hydration process of the fresh paste.

The main aim of this study is to constitute a blended cement mortar with high mechanical properties determined by the tetraethylorthosilicate (TEOS) functionalized zinc oxide nanoparticles obtained by sol-gel method.

The blended cement used consists of ordinary Portland cement (OPC) and functionalized Zinc Oxide Nanoparticles (TEOS/ZnO NPs). In this case the cement was partially substituted by TEOS/ZnO NPs of 0, 1, 2, 3 % by weight of cement. The blended mortar was prepared using the standard mortar mix formula. Structural and morphological studies of samples performed by X-ray diffraction, optical microscopy, scanning electron microscopy. The mechanical properties such as the compressive strength, split tensile strength and flexural strength were experimentally studied. As a result, presence of the (TEOS/ZnO NPs) had prominently higher mechanical properties compared to that of the traditional mortar.

Experimental testing will be achieved using an advanced experimental planning method that can indicate high accuracy of the nanoparticles influence added to the mortar recipe but with a very small number of tests that considerably diminish research costs.

Keywords: ZnO Nanoparticle, Cement Mortar, Blended Mortar, Mechanical Strength, advanced design of experiment method

Water-regulated synthesis of homogeneous Al₂O₃-SiO₂ monolithic aerogel composites

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Abstract: Alumina-based mixed metal oxide aerogels are well known for their thermal stability. They are typically prepared by controlled hydrolysis of metal alkyl esters, subsequent condensation, drying and heat treatment. Recent progress in the synthesis of pure alumina aerogels involved the hydrolysis of aluminum tri-sec-butoxide (ASB) using acetone and aniline thus releasing water in a defined manner [1, 2]. In that context, we investigated into the ASB route for the synthesis of mixed alumina silica aerogels alternatively to existing routes which are based on aluminum chloride (AlCl₃) and tetraethyl ortho silicate (TEOS) [3]. Within these studies it was revealed that water is still present after hydrolysis of TEOS and hampers homogeneous gel formation by a simple subsequently addition of ASB. To overcome this issue, we developed a new method featuring the addition of (non-toxic) trimethyl orthoformate (TMOF) to the silica sol for an irreversible removal of water before ASB was added. The homogeneous gel bodies were dried under supercritical CO₂ conditions. One mayor advantage of the new developed method is the avoidance of toxic reagent.

Within the presentation we will report on systematic studies of synthesis to achieve monolithic aerogel samples with varied molar ratios of Al:Si and Al:Si:solvent and the aerogel materials properties received after characterization with respect to shrinkage, density, thermal conductivity, mechanical properties, as well as microstructure by SEM and TEM. Furthermore, the effect of heat treatment (800 – 1200 °C) on the monoliths will be illustrated, too. All these properties are critical issues for the design of thermally resistant materials used for mobile and semi-stationary applications in aeronautics, space, and the transportation sector.



Figure 1: Wet gel body of homogeneous alumina silica (molar ratio 1:1).

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Preparation and properties of alumina nanoparticles modified with phenolic antioxidants

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Abstract: Alumina is one of the safest inorganic oxides and it is approved by FDA for use as an adjuvant. However, there are a number of works in which the formation of ROS was caused by aluminum compounds [1]. Therefore, in this study, we attempted to immobilize phenolic antioxidants (e. g. gallic and caffeic acids) on alumina prepared via sol-gel route (fig. 1) to prevent possible oxidative effect of NPs. After immobilization of phenolic molecules on NPs, their morphology, crystal structure, remained unchanged. Slight difference was observed in colloid-chemical properties – surface charge, apparent size and isoelectric point. Although screening of gallic acid by water molecules was predicted by DFT theory calculations [2], our modified NPs demonstrated membrane-protective and antiradical activity.

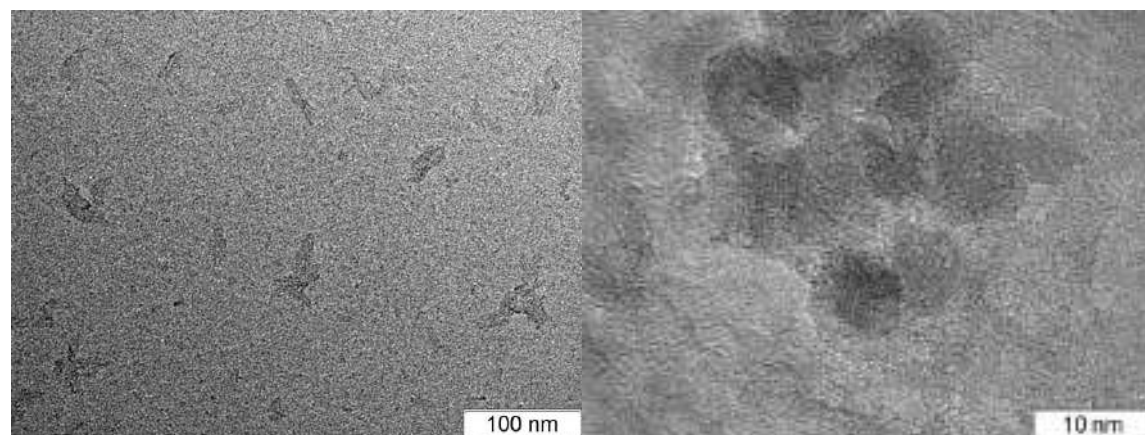


Figure 1. TEM images of alumina NPs.

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SiliOrange: Sol-gel microencapsulation of orange essential oil for sustainable pest control

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Abstract: The encapsulation of essential oils in silica-based spherical microcapsules via the sol-gel route may afford effective biopesticides for sustainable pest control.

The encapsulation in mechanically stable, porous silica particles of spherical geometry enhances the chemical and thermal stability of the entrapped essential oil, and prolongs its efficacy.¹ Silica, furthermore, is a safe and environmentally benign, biodegradable material which is of direct relevance to materials that will be employed in agriculture.²

Produced by cells within the rind of the orange fruit, and extracted as a by-product of orange juice production, orange oil is highly effective in killing or repelling several noxious insects, fungi, bacteria and even viruses. At least two broad-spectrum biopesticides based on orange oil have been lately commercialized.³ Orange oil terpenes, however, are easily oxidized and deteriorated when exposed to high temperature, oxygen, and humidity, namely, the conditions typical of open fields, making it a target for microencapsulation, and sol-gel microencapsulation in particular.⁴

The template-driven sol-gel entrapment of both d-limonene and orange oil in SiO₂ affords high loaded porous microspheres. Results were confirmed through structural and chemical characterization (TGA / DSC, SEM, BET surface area analysis, GC-MS, FT-IR). The bioactivity of the materials against different pests is currently under investigation.

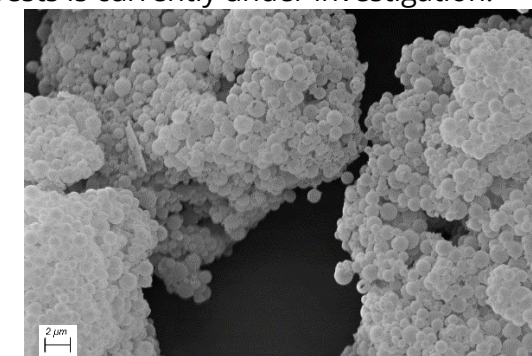


Figure 1. SEM of SiO₂ microcapsules embedding orange oil

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Nanorods synthesis and organization as building block for innovative porous materials: application to γ -alumina

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Abstract: γ -Al₂O₃ is a widely used material as industrial absorbent, catalyst or catalyst carrier. Its porous structure and its surface acidic-basic properties can be largely tuned by controlling particles morphology and aggregation. γ -Al₂O₃ is classically obtained by thermal activation of boehmite AlOOH precursor via a pseudomorphic transition: the use of AlOOH nanorods is also an exciting approach to obtain material with unique textural properties, improved diffusion properties and / or different exposed surfaces. If several examples of AlOOH nanorods synthesis are reported in literature, the precise control of their size and shape, as well as their aggregation, remain a difficult task, mandatory for the development of new porous shaped materials.

In this goal, we have developed a simple and scalable synthesis for boehmite nanorods with well-controlled size in water and without any additives (often detrimental for catalyst): the synthesis is based on chloride aluminum neutralization by NaOH, followed by hydrothermal treatment. Concerning the operating conditions, molar OH/Al hydrolysis ratio, temperature and duration of the thermal treatment appear as the key experimental parameters that induce morphology change, from platelets to nanorods. OH/Al ratio lower than 3 and temperature higher than 160°C are mandatory to ensure rods formation in fair reaction time. Effect of OH/Al ratio (from 2.3 to 3), Al concentration (from 0.0075 to 1.5 mol.L⁻¹), temperature (160 to 200°C) and duration (from 12 to 72h) have been rationalized: pure rods morphology is obtained, with diameters between 10 and 20 nm and aspect ratios (length/diameter) from 1 to 20. The specific area of the corresponding γ -Al₂O₃ (540°C calcination) stands between 100 and 250 m²/g.

To further characterize the nanorods and their formation, coupled structural (XRD) and morphological (TEM, including tilt mode) analyses have been performed: we unambiguously demonstrate that the nanorod is not formed by a single anisotropic crystallite, but results from the oriented aggregation of primary nanoplatelets with a defined growth direction. The use of electron diffraction (SAED) on both boehmite and alumina samples allows us to determine this preferential growth direction, ie the [100] boehmite crystallographic direction (Cmcm space group). The presence of (100) surface on the primary boehmite particle seems to be necessary to initiate the nanorods formation. By combining these results with surface sensitive techniques (CO probe adsorption followed by IR spectroscopy and ethanol TPD), the nature of the exposed surfaces has been revealed, leading to the whole determination of nanorod shapes.

The last step to prepare catalytic material is the development of porous shaped bodies (for instance, via kneading-extrusion processes): at the microscopic level, it requires the carefully control of the nanorods aggregation, especially to limit the bundles formation. Different strategies have been evaluated in this goal (powder drying, peptisation via mineral acids and bases, mechanical stress...) and insights about the nanorods organization were obtained by SAXS and TEM analyses. The obtained extrudates have been compared in term of textural properties to those obtained from nanoplatelets using similar protocol. Furthermore, improved molecular transport properties of these nanorods-based extrudates (evaluated by pulsed field gradient NMR) were demonstrated.

Fabrication and characterization of Zr-induced P (AM/NVP/AMPS) mesoporous networks hydrogel nanoparticles and the temperature resistance mechanism

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Abstract: Polymer hydrogel particles with size varying from 100 to 170 nm were prepared through inverse emulsion copolymerization of acrylamide (AM), N-vinylpyrrolidone (NVP), 2-Acrylamide-2-Methylpropanesulfonic acid (AMPS) with N, N-methylene bis acrylamide (MBA), zirconium acetate (ZA) in water with ammonium persulfate as the initiator. The crosslinked particles were fully characterized with several means including SEM, TEM, DLS, BET, FT-IR, ¹³CNMR, elemental analysis and long term thermal stability. The SEM, TEM, DLS, BET experimental results indicate that the polymer hydrogel particles exhibits regular spherical shape and smooth surface, has mesopores ranging from 4.9–7.1 nm with a typical diameter centered (BJH pore size distribution) at ~5.7 nm. FT-IR, ¹³CNMR, elemental analysis experimental results indicate that the monodisperse mesoporous networks hydrogel nanoparticles were crosslinked by AM, AMPS, NVP and Zr. This crosslinked Zr-AM/NVP/AMPS nanoparticles exhibit super- and high-temperature thermal stability, swelling capability and has wide application prospects in many fields, such as high temperature reservoirs and molecular sieve template. The temperature resistance mechanism of the crosslinked Zr-AM/NVP/AMPS nanoparticles was also given.

Reversibly Compressible Carbon Spherogels

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Abstract: Carbon aerogels are open porous solids with surface areas up to 2500 m²/g. Offering also electrical conductivity, these materials are also highly promising for applications such as energy storage (electrodes for supercapacitors), capacitive desalination, catalysis, adsorption, or filtration. We have developed a facile templating strategy to tailor the morphology and pore structure of carbon aerogels.¹ By applying an adequate amount of polystyrene spheres to a resorcinol-formaldehyde sol, subsequent gelation, supercritical drying and carbonization, monolithic carbon aerogels are designed with a substructure only consisting of hollow spheres, which we call spherogels (Fig. 1).² We show the versatility of this approach to a) adjust the hollow core diameter, b) obtain a controlled pore wall thickness with microporosity, and c) control the chemical and structural homogeneity. All materials were characterized by electron microscopy (SEM, TEM), small angle X-ray scattering (SAXS), and nitrogen gas sorption. The mechanical and electrochemical properties are discussed with respect to their structural characteristics and compared to reference carbon aerogel materials.

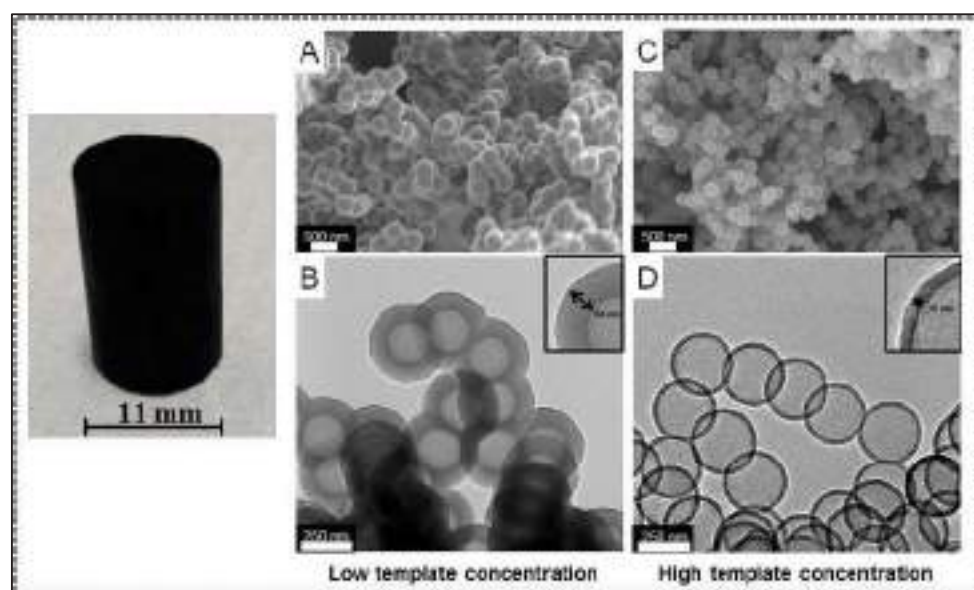


Figure 1. Photograph of a monolithic, reversibly compressible carbon aerogel (left) and SEM (A, C) as well as TEM images (B, D) for two cases (low vs. high template concentration) indicating the adjustable microstructure.

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Sol-gel surface coating of cathode materials for lithium ion batteries

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Abstract: Lithium ion batteries play an important role in the field of electromobility and stationary energy storage. Unfortunately, their improvable energy density, efficiency and lifetime still limit their comprehensive application. Major issues with respect to cathode degradation involve metal ion dissolution due to hydrofluoric acid etching, cation disorder or unwanted phase transitions. The sol-gel method is a useful and widely used strategy to apply functional cathode coatings which prevent the direct contact with the HF-containing electrolyte [1,2]. These protective coatings not only prevent unwanted side reactions but also reduce heat generation during cycling resulting in an improved electrochemical performance.

An initial evaluation of chemical and electrochemical influence of sol-gel coatings (e.g. ZrO₂, ZnO) on planar model electrodes produced by radiofrequency magnetron sputtering (e.g. LiCoO₂) is conducted. Besides electric and ionic conductivities, surface morphologies and chemical compositions of the respective coatings are investigated. Based on the findings regarding wetting behavior of the sol-gel film and the intrinsic mechanism between the different thin film layers, the coating process is further optimized: Surface pretreatment, sol precursor selection, dip- and spin coating process parameters as well as heat treatment parameters are equally taken into account. In consideration of economic aspects, the previously identified coatings are transferred to commercial cathode materials in powder form. For this purpose, a variety of different precursors, solvents and dispersion agents are evaluated and optimized aiming for a uniform coating with a layer thickness in the nanometer range.

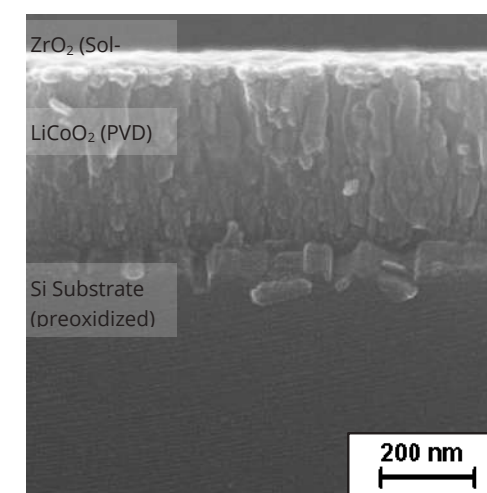


Figure 5. SEM image of a ZrO₂-coated LiCoO₂ thin film cathode.

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Sol-gel Fe–Alumina Films for Optical, Catalytic and Adsorption Applications

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Abstract: The problem of creating nanostructured materials with specific properties and functions is undoubtedly relevant. This interest in nanoscale structures is not only due to them manifesting fundamentally new and unique properties when compared with bulk materials, but also the possibility of creating entirely new devices and systems with a wide range of functionalities. They also have promising impact on next-generation technologies, communication, etc.

In recent years, the scientific community has become interested in studying various types of nanoparticles embedded in a polymer or oxide matrix. When the size of the embedded particles is reduced to the nanoscale, a significant number of new dimensional effects are manifested when compared to systems in bulk form. Materials containing monodisperse magnetic nanoparticles uniformly distributed in the matrix are promising as high-density data storage systems. Composite nanomaterials with embedded nanoparticles often have a large surface area, which is promising when used in catalysis and adsorption.

Films and coatings are of special scientific and practical interest. Unlike powders, they can be directly used in a wider range of technological applications. Inorganic films and coatings have been intensively studied during the last century, with special attention being paid to thin films which are two-dimensional (2D) nanostructures. At the same time, when films are used as filter layers of membranes, catalyst carriers, anticorrosive and abrasion-resistant coatings, the layer thickness should be in the micron range. The development of new films and coatings with characteristics inherent to a particular field of application, as well as the development of simple, inexpensive and easily scalable methods of their preparation are topical tasks. The sol-gel approach is also often used to produce oxide films. The simplicity, inexpensiveness, and ability to control the final product properties are the advantages of this method.

In our work, composite self-supporting Al_2O_3 -Fe films with different component ratios and multilayer Fe-alumina films were obtained using sol-gel and selective reduction approaches. A comprehensive study of the composition, microstructure, as well as the textural, optical, catalytic and adsorption characteristics was carried out. In general, the resulting films are excellent as adsorbents and optical sensors for Cr(VI). They are likely to have other optical applications and be used in water purification due to their low and slightly varying roughness, variable spectral characteristics, high adsorption activity to highly toxic Cr(VI) anionic forms, easy regeneration and magnetic separation, and reusability. This device can also be useful for estimating the Cr(VI) concentration in water or its proximity to maximum acceptable concentration. In the water treatment, the films can be used both in the original film form and in the form of a layer deposited on the surface of the ceramic membrane.

The reported study was supported by a Grant of the Russian Science Foundation (project No. 17-73-10272). Investigations were partially carried out using the equipment of the "Khimiya" Common Use Centre (Institute of Chemistry, Federal Research Centre "Komi Science Centre of the Ural Branch of the Russian Academy of Sciences").

Preparation of small multifunctional silica nanoparticles for the generation of vaccine formulations

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Abstract: Silica particles, among other nanomaterials, are specifically interesting for biomedical applications due to their biocompatibility^[1], deliberate adjustment of particle size^[2] and versatile surface functionalization^[3]. In this work highly monodisperse, multifunctional silica nanoparticles have been prepared with sizes ranging from 20-40 nm.

The particles were prepared based on the L-lysine controlled co-condensation of tetraethylorthosilicate with an azido-functionalized silane in a biphasic water/octane system. Temperature increase of the reaction mixture resulted in an increased particle size of high reproducibility. The second functional group, a carboxy-modified silane^[5], was post-synthetically grafted onto the particle surface. Those surface functionalities are used for binding an antigen and respective polysaccharides. Alkyne functionalized polysaccharides are conjugated to the azido groups on the particle surface via Cu(I) catalyzed alkyne-azide "click" reaction, while antigens are bound by their lysine residues to the carbodiimide activated COOH group. It is hypothesized that this novel carrier allows to deliver an increased concentration of antigen to its target cell, while additional polysaccharides are meant to enhance the uptake of particles via cell specific receptors.

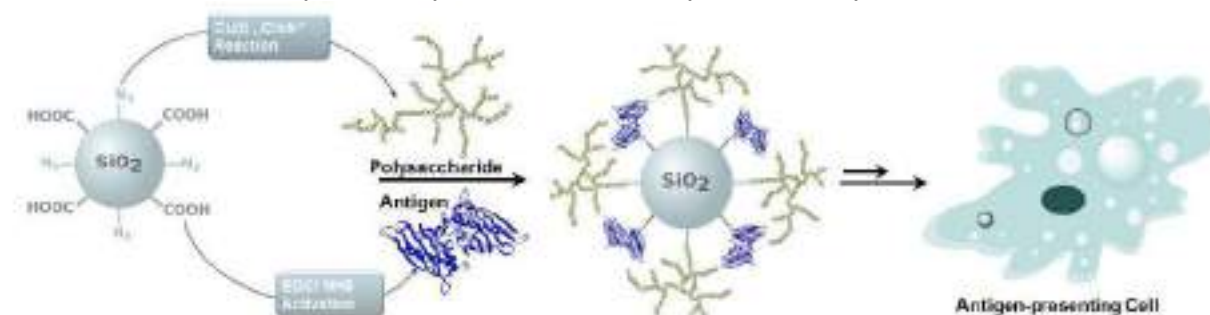


Figure 1. Illustration of the overall concept of the silica particle based vaccination platform.

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Hybrid Carbon Spherogels

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Abstract: Carbon aerogels are promising materials for state-of-the-art energy storage applications, such as supercapacitors, due to their excellent electrical conductivity in combination with high specific surface areas and their mechanical properties can be enhanced by polystyrene latex templating.^{1,2} We have recently published a facile synthesis route towards reversibly compressible monolithic carbon aerogels comprising a microstructure which is built-up of homogeneously sized hollow spheres, perfectly described as spherogels.³

In this study we extend the resorcinol-formaldehyde based sol-gel approach combined with templating with polystyrene nanospheres to hybrid carbon aerogels. We present for the first time a one-pot method to prepare hollow spherical carbon aerogel microstructures in which the individual shell consists of separate carbon and titanium dioxide layers (Figure 1). We process a condensable mixture of aqueous resorcinol/formaldehyde with a titanium acetylacetonate complex in the presence of a thermoplastic sphere template to obtain a titania coated polystyrene latex sphere surface. Only in a latter stage of the reaction, the titania surface reacts with the condensing resorcinol-formaldehyde to give a 3D nanocomposite network of polystyrene latex, titania, and resol. After carbonization of this composite, we prepare hollow spherical carbon aerogel microstructures in which the individual shell contains a layer of titanium dioxide (Figure 1). The versatility of our sphere templating method together with the introduction of inorganic components is demonstrated by scanning and transmission electron microscopy, thermogravimetric and electrocatalytic investigations.

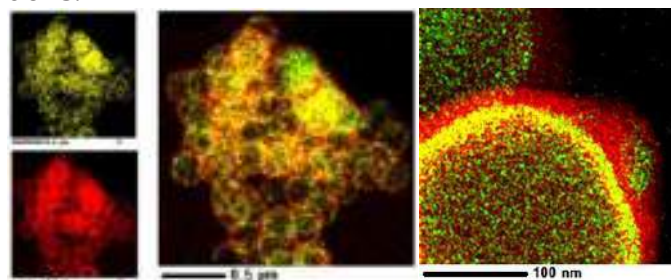


Figure 1. STEM EDX maps of a hollow sphere carbon (red) and titanium dioxide (green; oxygen omitted; yellow: carbon and titanium dioxide overlap) aerogel network.

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Preparation of quadruple-chain polysiloxane by intramolecular polycondensation of dialkoxysilane side chains in ladder-like polysilsesquioxane

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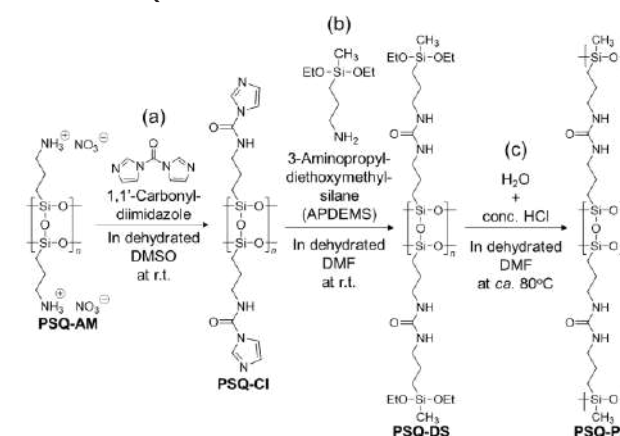
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Abstract: The double-chain polymers are expected to have different properties compared with the single-chain polymers, because the conformational freedom of the double-chain polymers is limited. As a method of representative preparation of the double-chain polymers, it is known that polymerizable groups are introduced into the side-chains in base polymers, and intramolecular polymerization of these polymerizable groups were performed.¹ Meanwhile, we have reported that soluble ionic ladder-like polysilsesquioxanes (PSQs), which have double-main-chain composed of Si-O-Si bond, can be prepared by the hydrolytic polycondensation of the organotrialkoxysilanes.²

In this study, the quadruple-chain polysiloxane (PSQ-PS) was prepared by combining the above two preparation methods for double-chain polymers, i.e., by intramolecular polycondensation of dialkoxysilanes as a polymerizable group introduced into side-chains in ladder-like PSQ (Scheme 1).

First, as a precursor for introducing dialkoxysilanes, ladder-like PSQ containing carbonylimidazole groups (PSQ-CI) was prepared by the reaction of ammonium-functionalized ladder-like PSQ (PSQ-AM) with 1,1'-carbonyldiimidazole (Scheme 1a). Then, 3-aminopropyldiethoxymethylsilane (APDEMS) as a dialkoxysilane was introduced into the side-chains in PSQ-CI to obtain PSQ containing dialkoxysilane (PSQ-DS) (Scheme 1b). Finally, intramolecular polycondensation of APDEMS component in PSQ-DS was performed in dilute dehydrated DMF solution under acidic conditions to obtain PSQ-PS (Scheme 1c).

PSQ-PS was soluble in DMSO, DMF, and methanol. From the results of GPC, the weight average molecular weight of PSQ-PS was estimated to be ca. 10,000. In IR and ¹H NMR spectra, it was found that APDEMS component was introduced into the PSQ sidechains via urea bonds. Furthermore, ²⁹Si NMR spectrum indicated broad peaks in the T³ region for the PSQ chains and the D Scheme 1. Preparation of (a) PSQ-CI, (b) PSQ-DS, and (c) PSQ-PS. with an integrated ratio of ca. 1:1. These results suggested that the APDEMS component was introduced into almost all PSQ units. In addition, the integrated ratio of (D²+D¹)/(D²+D¹+D⁰) was ca. 0.89. This indicates that 89% of the APDEMS component was intramolecularly polycondensed. Based on the above results, we consider that the quadruple-chain polysiloxane was successfully prepared by intramolecular polycondensation of APDEMS component introduced into the PSQ side-chains.



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Formation of ZrTiO₄ film by anodic oxidation of titanium under spark discharge

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Abstract: Recently, BaTiO₃ thick film was successfully prepared by anodic oxidation of titanium in Ba(OH)₂-containing bath under electric spark discharge. Other perovskites such as ZrTiO₄, (Ca, Sr)TiO₃ and ilmenites (LiMO₃ (M = Nb, Ta)) films were also prepared by this method with pulse current density. However, precise formation mechanism for preparing multicomponent metal oxide films in metal hydroxide particles bath is not clear. Therefore, the formation process was mainly investigated by XRD analysis with various shallow diffraction angles. Titanium plate (30^W×20^L×0.5^T(mm)) was anodized in NaOH-Na₃PO₄ bath with Zr(OH)₄ (or ZrO₂) fine particles under the rectangular wave of current density (5-30 A/dm²). ZrTiO₄ thick film was obtained over 10 A/dm² of the current density, whereas titanium dioxide thin film was formed at 5 A/dm² because the spark discharge didn't occur under this condition (Fig. 1). Figure 2 shows the depth profiles of Zr, Ti and O for the film prepared at 100 Hz of rectangular wave (30 A/dm²) for 60 minutes of anodizing time. As zirconium exists at the whole area regardless of the depth less than 1.5 micron thick, ZrTiO₄ was formed inside the film. Figure 3 shows the proportion of various crystals for the anodizing film prepared for 60 minutes as a function of thickness. ZrO₂ particles react with anatase to form ZrTiO₄ at the film surface.

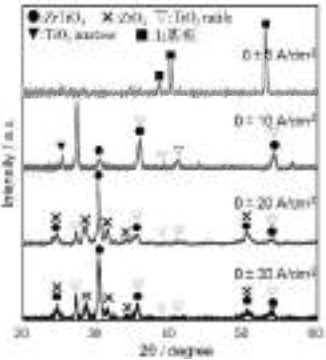


Figure 1. XRD patterns of the anodizing film at various current densities. (100Hz, 60 min, Zr(OH)₄)

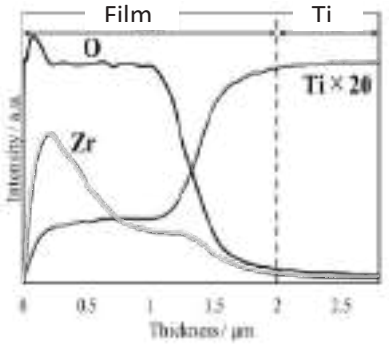


Figure 2. Depth profiles of Zr, Ti and O for the film. (30 A/dm², 100 Hz, 60 min, Zr(OH)₄)

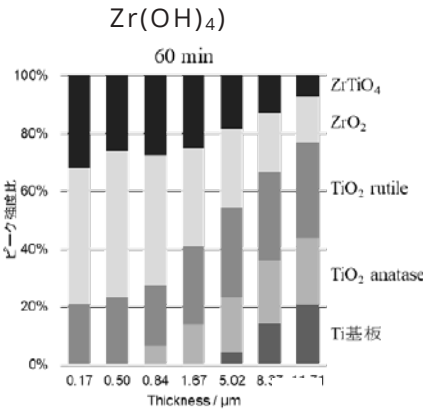


Figure 3. The proportion of various crystals

In situ Preparation of Epoxy-SiO₂ Nanocomposites as High Voltage Insulation

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Abstract: Epoxy-based nanocomposites, containing inorganic oxide nanoparticles as the dispersed filler, can exhibit novel properties such as reduced complex permittivity and higher dielectric breakdown strength that make them attractive nanodielectrics for high voltage power applications [1]. A homogeneous dispersion of non-agglomerated nanoparticles is crucial to optimize the dielectric properties [2].

In this work, an *in situ* sol-gel based method was used to synthesize SiO₂ nanoparticles (surface functionalized with coupling agents) directly in the epoxy monomer (DGEBA), followed by polymerization. This approach to the production of nanocomposites is an attractive alternative to conventional *ex situ* methods where the dispersion of the nanoparticles in the epoxy is challenging [3].

The formation of the surface functionalized SiO₂ in the epoxy was confirmed by FTIR and Raman (Figure 1(a)) spectroscopy. SAXS measurements, combined with TEM images (Figure 1(b)), confirmed the formation of fractal-like SiO₂ domains (10-50 nm) that are homogeneously distributed in the polymer. The thermal stability and the glass transition temperature was observed to increase for the nanocomposites with increasing SiO₂ content (above 2 wt%) compared to pure epoxy. The complex permittivity of the nanocomposites was comparable to that of pure epoxy, showing only slight changes in the dielectric constant and the dielectric loss depending on SiO₂ content (for 0.1 Hz – 1 MHz). The *in situ* approach thus proves to be a promising alternative for the fabrication of nanocomposites with good dispersion quality and improved thermal and similar dielectric properties.

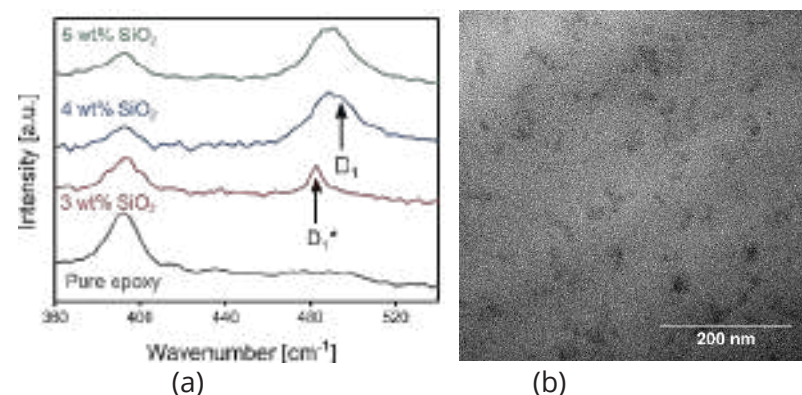


Figure 1. (a) Raman spectra showing the breathing modes (D₁ and D₁*) of surface-functionalized SiO₂ in the nanocomposites with varying SiO₂ content (b) TEM image of the nanocomposite with 5 wt% of SiO₂.

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Ir/SBA-type catalysts active in the hydrogenation reaction - synthesis, characterization and catalytic application

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Abstract: Recently catalytic hydrogenation of aromatic compounds has attracted great attention. This class of reactions is very important due to environmental issues as well as industrial applications. Noble metals (particularly platinum) based catalysts are often used in hydrogenation reactions. However due to the fact that platinum is sensitive to poisoning with impurities, especially sulphur compounds, other metallic active phases are investigated. An interesting alternative could be iridium, other platinum group metal, which is distinguished by high corrosion resistance. The catalytic activity in hydrogenation reaction depends on both active phase and support of the catalyst.

Ordered mesoporous materials, particularly SBA-type, seem to be promising supports because of their unique properties like high surface area, uniform pore system and higher thermal/hydrothermal stability in comparison to MCM materials. The presented work compares the activity of iridium particles as the active metal species supported on the ordered mesoporous silica (SBA-3, SBA-15) and commercial (Al_2O_3 , SiO_2) supports in hydrogenation reaction.

The SBA-3 and SBA-15 supports were prepared by hydrothermal synthesis performed under acidic conditions according to the procedures described elsewhere [1]. The catalysts with Ir loading of 1 wt % were prepared by the conventional impregnation method using H_2IrCl_6 as a metal precursor. The catalysts were characterized by XRD, BET, TPR- H_2 , hydrogen chemisorption, XPS and TEM techniques. The obtained supports and catalysts show high surface areas and ordered mesopore systems. After H_2 reduction the iridium catalysts contain small iridium nanoparticles <1.5nm. Generally, in hydrogenation reaction the catalyst supported on SBA-3 indicates higher activity than catalyst supported on SBA-15. Higher activity of Ir/SBA-3 catalyst arises from its higher surface area when compared to Ir/SBA-15 or Ir/ SiO_2 samples.

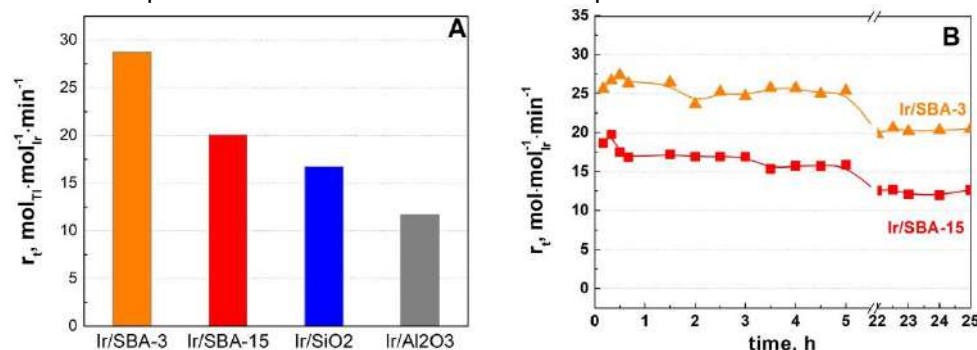


Figure 1. The effect of support (A) and reaction time (B) on the apparent rate of toluene hydrogenation at 150°C

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Preparation and characterization of Fe-exchanged anatase-type titania for nitrous oxide decomposition

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Abstract: This study has been devoted to the preparation of Fe-exchanged anatase-type TiO_2 samples using a sublimation technique. The chemical nature and surface molecular structure of the Fe species have been extensively characterized by using XRD, XPS, Raman, DRIFTS, and N_2O adsorption measurements. To see if those materials as a support of V_2O_5 and WO_3 can play a role in depressing N_2O production levels in the selective reduction of NO by NH_3 , their significance in N_2O decomposition has been tested.

Prior to preparing samples of Fe-exchanged TiO_2 under different conditions, an appropriate amount of TiO_2 (ca. 50 g) was dried at 110°C overnight and then hydroxylated in an aqueous solution of NH_4OH . The resulting titania was washed repeatedly in water before drying at 110°C. A solid-state ion exchange technique was employed to obtain Fe-exchanged TiO_2 . For this, the hydroxylated TiO_2 was well mixed with a desired amount of $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ using a laboratory-designed small bottle mixer. After this, the mixture was loaded into a quartz reactor combined with an electrical furnace, heated to 200°C in flowing a high-purity N_2 with a flow rate of 200 cm^3/min and kept for 3 h at the temperature. The Fe- TiO_2 was stored in a desiccator for later use. Other Fe- TiO_2 samples, that had been sublimed up to 550°C, were prepared according to similar protocols. A part of the coresponding samples was calcined at 500°C for 1 h in a flowing mixture of 5% $\text{O}_2/95\%$ N_2 . The Fe- TiO_2 prepared here was denoted to (n)FETnC, where (n) is the Fe content in %, n is the first digit of the sublimation temperature and C presents the calcination. Different amounts of V_2O_5 were loaded onto the Fe-doped samples using a wet impregnation technique. N_2O decomposition over the (n)FETnC catalysts was conducted using a Thermo Nicolet 6700 IR spectrophotometer equipped with a gas cell.

All Fe-doped samples give original diffraction signals due to TiO_2 , indicating no significant chemical reaction between the titania and the iron. Although 2.73% Fe- TiO_2 gives, in a comparison with XRD pattern of the TiO_2 , new peaks, all these are not indicative of hematite ($-\text{Fe}_2\text{O}_3$) and magnetite (Fe_3O_4). In contrast, 1.36% Fe- TiO_2 shows only peaks corresponding to the TiO_2 . XPS measurements disclose that all Fe- TiO_2 samples have Fe^{2+} and Fe^{3+} species, regardless of the iron content. Raman spectra of Fe-exchanged TiO_2 samples are very complicated and depend strongly on the preparation technique. Even Fe-exchanged titania-supported $\text{V}_2\text{O}_5\text{-WO}_3$ catalysts have phonon signals of TiO_2 , regardless of the synthesis protocol. This indicates that the Fe ions could create no significant change in the support molecular structure. Calcination at temperatures > 300°C showed peaks at 2980 – 2870 cm^{-1} due to FeOOH . Peaks at 1590 – 1680 cm^{-1} and 1450 – 1280 cm^{-1} are assigned to Fe(O)_x species that are strongly bound to the surface of TiO_2 .

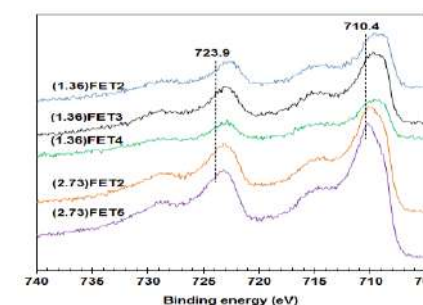


Figure 1. Fe 2p XPS spectra for Fe- TiO_2 samples with different sublimation conditions.

Properties of microporous TiO₂ and SiO₂-TiO₂ spheres, prepared via the peroxo route.

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Abstract: Materials on the basis of TiO₂ and SiO₂-TiO₂ are widely investigated as: photocatalysts, adsorbents, acid catalysts, membranes for gases separation because of their non-toxicity, low cost, high chemical stability. High surface area and finely tuned pore sizes allow them to act with higher performance and selectivity. Spherical morphology is important for the flow processes, it gives stable and laminar flow of tides. Mixed oxide SiO₂-TiO₂ has some helpful features in comparison to individual oxides SiO₂ and TiO₂ – namely it has higher stability of structure in conditions of high temperature and humidity and also it has Lewis acid centers, which are useful in acid catalysis. Despite of such an interest the ways of materials' preparation are full of limitations. Toxic, unstable and expensive titanium alkoxides are used as precursors for preparation of particles with spherical morphology. High surface area and finely tuned pore sizes are the results of template synthesis, while templates are mandatory to exclude from the structure of material by the means of calcination or extraction - this process consumes a lot of additional energy and solvents.

In this work we suggest the preparation way for microspheres with high surface area and finely tuned pore sizes without Ti alkoxides and templates. Instead of Ti alkoxides aqueous peroxotitanate solution was used as TiO₂ precursor. Temperature of post-synthetic treatment allows to control the phase composition of materials while the solvent used controls the size of microspheres [1]. Obtained materials were used as adsorbents of Pb²⁺ ions from the aqueous solutions, they demonstrate adsorption capacities up to 300 mg/g. Such values are higher than those of polymer adsorbents, mineral adsorbents presented in literature. Furthermore, our materials demonstrate more than 60 % of initial adsorption capacity during 5 cycles of regeneration by the means of EDTA [2].

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Preparation of organic-inorganic hybrid emissive thin films by sol-gel reaction using photo-curing binary crosslinking

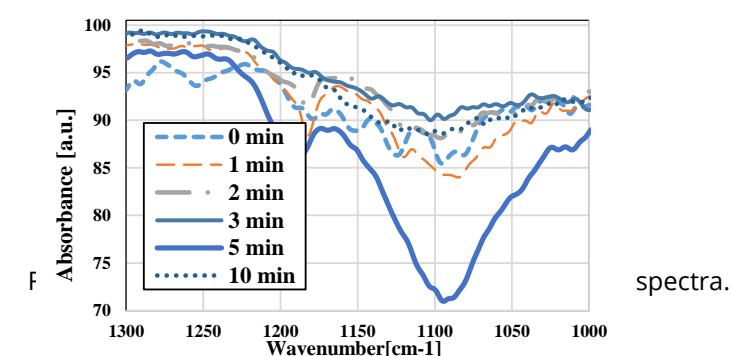
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Abstract: Recently, we have prepared organic-inorganic hybrid emissive thin films by sol-gel reaction [1] and applied them to organic light-emitting diodes (OLEDs) as active layers [2, 3]. However, when using perhydropolysilazane (PHPS) as the reaction accelerator, more than three hours are needed to complete the sol-gel reaction. In this study, to fabricate organic-inorganic hybrid emissive thin films in a short sol-gel reaction time, we formulated a solution of a silane-coupling agent having a vinyl group plus a light acid-generating agent and a photo-radical generating agent and then irradiated these with ultraviolet (UV) light to accelerate the sol-gel reaction.

We used bis(t-butylsulfonyl) diazomethane as a light acid-generating agent and vinyltrimethoxysilane (VTMS) as a reactive group. In addition, we used a photo-radical-generating agent, 2-hydroxy-2-methylpropiophenone as a reactive vinyl group. Moreover, poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) was used as an emissive polymer. Next, these agents were dissolved in toluene. Their thin films were prepared using a spin-coating method and by irradiation with UV light in air or water. By observation of the FT-IR spectra, we confirmed that the VTMS decreased while hydrolysis reaction was generated due to UV irradiation. In addition, we confirmed a decrease in C=O couplings of the photo-radical-generating agent and a decrease in vinyl groups of the silane-coupling agent, indicating that the vinyl groups were decomposed by the generation of radicals and that radical polymerization was accelerated. These results demonstrate that the alkoxyl groups of VTMS were hydrolyzed and that VTMS's vinyl groups and MDMO-PPV's vinyl groups were radically polymerized at the same time. Moreover, when the sol-gel reaction proceeded for 5 minutes, a wide absorption signal band at around 1100 cm⁻¹ was found, originating from the generation of siloxane bands (Si-O) (Fig. 1). This clearly indicates that the sol-gel reaction was completed in only 5 minutes.



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Hierarchically ordered porous materials using hydroxide-based organic-inorganic hybrid crystals

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Abstract: Transition metal hydroxides, having a crystal structure of inorganic hydroxide layers and organic molecules in interlayer spaces, are known as potential candidate catalysts for efficient oxygen evolution reaction, which is significantly important to realize using renewable energy. To fully exploit catalytic property of hydroxides, it is essential to introduce nm- and μ m-scaled pores with well-controlled size, shape, and volume. However, in general, transition metal hydroxide crystals grow and aggregate rapidly, which makes difficult to design porous structures. Recently, we reported synthesis of tiny hydroxide crystalline colloids (< 5 nm) by controlling the alkalization process and inducing high supersaturation condition.¹ Subsequent assembly of colloidal crystals and templates allows formation of ordered meso-structures.² It was found that incorporation of carboxylic acids was essential to synthesize tiny nanocrystals due to their multi role during crystallization. In this study, the hydroxide-based nanocrystals were prepared using different types of carboxylic acids. Synthesized colloidal crystals were assembled with hard and soft templates to form hierarchically ordered structures.

Nickel chloride hexahydrate, mono-carboxylic acids, and ethanol were used as metal source, crystallization control agents, and solvent, respectively. Addition of propylene oxide triggered pH increase and nucleation and crystal growth. The crystallite size strongly depended on the molecule structure of carboxylic acids; carboxylic acid with hydrophilic groups retarded crystallization and with hydrophobic groups improved crystallization. Obtained colloidal nanocrystals formed ordered meso-structures with block-copolymer mesotemplates through evaporation-induced selfassembly. By using ordered photonic crystals of polystyrene spheres as macro-templates, wellordered hierarchically porous structures were obtained (Figure 1). It was found that carboxylic acid determined the thermal stability of hydroxide crystals and subsequent mesoporous structures. In summary, carboxylic acids were essential not only to control crystal growth but also to control thermal robustness of porous structures.

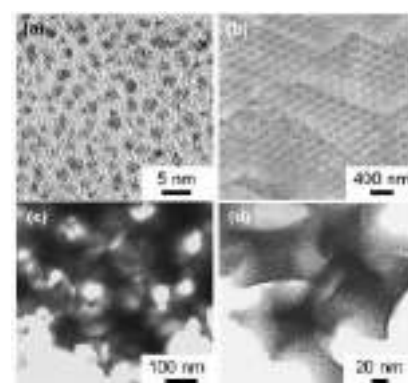


Figure 1. (a) TEM image of hydroxide nanocrystals. SEM and STEM images of synthesized hierarchically porous materials; (b)(c) macro- and (d) meso-porous structures.

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Tunable-sized perovskite BaMO₃ (M= Ti, Zr and Hf) nanoparticles stable on YBa₂Cu₃O₇ superconducting nanocomposites

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Abstract: Nowadays, one of the most promising strategies in the enhancement of superconducting properties of High Temperature Superconductors (HTSC) is the use of preformed nanoparticles in the Chemical Solution Deposition approach to YBCO superconducting layers. In particular, all general methods to obtain metal oxide nanoparticles fail in the synthesis of BaZrO₃ and BaHfO₃ (e.g. controlled size and shape). Herein, a tunable-size synthesis of well-defined BaMO₃ (M= Ti, Zr, and Hf) perovskite nanoparticles has been reported using a modified polyol route. With our approximation, purely crystalline nanoparticles with cubic shaped were obtained. Exhaustive experiments reveal feasibility of a fast synthesis by using solvothermal route (minutes rather than hours) without the need to use microwave activation, and without significant changes on crystal parameters or size. We are able to tune the size of BaMO₃ nanoparticles, from 4 to 40 nm, accomplishing the suitable and specific conditions for their further applications. In addition, the long-time stability (months) of the colloidal solution in alcohol media has been stated in a deep range of sizes and concentrations. This synthetic approximation is prone to be applied in a deep range of metal oxide nanoparticles, specifically in those perovskites that are not allowed with conventional approaches. Concerning their applicability, Chemical Solution Deposition is one of the most promising strategies in YBa₂Cu₃O₇ superconducting nanocomposites fabrication. This strategy allows the suitable match between stable oxide nanoparticles and YBa₂Cu₃O₇ precursors in high ionic strength solution media. Hence, Chemical Solution Deposition of colloidal solutions is highlighted as an encouraging alternative being a low-cost route with enhancement of final superconducting properties with our as-synthesized nanoscaled system.

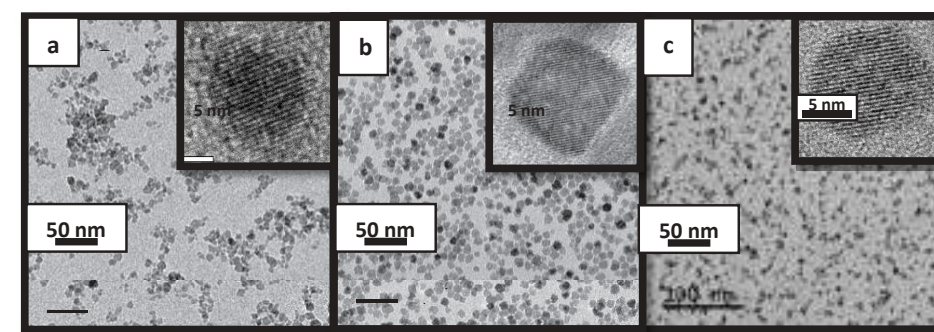


Figure 1. TEM image of BTO (a), BZO(b) and BHO(c) by using solvothermal reaction "Severo Ochoa" Programme for Centres of Excellence in R&D (SEV-2015-0496), CONSOLIDER Excellence Network (MAT2015-68994-REDC), COACHSUPENERGY project (MAT2014-51778-C2-1-R, cofinanced by the European Regional Development Fund) and SUPERINKS project (RTC-2015-3640-3, cofinanced by the European Regional Development Fund). Acknowledges Departament de Química from UAB for the financial support of PIF scholarship.

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Fluoride nanocrystals MF₃ (M = La, Y) in sol-gel materials

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Abstract: Over the last several years, there has been observed a dynamic development of researches in a field on synthesis and characterization of fluoride nanocrystals dedicated for diverse range of optoelectronic applications. Hence, the development of transparent oxyfluoride glass-ceramics (GCs) is a forefront direction in current materials engineering [1]. The GCs combine the advantages of individual fluoride nanocrystals related with their low phonon energies and large solubility of rare earth dopants (RE³⁺) with good mechanical strength and thermal durability of oxide hosts. Moreover, the successful incorporation of RE³⁺ ions into fluoride crystal lattice results in high luminescence efficiency. Therefore, from the optical point of view, RE³⁺-doped nanocrystalline materials have been recognized to hold tremendous promises as luminescent materials in a variety of applications, such as novel light sources or luminescent tracers in forensic and bioimaging [2].

Generally, glass-ceramic materials are fabricated via controlled annealing process of glasses derived by conventional melt-quenching method or xerogels obtained using sol-gel technique. Due to the fact, that heat-treatment of xerogels could be conducted at significantly lower temperatures compared with melting of glass-forming components, the sol-gel method seems to be particularly attractive technique to fabricate the oxyfluoride glass-ceramic materials [3].

In this work, the glass-ceramic materials containing MF₃:Eu³⁺ (M = La, Y) nanocrystals were obtained by controlled heat-treatment of precursor xerogels synthesized using sol-gel method. The nucleation of LaF₃ and YF₃ nanocrystals was induced from thermal decomposition of M(CF₃COO)₃ (M = La, Y) inside the silicate gels. Based on Scherrer equation the average crystal sizes of LaF₃ and YF₃ were estimated to 8.1 nm and 15.4 nm, respectively. The optical behavior of sol-gel samples were evaluated based on photoluminescence excitation and emission spectra as well as luminescence decay analysis. Registered luminescence lines are attributed to the typical ⁵D₀ → ⁷F_J (J = 0-4) emissions within reddish-orange spectral scope. The Stark splitting of luminescence bands, double-exponential character of decay curves and long-lived emission for fabricated glass-ceramic samples clearly evidenced the partial substitution of La³⁺ and Y³⁺ by optically active Eu³⁺ ions in fluoride nanocrystals.

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The role of polymeric templates in the stabilization of inorganic oxide particles

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Abstract: Removable templates - supramolecular structures (surfactants, polymers) are often used alongside with sol-gel synthesis for design and preparation of highly structured, hierarchical or porous materials. Their primary role is a structure molding at the micro- and nano-levels. However, we have shown that there are also additional effects, such as inadvertent doping in case of sol-gel synthesis of titanium dioxide materials by template method or stabilization of small particles in case of impregnation of iron (III) oleate within polymeric matrix.

Monodisperse polymeric beads with diameters in the range of 0.2-4 μm were prepared using dispersion and emulsion polymerization techniques. The variation of particles' size was realized by fine tuning of the reaction mixture composition while the porosity was changed by varying the amount of cross-linking agent.

In these work it was shown that impregnation of polystyrene beads with iron (III) oleate with subsequent calcination at 500°C leads to stabilization of smaller iron oxide particles (~20 nm) than they are produced without the presence of polymeric material (~1 μm). The stabilization effect increases with the increase of PS beads swelling. The differential thermal analysis and thermal gravimetric analysis suggest that a smaller size of the iron oxide particles produced by calcination within the polymeric particles could be related to, firstly, the longer temperature stability of the polymer decomposition products, which does not allow the iron oxide particles to form larger crystals and, secondly, to the decrease of the total heat release during calcination due to the melting of polymer.

A set of TiO₂ photocatalysts with a macropore network has been prepared by combining sol-gel synthesis and "hard" template method using PS and PMMA microspheres with different functional groups on the surface originated from three types of initiators. The influence of template removal conditions was found to be crucial because the nature of template themselves effects the phase composition and electronic structure of titanium dioxide. Moreover, the elements constituting the polymer particles could be embedded in the oxide lattice affecting the physical properties of the material. Therefore, it is important to recognize the possibilities and conditions for the introduction of impurities from the polymeric template into inorganic oxides lattice. The TiO₂ samples were tested on continuous gas phase flow unit using a model reaction of acetone photocatalytic oxidation under visible light irradiation. For macroporous TiO₂ samples an increased photocatalytic activity was observed compared to nanocrystalline reference TiO₂. This increase was attributed to the difference in phase composition, ability to absorb visible light and the presence of small quantities of non-metallic dopants (C,N,S) remained after incomplete template elimination at 500°C.

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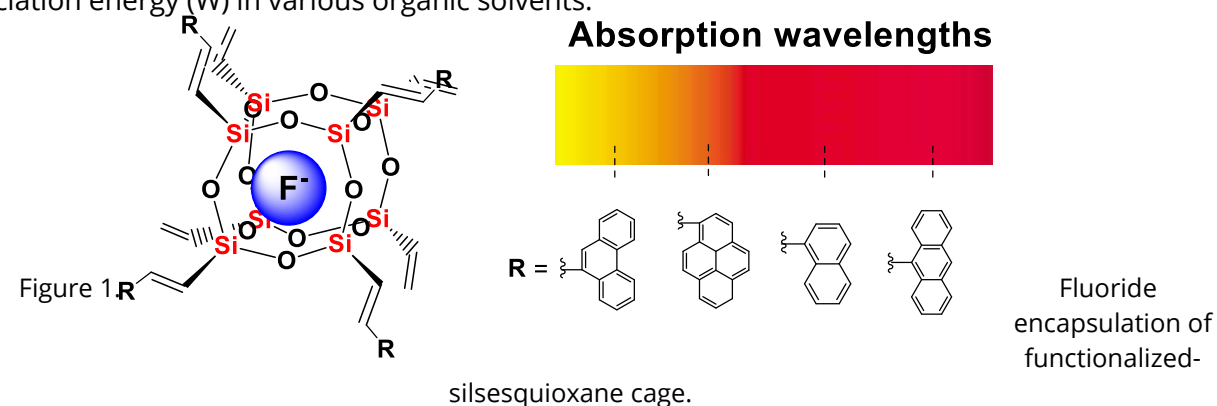


Charge transfer complexes of silsesquioxane cages with polycyclic aromatic hydrocarbons and fluoride in organic solvents

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Abstract: Polyhedral oligomeric silsesquioxanes (POSS) are a class of cage-like molecules having inorganic silica core with peripheral organic substitution in a structure.¹ Silsesquioxane cages (SQ) or POSS have become more attractive than silica because of their high solubility in organic solvents, which widely used in various applications as catalysis, biomaterials, nanocomposites and sensor.² Previous work, after pyrene and anthracene functionalized-silsesquioxane cages were encapsulated with fluoride, the desired products became naked-eye colorful solutions.^{3,4} Herein, this study has focused on the proof of charge-transfer complexes in silsesquioxane cages with polycyclic aromatic hydrocarbons (1-bromopyrene, 1-bromonaphthalene, 9-bromoanthracene and 9-bromophenanthrene) and fluoride, which were investigated spectrophotometrically (formation constants of the charge transfer reactions (KCT), stoichiometric ratios of the formed complexes by Job's method, molar extinction coefficient (ϵ), oscillator strength (f), dipole moment (μ), charge transfer energy (ECT), ionization potential (IP), and dissociation energy (W) in various organic solvents.



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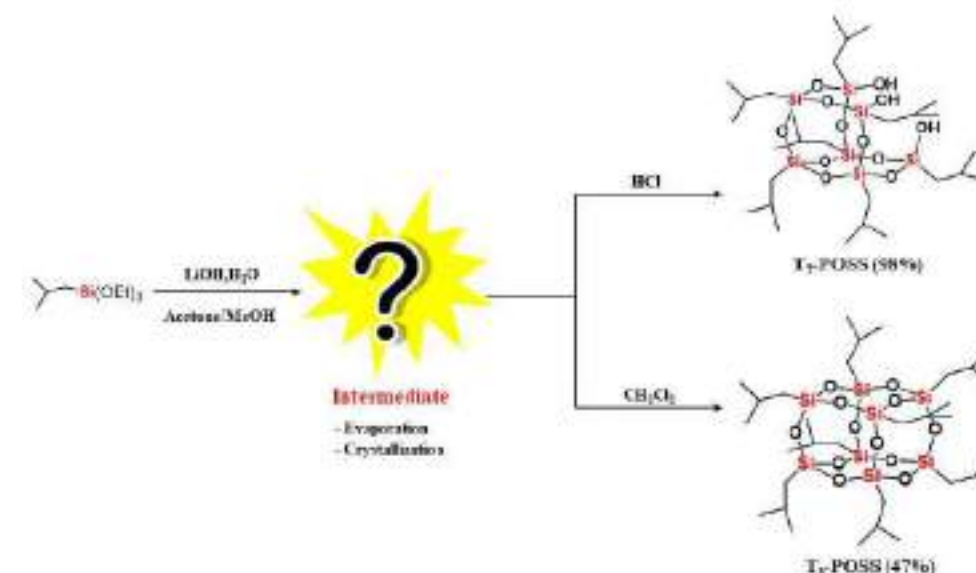
Lithium inspired silsesquioxane cage formation

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Abstract: The trisilanol hepta(*i*-butyl)silsesquioxane (T₇) as an incompletely condensed cage, which can be considered to be very useful and approachable precursors to prepare other mono functional T₈. Moreover, T₇ can serve as model for metal-doped silica surfaces because of the presence of silanol group.¹ Previously, T₇ was prepared from *i*-butyltriethoxysilane with LiOH as catalyst to form intermediate salts and then neutralized by HCl to form T₇ in very high yield of 98%.² To find out what the reason behind of high yield of T₇ could be very interesting hypothesis. In this work, we attempt to isolate intermediate on each step. The addition of chlorinated solvent into the reaction solution can form crystalline T₈ product in 47%. In contrast to evaporate of reaction solution, the crude product was further recrystallized in the solvent mixture to obtain colorless crystals. The new compound was formed and further characterized by FTIR, ¹H, ¹³C and ²⁹Si NMR. The precise structure of each has been under investigation.

Figure 1. Synthetic approach T₇ and T₈



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Novel Drying Method of Polymethylsilsesquioxane Xerogels Suitable for Large-Sized Monoliths

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Abstract: Aerogels, having low thermal conductivity and visible-light transparency, have been also expected as next-generation thermal insulation materials for buildings. Specifically, large-sized transparent monoliths, e.g. over 1 square meter size, are suitable for window components. Monolithic xerogels have been obtained from the hybrid network based on polymethylsilsesquioxane via ambient pressure drying [1,2], which gives a formidable cost advantage over. For mass production of larger size monoliths, however, a significant improvement of the drying process is still required. In this study, we have established the novel drying method of polymethylsilsesquioxane xerogels suitable for large-sized monoliths, by floating on a water surface. The scheme of the drying method is shown in fig.1. After the solvent exchange process (a), water was poured under the solvent (b), and the solvent was evaporated through a breathable film (d-f), finally xerogels were obtained on a water surface (h). This method can reduce friction between gels and solid materials under the gels such as non-woven fabrics in a commonly used drying process, among the shrinkage and the spring-back. Furthermore, it was considered that water vapor functioned to decrease crack generations caused by ununiform nano-structures containing in gels.

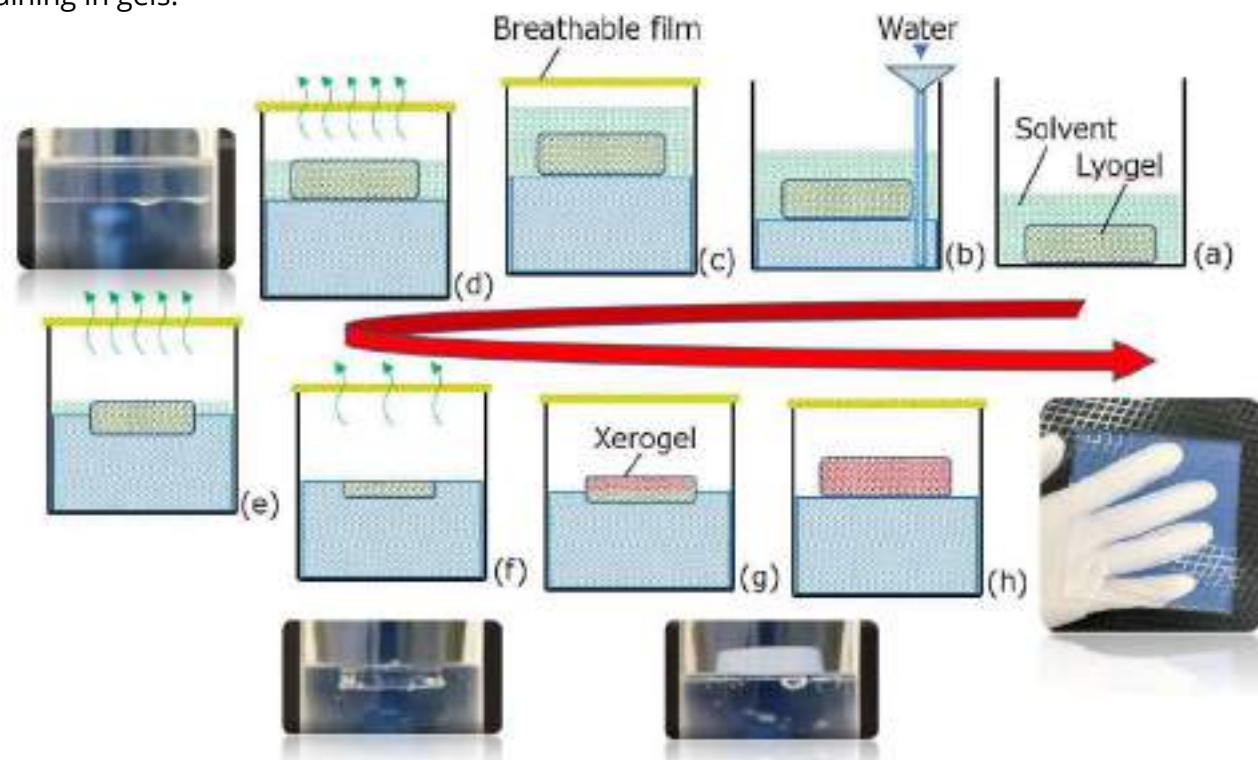


Figure 1. Scheme of the novel drying method of polymethylsilsesquioxane xerogels by floating on a water surface

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Comparison of In-Plane Stress Development in Sol-Gel and Nanoparticle Derived Mesoporous Metal Oxide Thin Films

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Abstract: The research area of mesoporous thin films became more popular in the last decade as these films enhance the material properties for several applications in (photo-)catalysis, energy storage, photo-/electrochromics, thermal insulators or sensors. As there is still a lack of fundamental understanding the relationship between the pore structure and the mechanical properties, ordered mesoporous thin films of TiO₂ and ZrO₂ were prepared via an evaporation-induced self-assembly process (EISA) using PIB₅₀-*b*-PEO₄₅ as the structure directing agent. In order to evaluate the stress development during heat treatment up to 500 °C in regards to solvent evaporation, template decomposition and crystallization, metal alkoxide solutions and nanoparticle dispersions were used as precursor sources for the mesoporous films which were compared to dense films prepared analogously without the addition of the template yielding lower stress values for the PIB₅₀-*b*-PEO₄₅ templated films. A comparable behavior was observed for the residual stress at room temperature for several annealing temperatures indicating the distributed polymer and the corresponding mesopores act as relaxing agents for the system. These insights about the in-plane stress development are fundamental for understanding and tailoring stress-related mechanical properties of mesoporous metal oxide thin films in the future.

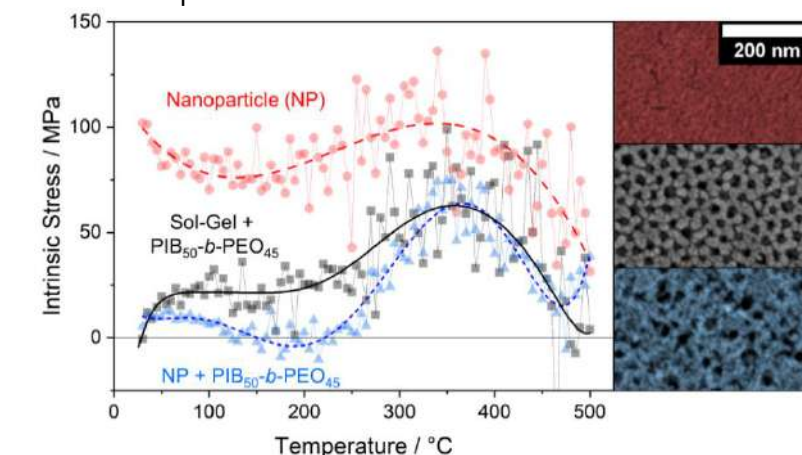


Figure 6. Intrinsic in-plane stress development during the heat treatment up to 500 °C with a heating ramp of 5 °C min⁻¹ of the nanoparticle and sol-gel derived dense and mesoporous TiO₂ thin films. SEM images of the films after the investigation are shown.

Coupling and decoupling of building blocks in nanocrystal network structures

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Abstract: The assembly of nanoparticles into interconnected macroscopic network structures, also referred to as gels, is a promising approach to combine the characteristic nanoscopic properties of the nanoparticle building blocks with the formation of a solid that can be handled macroscopically such as lyo- and aerogels. In recent years several methods have been established to assemble these network structures.^{1,2} However, in general this process only went so far as to build up the networks and applying them e.g. as a catalyst.³ We propose to further modify the original network structure with a thin silica shell surrounding the continuous network structure.⁴ By growing the shell around the network we are able to mechanically reinforce the macroscopic body of the network. As the mechanical stability is usually a weak point of these networks this step is important to broaden the possible applications of these materials. Furthermore, we are able to selectively couple and decouple our nanoparticle building blocks electronically and thereby tuning their optical properties by growing the silica shells before or after network formation.

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Effect of surface functionalization of Fe₃O₄ nanoparticles on thermal energy conversion induced by alternating magnetic field and laser radiation

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Abstract: The ultimate goal of presented study was to assess the effect of the magnetite (Fe₃O₄) nanoparticles surface functionalization on the efficiency of heat generation induced by mutual action of alternating magnetic field and laser radiation within 1st biological window (808 nm).

Ferrite nanoparticles were synthesized by using two distinctly different techniques: co-precipitation reaction under protective atmosphere of inert gas as well as thermal decomposition of metalorganic precursors in nonhydrolytic solvent, respectively. Different nanoparticle surface functionalization protocols were utilized using several phosphonic acid derivatives and silica. Structural properties of magnetite particles were characterized by means of XRD technique whereas particle size and morphology were analyzed by transmission electron microscopy (TEM, HR-TEM, SAED). Effectiveness of surface functionalization was assessed by using FT-IR spectroscopy whereas colloidal stability (zeta potential) and hydrodynamic size were determined by dynamic light scattering technique (DLS). Effect of surface modification with organic ligands on the heat generation was studied using G2 (nB nanoscaleBiomagnetics) set-up equipped with specially modified calorimetric (CAL1) coil.

Molecular simulation-based study of composites of silica aerogels and polymers

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Abstract: Silica aerogels have found applications in a wide range of fields in virtue of their outstanding structural, thermal and optical properties. Nevertheless, the poor mechanical resistance of these materials continues to be a serious limitation to their large-scale use. Mechanical reinforcement of the gel matrix with polymers has been a widely explored route to solve this issue, but successful developments in this area require deep knowledge on the nature of the chemical and physical interactions between the silica matrix (often modified by organic functionalities) and the polymer moieties. Molecular modelling and simulation (M&MS) tools are a practical way to systematically address this kind of fundamental questions. Despite several M&MS studies have been conducted on silica sol-gel reactions for unmodified silica aerogels – i.e. derived from the precursor tetramethylorthosilicate (TMOS) – studies regarding organically-modified silica (ORMOSIL) aerogels and their composites with polymers are rather lacking.

In this work molecular dynamics (MD) simulations paved the way to study composite systems of silica aerogels based on 100% TMOS, 100% vinyltrimethoxysilane (VTMS), and 50% TMOS/50% VTMS (henceforth designated TMVT) with hydroxyl-terminated polydimethylsiloxane (PDMS), as well as composites of 50% tetraethylorthosilicate (TEOS)/50% aminopropyltrimethoxysilane (APTMS) (here abbreviated as TMAP) and 50% TEOS/50% (3-glycidyloxypropyl)trimethoxysilane (GLYMO) (designated as TMG) aerogels with two distinct polyimides and their respective polyamic acids, with the aim of understanding the interactions between the silica aerogel matrix and the polymer chains.

In the case of the first 3 systems, aggregation of silica clusters into secondary particles was observed in the pure aerogel simulations, which in the case of TMOS and TMVT could be largely attributed to hydrogen bonds (H-bonds) between silica species, while in the VTMS system van der Waals interactions play the predominant role in aggregation. The addition of PDMS to these systems has a profound impact on the extent of clustering, as increasing the concentration of PDMS to 50% prevents the formation of any noticeable aggregates. This effect could be explained from a H-bond analysis to the MD trajectories, showing that an increase in the polymer concentration results in the formation of more H-bonds between polymer chains and silica species (while also strengthening van der Waals interactions between both molecules), at the expense of reduced H-bonding between silica clusters.

In the case of the systems based on the TMAP or TMG mixtures of precursors, both van der Waals and electrostatic interactions play significant roles in the overall attractive interaction between the silica species and the polyimide/polyamic acid chains. Strong H-bonds were identified between the amine groups of TMAP species and anhydride and carboxylic groups of the polymer chains. On the other hand, for the TMG-based systems, the H-bond pairs were mostly found between epoxy or ether groups of silica species and the amine terminal groups of the polymer chains.

This work was developed under the project AerogelDustFree - “Aerogel for Space applications ISO8 without dust release” (Contract No. 17815), developed by the consortium Active Aerogels / University of Coimbra, funded by the European Regional Development Fund (FEDER) through the Regional Operational Program of the Center of Portugal (Centro2020) of PT2020.

Effect of different silylating agents on the properties of ambient pressure dried TEOS/VTMS silica-based aerogels: a scaling-up study

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Abstract: Pure silica aerogels, in spite of exceptional properties that make them widely used for a remarkable list of applications are inherently brittle and possess poor mechanical properties. Their fragility while handled often hampers a large-scale production. Therefore, different reinforcement strategies are highly attractive to overcome these drawbacks. For this purpose, co-precursors are used to impart flexibility and to adjust the pore size of the final aerogels, and the reinforcement with fibers acts as the supporting skeleton of the silica matrix [1]. Such modifications are extremely useful, although they must be combined with non-polar groups by silylation prior to ambient pressure drying (APD). To study the effect of different silylating agents on the properties of tetraethoxysilane/vinyltrimethoxysilane (TEOS/VTMS) aerogels, trimethylmethoxysilane (TMMS), trimethylethoxysilane (TMES) and hexamethyldisilazane (HMDZ) are proposed. The higher number of methyl groups and the reactivity of the agent lead to smaller volumetric shrinkage of the samples, thus lowering both bulk density and thermal conductivity. Under optimal conditions, a scale-up of the aerogels is performed to plates of 17x17x1 cm after modification with HMDZ (Figure 1). Their thermal conductivity was characterized by two different methods, viz. HotDisk® *Transient Plane Source* (ISO 22007-2) and *Guarded Hot Plate* (EN 12667:2001). After scale-up, as revealed by the *Guarded Hot Plate* method, the thermal insulation performance is still guaranteed, with thermal conductivities of 0.023 W.m⁻¹K⁻¹.



Figure 1. Scheme of the scale-up of TEOS/VTMS aerogels reinforced with fibers, and modified with HMDZ prior to APD.

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This work was developed under the project AerogelDustFree - “Aerogel for Space applications ISO8 without dust release” (Contract No 17815), developed by the consortium Active Aerogels / University of Coimbra, funded by the European Regional Development Fund (FEDER) through the Operational Program for Competitiveness and Internationalization and/or the Regional Operational Program of the Center of Portugal (Centro2020) of PT2020.

Controllable Photothermal Temperature of Redox-responsive Polymer Dot-incorporated Hydrogel for Memory Storage

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Abstract: Herein, a near-infrared light-induced redox-sensitive hydrogel was synthesized by the incorporation of IR825 loaded-polymer dot (PD-IR825) into thermosensitive poly(N-isopropylacrylamide) hydrogel network for study of nanoparticles mobility inside gel network via reversible temperature memory phenomena by environmental redox changes. The PD-IR825 inside the hydrogel network performed fluorescent and photothermal properties to the hydrogels, exhibiting shrinking in volume behavior upon NIR exposure in response to redox condition. The photothermal effect, fluorescence, and microstructure of the composite hydrogel could be controlled under the NIR on/off cycles. Furthermore, MDAMB cancer cells were incubated with the composite hydrogel with the addition of exogenous GSH showed an enhanced photothermal effect, that effectively killed cancer cells under NIR laser irradiation. Hence, the light-induced redox-sensitive composite hydrogel has shown its potential in photothermal cancer treatment with subsequent study of the motion of nanoparticles inside hydrogel networks.

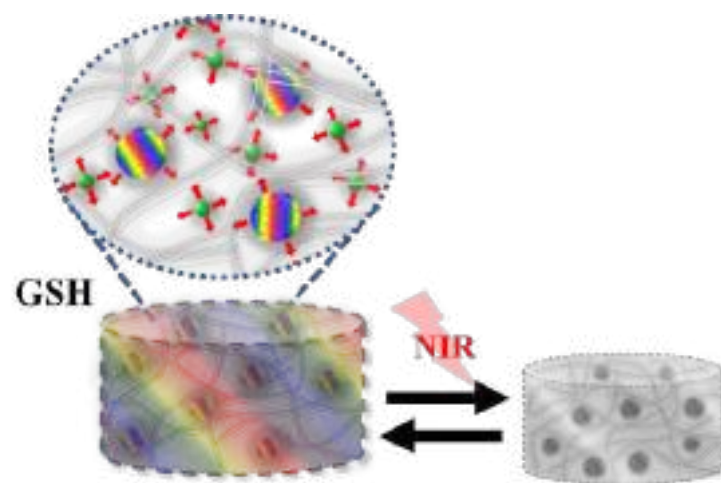


Figure 1. Redox-responsive Polymer Dot-incorporated Hydrogel for Controllable Photothermal Effect of Reversible Memory Storage.

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Novel 3D open-structures using sol-gel chemistry and stereolithography

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Abstract: Stereolithography-based additive manufacturing (AM) is increasingly becoming the technology of choice for small series production or material complex shapes preparation. It also allows the material-by-design fabrication, prime concern for most material chemists. Thus, three-dimensional (3D) printing enables a big leap in geometrical flexibility and microstructured architecture. 3D-structured organic-inorganic hybrid materials will be described and focus onto combined 3D printing technology and sol-gel ceramic-based material preparation will be emphasized.

We will report work on synthesis of new ceramics prepared from preceramic polymers or inorganic powder loaded resins cured using ultraviolet laser in a stereolithography 3D printer. After a thermal debinding and sintering step the part turns into a ceramic open-structure and gains its final properties, with uniform shrinkage and porosity control.

The paper will discuss the critical process parameters influencing polymerization uniformity and structure quality. Currently it is possible to print 3D-open structures with a spatial resolution down to 50 μm , exhibiting complex shape and cellular architecture. The photosensitive resin formulation specifically developed is a key parameter and enables the printing resolution control, and so the geometry of the final ceramic. Innovative approach for loading the photosensitive resin with optimized particle size distributions associated with preceramic precursor allows us to vary and optimize mechanical stiffness of the prepared 3D-porous structures.

Moreover, composite-structures made of 3-D printed ceramic framework embedded in an aerogel matrix have been produced with the prospect of reinforced-stiffness thermal super insulator application.

A numerical modelling supports interpretation of mechanical property results and permits the grading of different 3D-open architectures regarding the increase of mechanical toughness of such highly-porous structures.



Figure 1. 3D-printed ceramic sample with 200-micron features prepared using stereolithography printer. Sample A is a 3D-structured silica aerogel.

Alkoxyamine as a probe to quantify the efficiency of the photochemical or thermal homolysis of C-O bond in nanostructured silica

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Abstract: Development of new materials with unusual functional groups, such as radicals, is of topical interest to enable new advances in spin sciences. Properties related to the presence of unpaired electrons, such as conductivity or magnetism, have been studied in order to develop smart devices.

Recently, our group focused his attention on the effect of nanostructuration on the behavior of transient radical. Therefore, it has been shown that confinement of organic radicals in porous material allows a great increase of radical lifetime.¹⁻⁶ Mesoporous silica, obtained via sol gel process is a powerful and intricate tool to stabilize elusive organic intermediates.

In extension of this work we focused our attention on confined alkoxyamines within porous matrices. Indeed, we report the design of a nanostructured silica functionalized with an alkoxyamine which can led to a stable nitroxide radical upon either light irradiation or thermal heating. The formation of the nitroxide radical can be quantify and enables to evaluate the efficiency of the C-O bond homolysis in a mesoporous material.

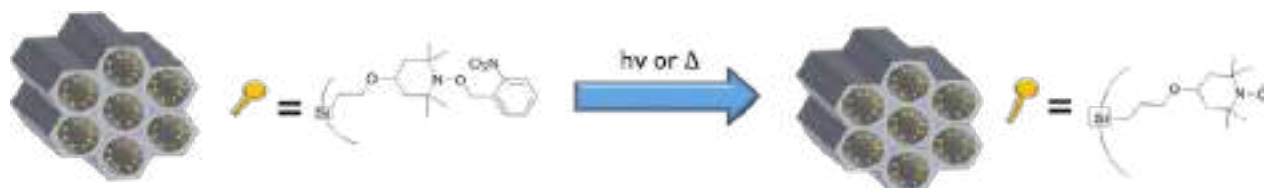


Figure 1: Formation of nitroxide radical on mesoporous silica

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Effect of malic acid concentration on yttrium oxide structure formation

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Abstract: Studies in the synthesis of yttrium oxyhydroxides are relevant due to the high prospects for using these compounds as catalysts for removing organic contaminants from water, as well as the basis for nanoceramics and phosphors. The structure and particle size of materials have a significant impact on their properties and reactivity as catalysts. In this connection an important factor in synthesis of these compounds is the ability to control the structure, which allows controlling the reaction process and product quality.

In the present study the samples were obtained by the sol-gel method with hydrothermal treatment. The sol-gel synthesis was carried out at final pH values (8, 9, 10) with the introduction of malic acid of various concentrations (0.1 M and 0.5 M). The primary hydrothermal treatment lasted for 24 hours. After the primary hydrothermal treatment the solution was adjusted to pH = 12 and subjected to repeated hydrothermal treatment within 24 hours. A study was carried out as to the effect of malic acid concentration on the structure of the samples obtained. On addition of malic acid with 0.1 M concentration, particles looking like hollow tubes 5–10 μm long and about 1–2 μm wide are formed. The wall thickness is about 100 nm (Figure 1). When 0.5 M acid is used, particles of a clear hexagonal shape are formed, which are not hollow. The particle length is 8–10 μm, the width is 3–4 μm, with the formation of particles of similar size (Figure 2).

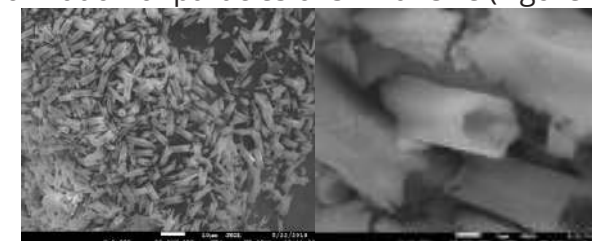


Figure 1. Micrographs of a sample obtained from yttrium chloride in the presence of 0.1 M malic acid (pH 8) after repeated hydrothermal treatment, adjusted to pH 12.

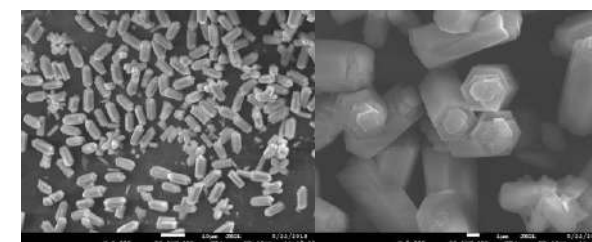


Figure 2. Micrographs of a sample obtained from yttrium chloride in the presence of 0.5 M malic acid (pH 9) after repeated hydrothermal treatment, adjusted to pH 12.

The analysis of the obtained diffractograms have shown that crystalline structures are formed only under the condition of repeated hydrothermal treatment with adjustment to high pH values. Analysis of the IR spectra suggests that malic acid is not included in the structure of the obtained samples, due to the absence of characteristic oscillations in the range of 1500–1750 cm⁻¹. For the samples obtained with the introduction of malic acid, formation of compounds with non-associated OH groups has been observed.

CO₂ Capture Adsorbents using Sol-gel Technology to develop a Carbon Neutral Cement

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Abstract: Cement is one of the two largest producers of carbon dioxide creating over 5% of total man-made emission in the world. However, it may be possible to capture CO₂ within the cement through carbonation process. CO₂ when added to cement during mixing reacts with water and cement to form calcium carbonate (calcite) minerals at the initial stages of hydration. These precipitated calcite particles in the microstructure can act as a seeding agent in the hydration of cement by providing additional nucleation sites. Furthermore, this approach can trap CO₂ permanently in the pore structure. This paper couples adsorbents synthesised by sol-gel material with engineered carbon capture technology which will be incorporated in cement. CO₂ captured aluminosilicates were synthesised using single step sol-gel process. The sol-gel technology aided in the production of high surface area and homogenous adsorbents which trapped large amount of CO₂ in its micro to mesopores of size ranging between 2-3 nm. These aluminosilicates were included in cement as an additive by partially replacing cement from 3% to 15%. The cement samples were cured in a carbonation chamber to maximise the CO₂ intake. Nitrogen Adsorption, FTIR, TGA and SEM of the synthesised cement samples showed significant changes in the microstructure of the resulting cement paste indicating accelerated carbonation reaction while at the same time reducing free water and bound water. The captured CO₂ in the adsorbents reacted with clinker and precipitated to form calcite inside the pores and aluminosilicate network helped in developing additional nucleation sites creating a less permeable structure. The resultant cement showed improved physical and chemical properties delivering a more durable and denser cement matrix. This work shows the potential to develop a novel carbon neutral construction material enhanced with sol-gel technology that will aid to close the loop of CO₂ emission during cement manufacturing. The creation of such a carbon neutral cement will be a breakthrough in the building construction industry.

Keywords: CO₂ Capture, Aluminosilicates, Adsorbents, Sol-gel, Calcite

Macro- and mesoporous sulfated tin oxide from an integrated sol-gel surfactant-template

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Abstract: Sulfated tin oxide was synthesized by a sol-gel process and pores were formed in the ceramic powders using Pluronic F-127 as a soft template. Sulfate ions linked to the tin oxide promoted the formation of acid sites on the particle surfaces. After calcination, the sulfate ions remained on the oxide particles as uni- and bidentate complexes, so changes in the tin atom coordination numbers at the second shells could be observed by X-ray absorptionspectroscopy. The tin oxides showed a cassiterite nanocrystalline structure consisting of aggregates of spherical particles, with crystallite size of around 8 nm, radius of gyration ~3.7 nm, and mean particle size between 7 and 10 nm, according to X-ray diffraction and small angle X-ray scattering measurements, together with the use of transmission electron microscopy images. The use of Pluronic F-127 as a template for the pores resulted in the formation of meso- and macro-pores sized around 7.5 nm and 60 nm, respectively, surface area of 128 m² g⁻¹ and porosities of 71%, after calcination at 500 °C. The porous sulfated tin oxide was used to catalyze the isopropanol dehydration reaction, with production of propene. The catalytic activity was indicative of the presence of acid sites on the catalyst surface, suggesting that this material could be employed as a heterogeneous catalyst in acid-catalyzed reactions

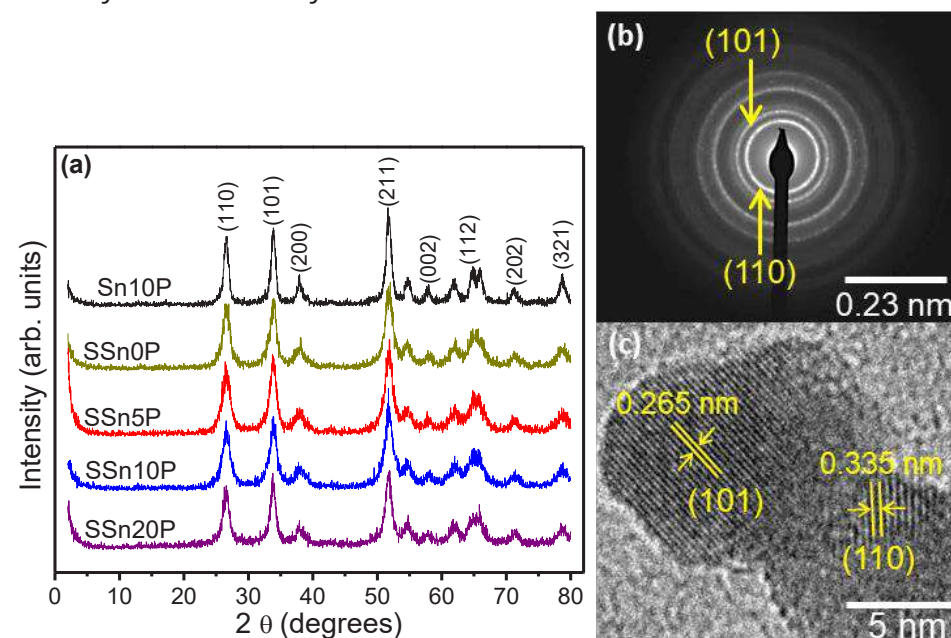


Figure1. (a) XRPD patterns of the samples prepared with different amounts of Pluronic, (b) SAED pattern and (c) TEM image highlighting the interplanar distances of the (110) and (101) atomic planes for the SSn10P sample.

FAPESP, CNPq and CAPES

Development of In-Situ Formation of Injectable Pegylated PLGA Thermosensitive Hydrogel to Deliver BiTEE (Bispecific Anti-CD3/Anti-EGFR T cell/EGFR Engager) for Enhancing Therapeutic Efficacy of EGFR-overexpression Cancer

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Abstract: BiTEE (Bispecific T cell Engager) antibody constructs comprise tandemly-arranged single-chain variable fragments (scFvs). One scFv binds the TCR CD3ε subunit and the other binds a tumor-associated surface antigen (TAA) that directly connect T cells with tumor-associated surface antigens (TAAs) to initiate T cell immunotherapy. However, the short half-life and the existence of effective therapeutic window of BiTEE antibodies limit their applications. Therefore, design of a drug delivery system with control and extended release ability is necessitate for extending its plasma half-life and maintaining stable blood level. In this study, mPEG-PLGA/PLGA-PEG-PLGA mix hydrogels (DPTPgels) were prepared with mPEG-PLGA (diblock polymer, DP) and PLGA-PEG-PLGA (triblock polymer, TP), both of which were synthesized according to the method as literature revealed. Three kind of pegylated PLGA thermosensitive hydrogels designated as DPTPgel01, DPTPgel02, and DPTPgel03 were prepared with different DP/TP ratio. All three DPTPgels showed thermosensitive property with a sol-gel transition temperature at 28-34 °C, which was suitable for injection. In addition, DPTPgels loaded stabilized BiTEE (Bispecific anti-CD3/anti-EGFR T cell/EGFR Engager) were found being able to keep stable for at least 14 days at 4 °C. The *in-vitro* release study showed that DPTPgel01, DPTPgel02, and DPTPgel03 could extend the release of BiTEE for up to 7 days. In animal pharmacokinetics study, subcutaneous injection of DPTPgel01, DPTPgel02, and DPTPgel03 prolong the half-life of BiTEE 2.6-fold, 1.4-fold and 1.33-fold, respectively, compared to subcutaneous injection of hydrogel-free BiTEE. In animal anti-tumor study, MDA-MB-231 and TALL-104 were used as EGFR-overexpression cancer model and human T cell model. The result indicated that subcutaneous injection of BiTEE loaded thermosensitive hydrogel showed to significantly improve anti-tumor efficacy than intravenous or subcutaneous injection of hydrogel-free BiTEE. In conclusion, in-situ formation of injectable pegylated PLGA thermosensitive hydrogel loaded with BiTEE was successfully developed to increase its half-life and maintain a constant blood level resulting in enhancing the treatment efficacy.

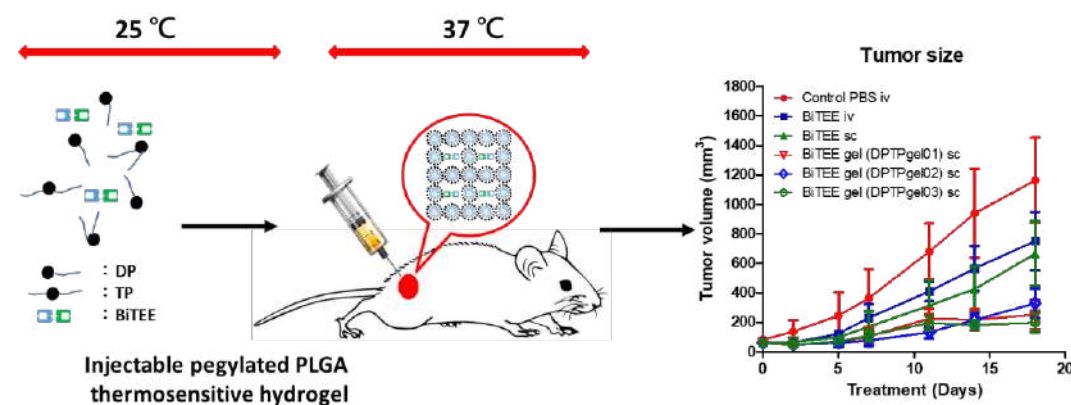


Figure 1. Illustration of BiTEE loaded injectable pegylated PLGA thermosensitive hydrogel.

Facile preparation and enhanced dielectric properties of organic-inorganic nanocomposite materials

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Abstract: In our work, we provide a new strategy to improve dielectric properties of organic-inorganic nanocomposite materials. A series of micro-nano inorganic particles with special morphology structure such as core-shell nanoparticle (e.g. TiO_2/Ag , $\text{BaTiO}_3/\text{PANI}$), hierarchical flower-like nanostructure (e.g. TiO_2 , TiO_2/C), Ag-loaded TiO_2 hybrid particles, and nanowire/nanoparticle self-assembled structure (e.g. SrTiO_3 nanowire grafted onto the surface of BaTiO_3 nanoparticle) were synthesized by wet-chemical method (e.g. hydrothermal method, vapor-thermal method). The dense well-distributed nanocomposite films were prepared by simple solution process using P(VDF-HFP) as matrix and synthesized inorganic particles as filler. The micro-nano inorganic particles effect on the dielectric properties and thermal behavior of P(VDF-HFP) organic film were comprehensively investigated. The P(VDF-HFP)-based nanocomposite materials exhibited enhanced dielectric properties over a wide frequency range, and the dielectric constant of polymer composite film at a low filler loading of inorganic particles is reached 3~30 times than that of pristine P(VDF-HFP), which were attributed to the interfacial polarization and micro capacitor effect provided by inorganic particle with sophisticated morphology. The obtained nanocomposite film can also maintain high breakdown strengths and low dielectric loss. All the improved performances suggest an easy method to fabricate nanocomposite films bearing potential electrical applications.

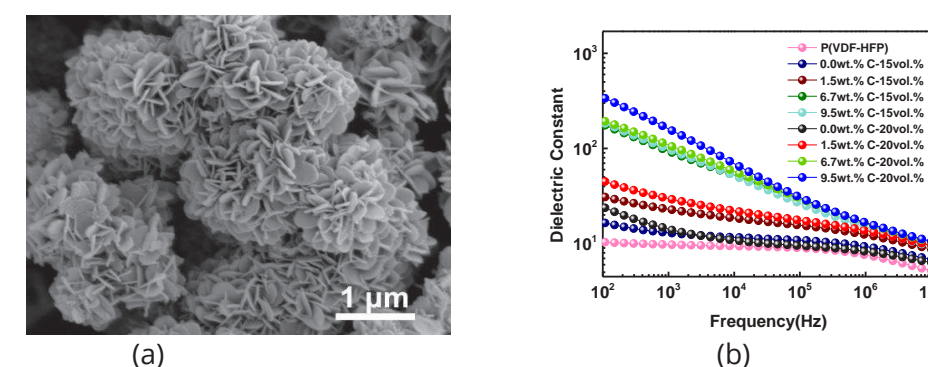


Figure 1. SEM of hierarchical flower-like TiO_2/C nanostructure and (b) dielectric constant of P(VDF-HFP) nanocomposites materials with TiO_2/C .

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Aqueous anatase TiO₂ sol towards nanorods via oriented attachment

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Abstract: Generally, alcoholic amorphous TiO₂ sol or gel prepared by hydrolysis of metal alkoxides, which crystallizes subsequently into anatase phase by heat treatment at 400-600°C, which depends on the preparation procedures. Both amorphous nature of TiO₂ and releasing a large amount volatile organic compounds (VOCs) limit their practical applications. Here, we describe some methods for preparation aqueous anatase TiO₂ sol including (1) peptization of titania precipitates using HNO₃ and CF₃COOH solution to acidic sols, (2) peroxotitanium acid derived neutral anatase TiO₂ sol and (3) titanium (IV) bis (ammonium lactato) dihydroxide transferred weak basic sols. Aqueous TiO₂ sols are suitable to prepare crystalline TiO₂ film on varying substrates including polymer and no heat treatment is need to improve its crystallinity (Fig. 1a). For example, a portion of titania precipitate dispersion was peptized by adding HNO₃, followed by refluxing at 80 °C to give a sol of pH ~1. XRD and TEM revealed that titania ultrafine crystallites is the resulting sol was in the anatase phase and with the size of 4 nm. By controlling the Zeta potentials of TiO₂ crystallites in aqueous sol, the anatase TiO₂ nanorods with a aspect ratio of more than 10 and with a diameter only less than 10 nm were obtained via the Oriented Attachment mechanism, and those nanorods were used to the photoanode of dye-sensitized solar cells with the higher open circuit voltage.

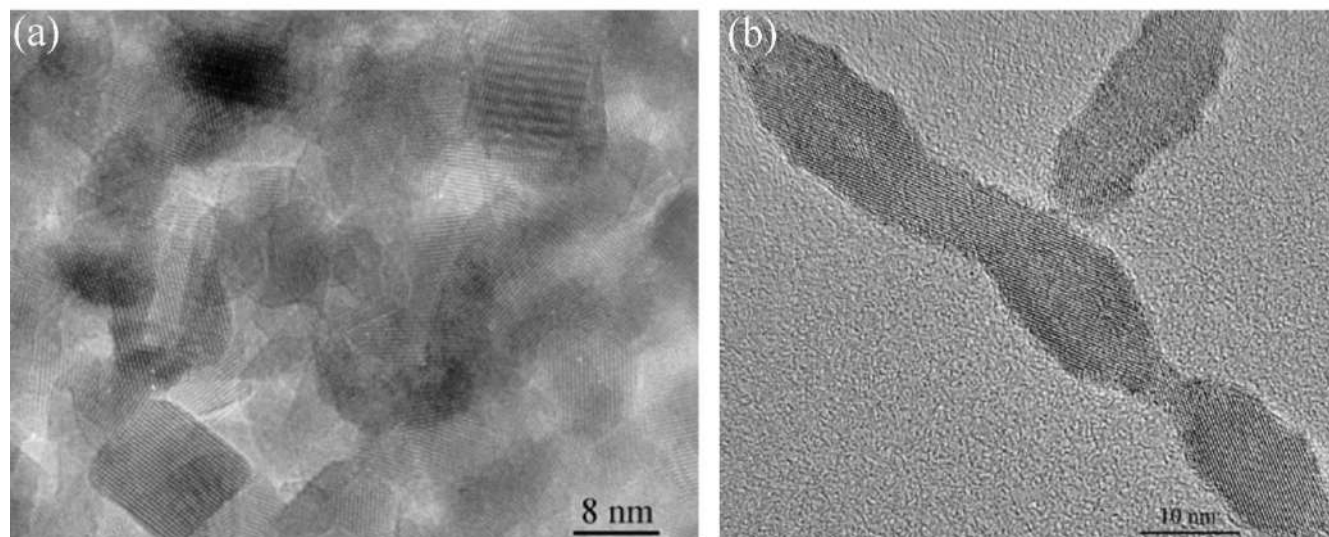


Figure 1. HRTEM images of sol-derived TiO₂ films (a) and anatase nanorods via Oriented Attachment (b)

Sol gel synthesis of Nano magnesia partially stabilized zirconia for thermoluminescence dosimetry

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Abstract: In this study, nanoparticles of magnesia partially stabilized zirconia were synthesized via sol-gel method followed by UV/Beta radiation dosimetry studies. Taguchi experimental design with L9 orthogonal matrix has used in order to optimize essential parameters. After optimizing the parameters, the synthesized powders were evaluated as a candidate for UV/Beta radiation dosimetry. Different analyses such as DLS, XRD, FE-SEM, and TLD were used. Variance analysis was used to achieve the smallest sol particle size. The optimized conditions were: solvent to precursor volume ratio 30, amount of magnesium 8 mole%, and reaction temperature 70 °C. Under these conditions, the average sol particle size was estimated 1.64 nm. After calcination at 600 °C, average particle size was determined about 25 nm. Under these conditions, TLD analysis showed that the synthesized powder was suitable for UV/ Beta dosimetry.

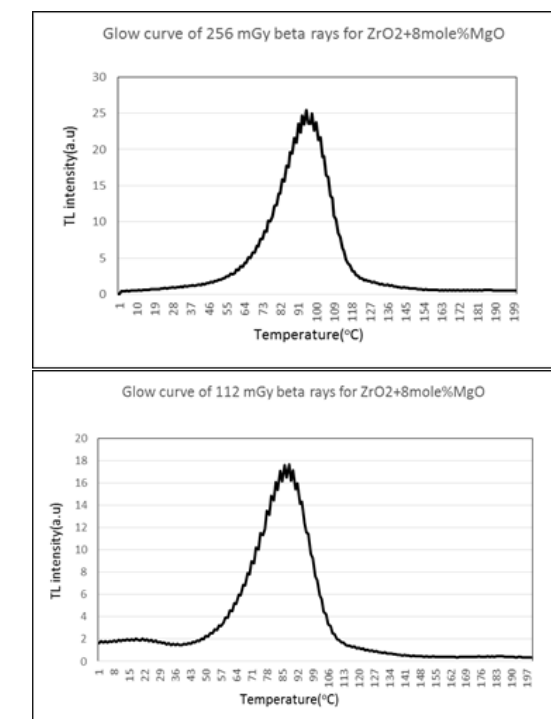


Figure 1. Glow curve of Beta radiation for ZrO₂+8 mole%MgO

Rapid Preparation of $\text{Li}_3\text{PS}_4\text{-LiI}$ Electrolytes by Liquid-Phase Shaking for All-Solid-State Lithium Batteries

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Abstract: The sulfide-based solid electrolytes are currently well known as a promising candidate for all-solid-state batteries and extensively studied due to their high lithium ionic conductivities and suitable plasticity for good contacts at the interface [1][2]. Li_3PS_4 and $\text{Li}_3\text{PS}_4\text{-LiI}$ electrolytes were prepared by a new liquid phase process using ethyl propionate as a medium with shaking for fabrication of all-solid-state lithium batteries. Figure 1 shows the formation of Li_3PS_4 precursor from Li_2S and P_2S_5 using the liquid phase shaking process.

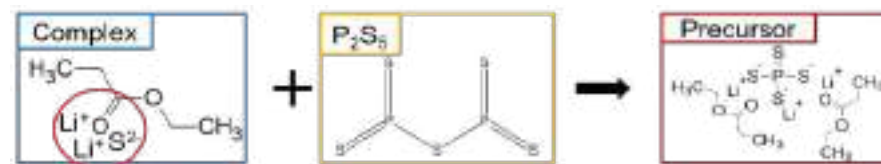


Figure 1 Formation of Li_3PS_4 precursor from Li_2S and P_2S_5 in the liquid phase shaking process using ethyl propionate as a medium.

By optimizing the liquid phase shaking time, 66.7 Li_3PS_4 :33.3 LiI (mol%) ($\text{Li}_7\text{P}_2\text{S}_8\text{I}$) electrolyte containing a new highly ion conductive phase (Phase I) was obtained (figure2). In the results of considering the drying process of the resultant products, crystalline $\text{Li}_7\text{P}_2\text{S}_8\text{I}$ thus obtained exhibited high ionic conductivity of 1.0 mS cm^{-1} at room temperature. All-solid-state lithium batteries fabricated using the electrolytes showed good charge-discharge performance, in which the electrolytes were used as the separator as well as the composed materials with active materials.

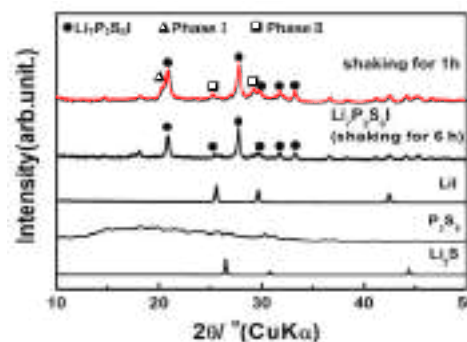


Figure 2. XRD patterns of $\text{Li}_7\text{P}_2\text{S}_8\text{I}$ (shaking time for 1h and 6h) and starting materials (Li_2S , P_2S_5 and LiI).

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This study was partly supported by Advanced Low Carbon Technology Specially Promoted Research for Innovative Next Generation Batteries (ALCA-SPRING) program of the Japan Science and Technology Agency (JST).

Preparation of flexible polysiloxane porous materials in non-aqueous condition and their characterizations

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Abstract: Organic-inorganic hybridization has been employed to improve mechanical strength and flexibility and to add functionality to polysiloxane-based materials. In fact, preparation of flexible polymethylsiloxane porous aerogels by using trifunctional and difunctional alkoxysilane precursors through the sol-gel process has already been reported, and the obtained materials were demonstrated to show selective absorption of oils from oil-water two-phase systems. In traditional sol-gel processes under aqueous conditions, however, it is challenging to obtain monolithic porous gels from more hydrophobic precursors, since the precursor and its condensates are more prone to be segregated in aqueous solution during gelation. In this work, uniform flexible porous materials have been prepared by copolymerization of tetramethoxysilane (TMOS) or methyltrimethoxysilane (MTMS) and polydimethylsiloxane terminated with silanol at both ends (PDMS-OH) in carboxylic acid as non-aqueous medium and a reactant.

The PDMS-OH and TMOS or MTMS were mixed and stirred at room temperature, and trifluoroacetic acid was then added under stirring. The resultant transparent homogeneous solution was left at room temperature for gelation and ageing, and the obtained gels were washed with alcohol and dried. The microstructure of the xerogels was characterized by scanning electron microscopy, and the mechanical properties were investigated by uniaxial compression and three-point bending.

The pore structures in the micrometer scale could be changed continuously from aggregated particles to co-continuous structure depending on the starting composition. In the copolymer system of MTMS and PDMS-OH, a xerogel with low density (0.13 g cm^{-3}) having co-continuous structure (Fig. 1) was obtained. The xerogel showed high strength and flexibility in uniaxial compression-decompression (Fig. 2) and in bending. In addition, these xerogels selectively absorbed oil (*n*-hexane) from the surface of water. This method can also be extended using different alkoxysilanes and carboxylic acids, and several different examples will be reported at the presentation.

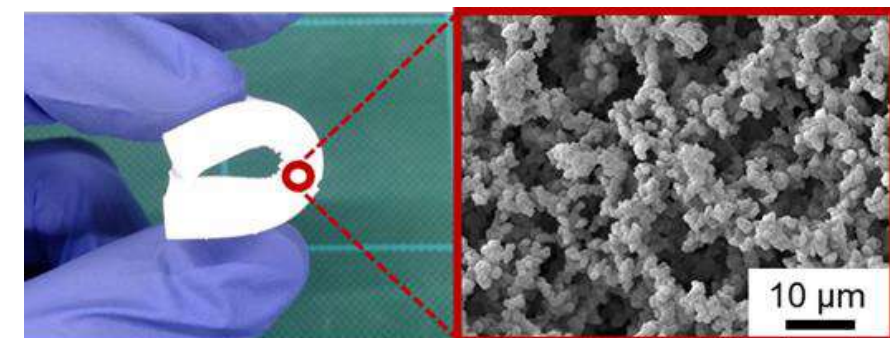


Figure 1. Photograph of a bended xerogel obtained from MTMS and PDMS-OH and its microstructure.

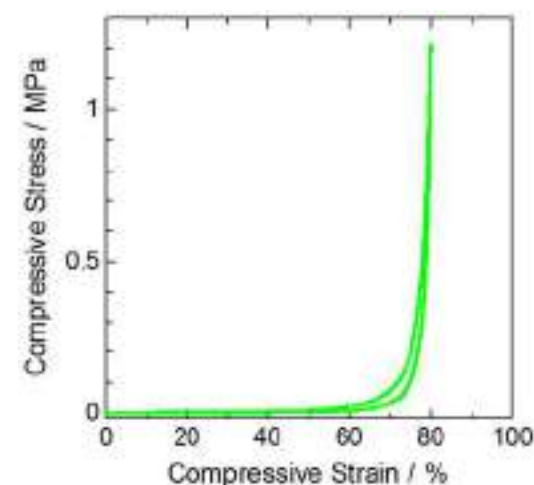


Figure 2. Stress-strain curve of the obtained xerogel.

Silica-coated carbon dots in titania-based photocatalysts for water decontamination

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Abstract: Water is essential for life and therefore any improvement in eliminating its pollutants is highly desirable. Carbon dots (CDs) hosting organic-inorganic hybrid materials can help to achieve increased photocatalytic activity of titania-based hybrids in the UV and visible light for degrading different organic pollutants.

Carbon dots are a class of (often non-toxic) fluorescent nanomaterials with a possibly high absorbance of the UV and visible light, which can be obtained by simple synthetic methods applied to easily accessible carbon sources.

The cheap and environmentally friendly citric acid is a frequently used CDs source. This compound, however, allows achieving only weak fluorescence, therefore it is often reacted in the presence of nitrogen-containing molecules. We introduced tris(hydroxymethyl)aminomethane and urea in the CDs synthesis in order to enrich the nitrogen content of the core in the nanoparticles, but in some cases the optical stability was not satisfactory (therefore reuse in a photocatalytic system would be limited). More stable CDs with further increased fluorescence were obtained after a simple surface functionalization with (3-aminopropyl)-triethoxysilane. Embedding these stabilized and protected CDs to a titania matrix through a sol-gel process can increase its photocatalytic efficiency and reusability against pollutants such as dyes or pesticides.

Wet-chemical processed thermochromic coatings for energy efficient glazing

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Abstract: Currently, buildings are responsible for approximately 40% of the world's energy consumption. An important loss in energy is obtained in existing low-E windows. This can be reduced by application of functional coatings that regulate the transmission of infrared (IR) radiation through windows. The ideal window would comprise a coating which is highly transparent for visible light, and smartly adapts its IR regulating functionality to the environmental conditions. Here, we present a proprietary thermochromic coating that can switch between transmission and blocking of IR light at a switching temperature between 25 and 70°C. This single layer coating comprises monoclinic vanadium dioxide as active ingredient. It is processed from solution and transparent in the visible. TNO/BMC investigated the switching temperature, the transmission change in the IR (800-2400nm) as well as the visible region (400-700nm) as a function of the coating composition and layer thickness. We have successfully demonstrated its working principle in a laboratory scale demonstrator, and anticipate to scale up the liquid coating formulation and the coating application and curing process to pilot scale in 2019-2021. Furthermore, we have managed to prepare solution processed thermochromic nanopigments with functionality similar to the glass coatings. We plan to integrate these in polymer foils for glass lamination in the near future.

AquaSun: An effective foul-release and antifouling marine coating

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Abstract: At sea, biofouling translates in the rapid attachment of marine organisms such as barnacles and algae to any submersed surface, including those of ships and boats comprised of widely different materials.¹ This makes the use of antifouling coatings compulsory, as a ship without antifouling (AF) paint after 6 months would consume 40% more fuel due to additional hull drag from fouling.¹ Since the ban of highly toxic tin biocides from AF paints, copper-based biocidal paints have become the main AF technology. However, around 5,000 tonnes per year of toxic copper compounds leach yearly at sea from the new AF paints, and over 208,000 tonnes of AF paint waste accumulate during ship repairing and dismantling operations every year.² In one of the most noticeable achievements of nanochemistry, several new ecofriendly marine paints have been lately commercialized which minimize the impact of AF coatings on the environment.³

Organically modified silicas (ORMOSILs) are excellent foul-release (FR) coatings, but they have poor antifouling activity.⁴ Showing exceptional biocidal activity, hydrogen peroxide, decomposing into innocuous water and oxygen, would be the ideal biocide.

We have recently discovered that ORMOSILs doped with nanoflower-like bismuth wolframate (Bi_2WO_6) are effective AF/FR coatings (Fig.1) suitable for the protection of boats and infrastructures in the marine environment. The presence of Bi_2WO_6 photocatalyst embedded in the ORMOSIL matrix endows the coating with high AF action thanks to the production of H_2O_2 driven by solar radiation.⁵ Dubbed *AquaSun*, the new coating has been successfully tested for several months in the Indian Ocean waters under simulated real life conditions.⁵

Forthcoming trials in the open sea on both boats and still immersed objects will be aimed to identify the optimal sol-gel coating composition and application parameters.

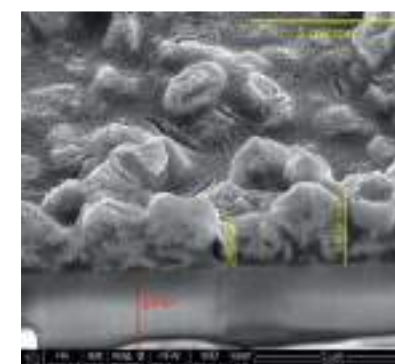


Figure 1. Cross-sectional image (by SEM-FIB) of the sample 50ME-50BW

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Highly Transparent Organic-Inorganic Hybrid Aerogels with Improved Mechanical Flexibility

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Abstract: Aerogels are highly porous materials. Silica aerogels, one of the typical aerogels, have unique properties such as high transparency, low bulk density, and low thermal conductivity. Hence, they are expected to be applied to thermally insulating window materials. However, silica aerogels have low mechanical strength and it is necessary to employ the supercritical drying process under high pressure due to their microstructure of weakly connected silica nanoparticles and high porosity. In order to improve their mechanical friability, organic-inorganic hybridization has been investigated and successful improvements in mechanical strength and flexibility have been reported; an example of which is transparent polymethylsilsesquioxane (PMSQ) aerogels with high strength and flexibility against compressive deformations [1]. This property facilitates monolithic aerogel-like xerogels by ambient pressure drying via temporal shrinkage and spring-back. There are, however, still remaining issues for improvement in bending flexibility. In addition, there is still room for improvement in optical property toward window insulating applications. Preparation of aerogels with improved transparency and bending flexibility has therefore been a challenge to be explored.

In this work, we have tried to prepare highly transparent aerogels based on PMSQ aiming at improved bending flexibility. We have prepared transparent PMSQ aerogels (up to 99 %/10-mm at 550 nm) using strong base tetramethylammonium hydroxide (TMAOH) as a polycondensation catalyst [2] and nonionic surfactant as a phase separation suppressor (an example shown in Figure 1). Obtained PMSQ aerogels with optimized starting composition and microstructure show improved bending flexibility. This synthetic system can be extended to other (co-)precursor systems, in which drastic improvements in mechanical properties are expected. Detailed properties of these aerogels will be discussed in the presentation.

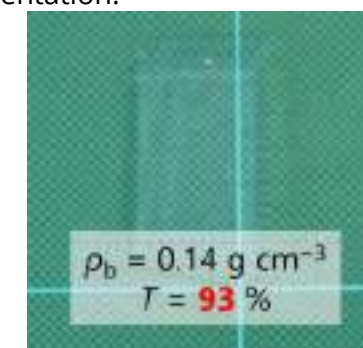


Figure 1. Appearance of an obtained PMSQ aerogel. ρ_b and T show bulk density and light transmittance of 10 mm thick sample at 550 nm.

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Preparation of cationic silsesquioxanes that can stably retain triiodide ion

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Abstract: Iodine is known as an excellent dopant (electron acceptor) for improving the conductivity of π -conjugated polymers, such as polyacetylene and polythiophene.¹ However, since iodine is volatile, practical application of iodine-doped π -conjugated polymers indicating high conductivity is difficult. Meanwhile, it has been reported that iodine is stably retained as triiodide ion and/or polyiodide ion in organic polymers, such as starch, polyvinyl alcohol, and a polymer containing imidazolium side-chain groups. Since triiodide ion also functions as an electron acceptor, it may have a possibility as a dopant for π -conjugated polymers. As mentioned above, most of the materials capable of retaining iodine are organic polymers. If iodine can be retained stably with inorganic materials, we believe that the application of materials will expand due to the durability of inorganic materials.

So far, we have found that cationic ladder-like polymeric silsesquioxanes (SQs)² and polyhedral oligomeric SQs (POSSs)³ as soluble inorganic materials were successfully prepared by the hydrolytic condensation of organotrialkoxysilanes containing functional groups convertible to cationic substituents during the reaction.

In this study, we investigated the preparation of cationic SQs capable of stably retaining iodine. Such a SQ could be prepared by hydrolytic condensation (sol-gel reaction) of an imidazolium-functionalized trialkoxysilane having an iodide counterion in a water/methanol mixed solution of iodine (Scheme 1). Based on UV-Vis and EDX measurements, it was found that this SQ contained triiodide ions. Furthermore, even when this was heated at 100 °C, the content of iodine did not decrease so much. Furthermore, the counterion of imidazolium-group-containing POSS, which was prepared according to our previous report,⁴ was converted into triiodide ion. Consequently, even when this product was heated at 100 °C, the triiodide ion was also retained stably.

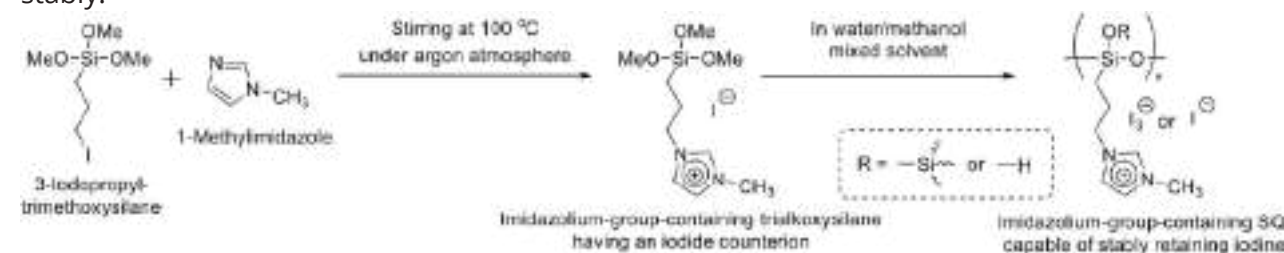


Figure 1. Preparation of imidazolium-group-containing SQ capable of stably retaining iodine.

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Combining sol-gel process and plasmonic nanostructures: an efficient strategy towards enhanced optical properties

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Abstract: Hybrid materials based on sol-gel technology have been widely investigated over the past 30 years as extremely interesting systems for optical and non-linear optical applications, such as LEDs, filters, sensors, optical protections, lasers¹. This large interest is based on the high optical and mechanical quality obtained for silica-based hybrids, and the possibility to dope them with either organic or inorganic active entities even at high loading². The difficulty in the preparation lies essentially on the compatibility between the hosting material and the guest one. Researchers have been putting large efforts in controlling the interface between the two systems, optimizing the dispersion up to large concentrations.

More recently, another alternative in improving the optical properties was explored, considering the use of plasmonic nanostructures. Plasmonics is nowadays an intense field of research in the scientific community of chemists and physicists, trying to understand and use the plasmonic response of large and sophisticated metallic nanostructures in different configurations. This communication will develop the different strategies explored to incorporate metallic nanostructures in transparent sol-gel matrices. The in-situ growth revealed important limitations in terms of dispersity, size and morphology control and the optical performances are strongly affected by those parameters. Thus, the alternative of producing the nanostructure in a first step followed by inclusion in a sol-gel system required important investigation on the interface but lead to broad range of possibilities with high quality materials³⁻⁵. Moreover, this methodology allowed numerous compositions to be prepared and unexpected optical performances to be reached in the fields of optics, nonlinear optics, photocatalysis.

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MgAl-Layered double hydroxides nanoparticles as additive for cement-based materials

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Abstract: Layered double hydroxides (LDH) are anionic clays also known as hydrotalcite type compounds, widely studied due to an important property called “memory effect”. The memory effect consists of the regeneration of the lamellar structure from the metallic mixed oxide in contact with water or anionic solutions. The mixed oxides obtained by the thermal decomposition of LDH can be incorporated into the hydrated cement in order to eliminate the cement pores due to the volumetric expansion of the particles caused by regeneration, filling small pores and improving the mechanical resistance of the cement matrix. Consequently, it is possible to obtain the increase in the mechanical strength and durability of the hydrated cement, besides that the use of additives can considerably affect the rheological properties of the material. MgAl-CO₃-LDH was prepared using the sol-gel method and the mixed oxides by the calcination of LDH. The *in situ* X-ray diffraction during calcination allowed the monitoring of structural changes of the LDH until the total collapse of the lamellar structure. The regeneration kinetics of the lamellar structure induced by the addition of deionized water and cement water (pore solution) were studied *in situ* by time-resolved wide-angle X-ray scattering (WAXS), evidencing the recovery of the LDH structure after 10 min. In addition, the WAXS results allowed verifying that the calcined LDH particles were able to regenerate the lamellar structure also when incorporated in the paste of the hydrated cement, leading to changes in the characteristic hydration phases of the cement. The basal spacing distance calculated for the regenerated samples demonstrated the high capacity of LDH to intercalate carbonate anions during the regeneration of the lamellar structure, which is one of the main ions responsible for the corrosion of the metallic structure by the carbonation process. This finding evidences the potential use of mixed oxides as a strategy to immobilize carbonate anions in the cementitious environment in order to reduce the aging effects induced by carbonation. Finally, the influence of the calcined LDH on the rheological profile of the cement was evaluated through rotational rheometry measurements with flow tests, in which the mixed oxides significantly change the shear stress curve *versus* shear rate and decreases the yield point and plastic viscosity of the hydrated cement.

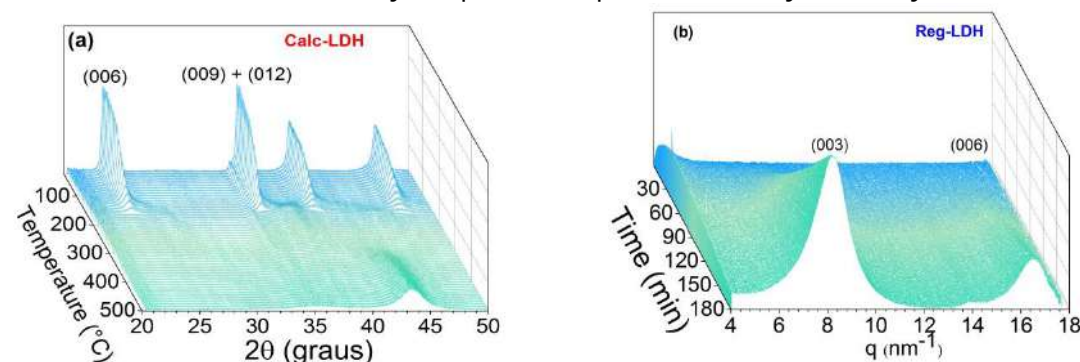


Figure 1: (a) XRD as a function of temperature during thermal decomposition of LDH and (b) WAXS monitoring of the LDH recovery at room temperature after addition of cement solution to calcined LDH.

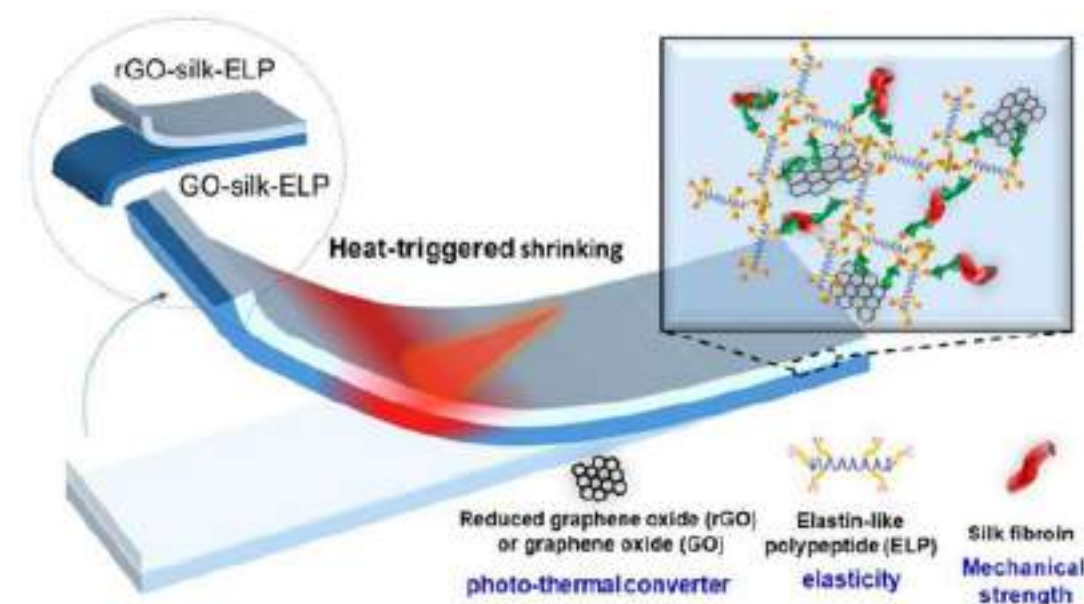
This work is a collaborative research of the members of National Institute on Advanced Eco-Efficient Cement-Based Technologies (FAPESP INCT 2014 50948-3; 465593/2014-3).

Elastin-like Polypeptide-based Hydrogel Actuation to Guide Skeletal Muscle Cells Alignment

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Abstract: The Cell alignment has been widely observed in organism which is a critical factor to differentiation and maturation in cell biology and tissue engineering. Despite several strategies including mechanical force, surface topography, electrical stimulation, and patterned chemical substrate had been studied over past decades, Herein, for the first time, a light-controlled soft actuator composed of elastin-like polypeptide, silk fibroin, graphene oxide, and reduce graphene oxide, named as ESGRG, is developed for driving cell orientation on soft actuator via remotely NIR laser exposure and high efficiency has been developed to guide cell orientation in this study. The bending force induced by photo-thermal NIR radiation response can promote cell alignment (or cell orientation effectively along the specific direction) of muscle cells, C2C12 seeded on ESGRG. Furthermore, hydrogel actuators could be easily molded into various shapes such as round and butterfly to generate different motion. This study provides the possibility, for the first time, for cell alignment achieved by bending motion of NIR-driven soft actuator, which can be utilized in applications of soft robotic and tissue engineering, such as maturation of cardiomyocyte and neuronal tissue repair.



Design of wrinkled SiO₂@TiO₂ particles for photocatalytic enhancement

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Abstract: The application of photocatalysis based on TiO₂ for environmental remediation presents several disadvantages, especially in the separation of the photocatalyst from liquid media. One way to solve this problem is to support TiO₂ nanoparticles (NPs), but TiO₂ – substrate interaction may reduce the photocatalytic activity. A strategy to increase the photocatalytic activity of TiO₂ (NPs) supported on SiO₂ spheres is to achieve an arrangement of NPs, such that the interaction with photons reaching the photocatalyst is enhanced. This work proposes to increase the photocatalytic activity of TiO₂ NPs using as support wrinkled SiO₂ spheres (w-SiO₂), in a way that the location of TiO₂ NPs leads to layers with variable effective refractive indexes that define the interaction with photons. w-SiO₂ particles (d = 460 ± 50 nm) were synthesized by bi-continuous emulsion method, and TiO₂ NPs (d = 7 ± 2 nm) were further grown by hydrothermal treatment. We designed two w-SiO₂@TiO₂ configurations by controlling the accessibility of the TiO₂ NPs to the porous system: HS, where highly dispersed TiO₂ NPs located in a SiO₂ - TiO₂ hybrid shell (~80nm); and TS, where TiO₂ is arranged as a quasi continuous shell (~15nm) of mesoporous TiO₂ on the geometrical surface of w-SiO₂ spherical particles. These configurations are schematized in figure 1. The photocatalytic activity was measured as the photodegradation rate of crystal violet (CV) at pH = 5 under UV-Vis irradiation.

Both configurations exhibit higher photo-activity per gram of TiO₂ when compared with unsupported TiO₂ NPs, but interestingly HS configuration is even more effective than TS. This fact is a consequence of complementary photon harvesting, as derived from Mie core-shell simulations combined with effective index models. Extinction numerical results have excellent accordance with experimental ones from which we conclude that enhanced photon harvesting in the HS configuration has two contributions: (i) intraparticle photon harvesting due to an effective optical path length which implies a major total absorbance in the hybrid SiO₂ - TiO₂ shell (despite the TiO₂ total mass is 2.4 times lower respect to the TS particles); (ii) inter-particle photon harvesting due to the design that combines refractive indexes, allowing greater light transmission that is then absorbed by neighboring particles. It is then demonstrated that the enhancement of photocatalytic activity can be optimized by tuning the refractive indexes of the TiO₂ support assembly through synthesis.

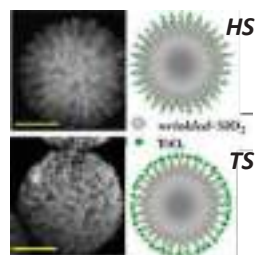


Figure 1: Schemes representing the location of TiO₂ in w-SiO₂TiO₂ HS and TS configurations and their corresponding SEM images. Scale bar = 200 nm

Thermal Insulation Materials based on Bridged Polysilsesquioxanes

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Abstract: The thermal insulation material is one of the key materials to our comfortable life and saving energy. Polyurethane foam, glass wool, and cellulose fiber are typical thermal insulation materials using around us in everyday life. In recent years, these materials are required for higher thermostability and lower thermal conductivity compared with before. To the development of new thermal insulation material, we focused on polysilsesquioxanes, that have attracted much attention as organic-inorganic hybrid materials. They exhibit remarkable thermal, mechanical, and chemical stabilities due to siloxane (Si-O-Si) bond frameworks. In particular, bridged trialkoxysilanes [(R'O)₃SiRSi(OR')₃] (R = organic bridging group) are useful as the sol-gel precursors, because the bridging part expands the siloxane network and adds various functionalities. In this study, we prepared polysilsesquioxane free-standing films and investigated their properties to explore the potential for thermal insulation material. Polysilsesquioxanes were synthesized from bis(triethoxysilyl)ethane (BTES-E1) by slightly modified acid-catalyzed hydrolytic polycondensation that was developed by Abe and Gunji [1]. We also prepared BTES-E1/polyhedral oligomeric silsesquioxanes (POSS) hybrid films by endcapping reaction of polyBTES-E1 sol, and following hydrosilylation of this sol with vinyl-POSS (Figure 1). Details of preparation conditions of sol and films and film properties will be shown on the poster.

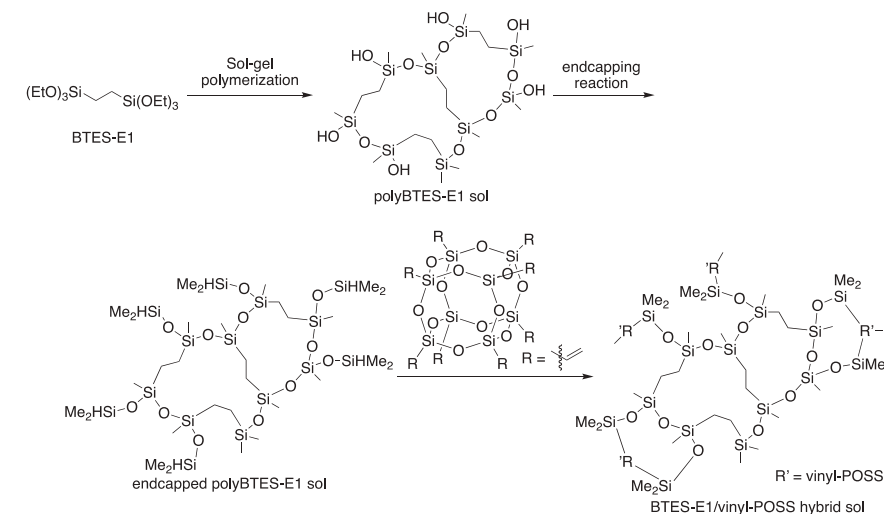


Figure 1. Synthesis of BTES-E1/vinyl-POSS hybrid sol.

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Synergistic Vertical Graphene Skeleton and S-C shell to Construct High-performance TiNb_2O_7 -based Core/Shell Arrays

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Abstract: Bespoke synthesis of wide-temperature high-power electrodes is of great importance for the development of advanced power-type lithium ion batteries (LIBs). Herein, we report a powerful combined solvothermal-electrodeposition (ST-ED) method to construct titanium niobium oxide (TiNb_2O_7) arrays sandwiched between highly conductive vertical graphene (VG) skeleton and S-C shell forming binder-free VG/ TiNb_2O_7 @S-C electrode. VG and S-C work cooperatively to establish an omnibearing conductive network on TiNb_2O_7 through internal and external integration. Positive advantages including large porosity, improved conductivity and enhanced structural stability are obtained in the VG/ TiNb_2O_7 @S-C core/shell arrays. Consequently, excellent electrochemical high-power performance at medium-high temperature (25 to 70 °C) is demonstrated for the designed VG/ TiNb_2O_7 @S-C electrodes, which show a high capacity from 284 to 354 mA h g⁻¹ at 1 C, and 181 to 241 mA h g⁻¹ at 160 C as the working temperature increases from 25 to 70 °C. Additionally, remarkable high-temperature (70 °C) cycling span is proven for the VG/ TiNb_2O_7 @S-C electrode with a capacity of 203 mA h g⁻¹ at 40 C after 5000 cycles. The synergistic positive effect from VG and S-C shell is responsible for the enhancement of high-power capability. Our work paves the road for fabrication of novel high-power electrodes for electrochemical energy storage.

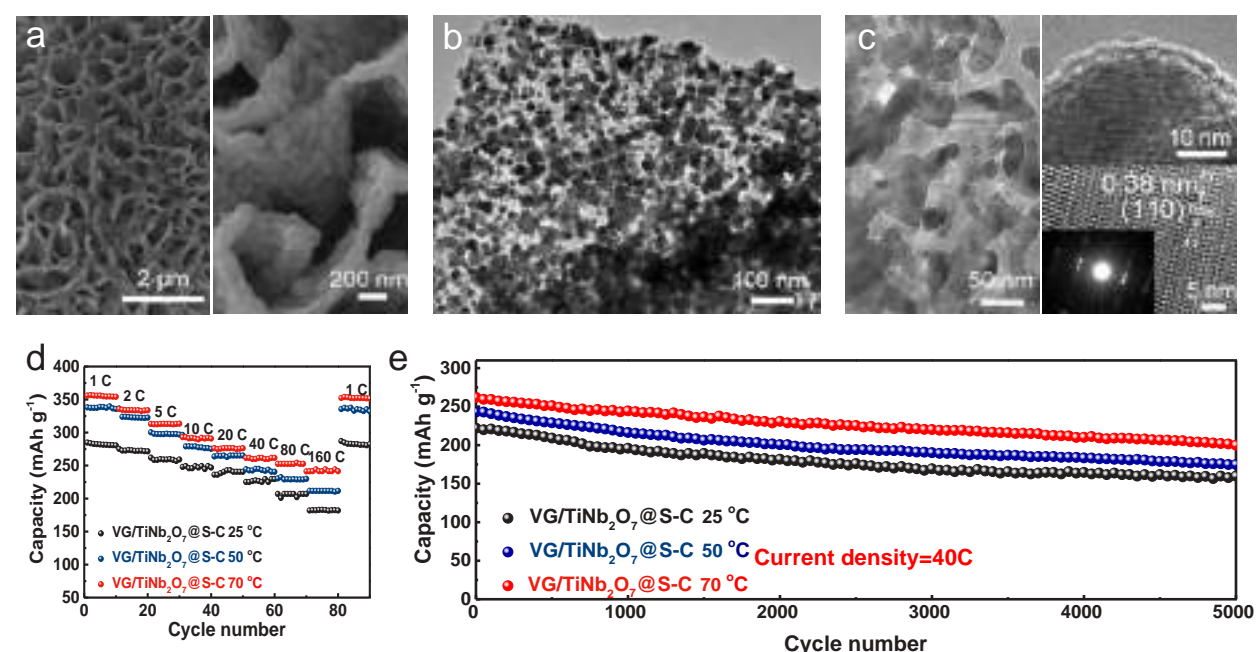


Figure 1. (a) SEM images and (b-c) TEM-HRTEM images of VG/ TiNb_2O_7 @S-C sample; (d) Rate performance and (e) cycling performance of VG/ TiNb_2O_7 @S-C electrodes at 25, 50 and 70 °C.

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Preparation of POSS-linking polymers containing catechol component and their adhesive properties

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Abstract: It is well known that mussels can strongly adhere to various organic and inorganic surfaces due to the function of adhesion protein excreted from mussels. This protein contains catechol components. Therefore, a number of synthetic organic polymers containing catechol components in the side-chains have been prepared so far.^{1,2} However, in consideration of long-term use in the natural environment, development of the adhesives excellent in UV and heat resistances are required.

Recently, we reported that soluble ladder-like polysilsesquioxane (PSQ) containing catechol component in side-chains [PSQ-Ph(OH)₂] were prepared by reaction of ammonium-group-containing ladder-like PSQ³ with 3-(3,4-dihydroxyphenyl)propionic acid using condensing agents.⁴ PSQ-Ph(OH)₂ could be adhered even at high temperature (200 °C). However, PSQ-Ph(OH)₂ could not endure the strain derived from the temperature change in the substrates with different thermal expansion coefficients, i.e., stainless-steel and glass, because this polymer has a rigid main-chains.

Therefore, we focused on ammonium-functionalized polyhedral oligomeric silsesquioxane polymer (POSSP-Am)⁵. This polymer was relatively flexible compared with PSQ-Ph(OH)₂ at high temperature. In this study, we investigated the preparation of a POSS-linking polymer containing catechol component in side-chains [POSSP-Ph(OH)₂] (Scheme 1). In addition, we evaluated the adhesion properties of this polymer and mixtures of POSSP-Ph(OH)₂ and PSQ-Ph(OH)₂ using different inorganic materials, such as stainless-steel plate and glass plate, at various temperature.

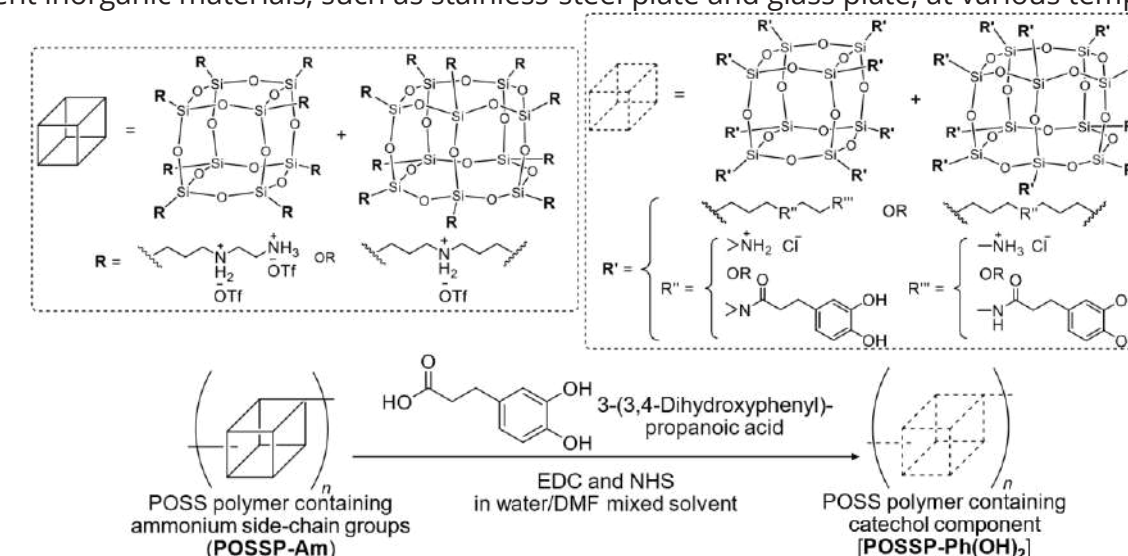


Figure 1. Preparation of POSS-linking polymer containing catechol component in side-chains.

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Preparation and Characteristic Evaluation of Quercetin-loaded Polyacrylate Adhesive Gel for Enhanced Activity of Brown Fat Cell

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Abstract: Obesity characterized by the excessive adipose tissue is a chronic disease with the associated risk on the development of other diseases. Recently, it has been pointed out that white fat can be browned into brown fat which contains a lot of mitochondria and can consume energy. Browning white fat may be a potential weight loss method. Quercetin, a widely consumed dietary flavonoid, has a great potential as an anti-obesity agent because of its ability to induce lipolysis and β oxidation in adipocytes. In addition, quercetin was found to induce browning in white adipose tissue. Therefore, in this study, the synthesis of quercetin-loaded adhesive composite would be first studied using polyarylate and quercetin in different solvents via low temperature drying process. The effect of composition and preparation process of quercetin-loaded composite on morphology, distribution and cell biological function are analyzed. In addition, we will further focus on the effect of the quercetinloaded composite on the browning of white into brown fat. The result showed that the composite prepared at low temperature in acetone displayed uniform morphology and achieved high quercetin encapsulation efficiency. The in vitro cell culture test showed that quercetin-loaded composites were biocompatible to L929 fibroblasts. Furthermore, the browning in differentiated 3T3-L1 adipocytes can be enhanced by controlling the quercetin release of the composite. As expected, this study can provide the possibility for achieving effective weight loss control using a low-cost intramuscular patch with quercetin-loaded composite adhesive gel through transdermal drug delivery.

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An AIE Chemosensor for Drugs Detection Based on POSS-core Dendrimer and Controlled Self-assembly Behaviors

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Abstract: Recently, the effect of "aggregation-induced emission" (AIE) has gained increasing academic interest in numerous scientific fields due to the unusual photophysical phenomenon that they are non-luminescent in the solution state but become strongly emissive when aggregated. Most of the working mechanism of AIE chemosensors is to detect target objects through impacting AIEgens aggregations with specific recognition groups, which are clearly limited in universal applications and suffer from poor fluorescence intensity. So developing a novel universally applicable AIE chemosensor with excellent photophysical properties for aromatic molecules by non-covalent interaction forces and supramolecular self-assembly is feasible and meaningful. Over the recent twenty years, the prevalence of synthetic drugs including methamphetamine and ketamine as the main illicit drugs is clearly increasing. Compared to analytical techniques of synthetic drugs that require large-scale inspection instruments, AIE chemosensors have unique advantages of its convenience, low cost, high sensitivity as well as on-site workability.

For this, an eight tetraphenylethene (TPE) modified polyhedral oligomeric silsesquioxane (POSS) dendrimer is designed and synthesized as an aggregation-induced emission (AIE) chemosensor. The photophysical properties of POSS-TPE were screened using UV-vis absorption and fluorescence spectroscopy in different solvents. The results showed that POSS-TPE exhibited great enhancement of unique monomer emission, aggregate emission and AIE quantum yields because of its special molecular structure and self-assembly properties. Then the aggregation structures of POSS-TPE solvents were observed to study the self-assembly behaviors by SEM and TEM. We can conclude that POSS-TPE had special self-assembly morphologies in different solvents at different concentration which improved the photophysical behaviors. What's more, the intriguing AIE effect of POSS-TPE prompted us to explore their potential applications as a chemosensor for synthetic drugs. It has been identified that POSS-TPE could on-site fast detect methamphetamine and ketamine even in artificial saliva through quenching aggregate emission, which is crucial to punish drug crime and maintain social security.

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Au/TiO₂ sol gel catalysts for hydrogen production under illumination with ultraviolet and visible radiation

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Abstract: Hydrogen is an interesting alternative to fossil fuels because its direct combustion does not generate pollutants or greenhouse gases. There are different ways to obtain H₂. Between them photocatalytic hydrogen generation from water splitting at room temperature under non-aerated conditions is a promising option. In this work bare mesoporous nanocrystalline support was prepared combining a hydrolysis process of titanium(IV) butoxide on Aerioxide® surface with sol-gel process. Au was deposited by the deposition-precipitation method with urea on the surface of modified-TiO₂. The samples were used for hydrogen production through the photocatalytic separation of water at room temperature and atmospheric pressure, using methanol as sacrificial reactive and simultaneous ultraviolet and visible radiation as excitation source. Figure 1a) shows the emission spectra of the lamps and Figure 1b) contains the hydrogen production as function of the illumination time. There is a clear dependence with the kind of lamp used. We also studied the H₂ generation dependence with the stirring speed, and amount and size of the Au particles. A discussion of the results is presented.

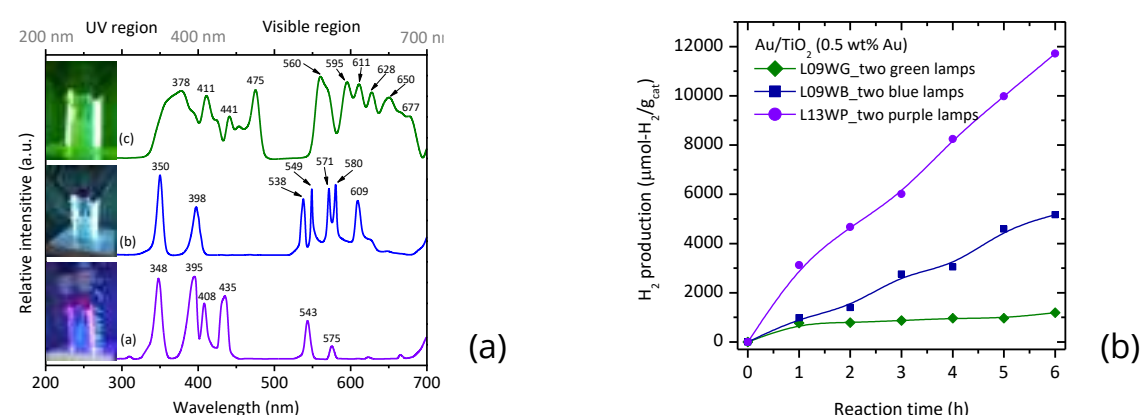


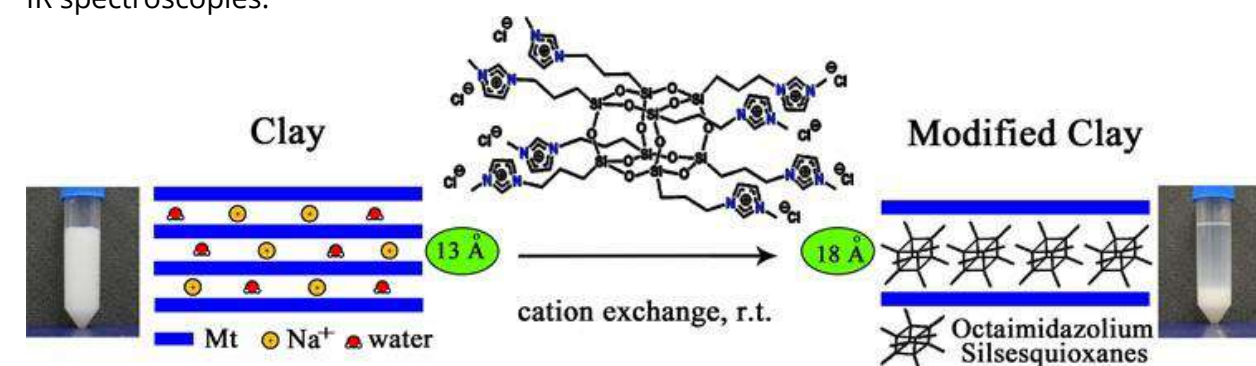
Figure 1. a) emission spectra of the used lamps. b) H₂ production as function of the irradiation lamp.

Acknowledgements We acknowledge the financial support from SECITI/053/2016 Project, Antonio Morales and Xim Bokhimi (XRD), Roberto Hernandez and Diego Quiterio (HRTM), V. Maturano and R. Zanella (N₂physorption).

Modifying interlayer space of montmorillonite with octakis (3-(1-methylimidazolium)propyl) octasilsesquioxane chloride

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Abstract: Highly water-soluble material of multi-imidazolium based silsesquioxane cages (material 2) is a promising candidate for modifying clay mineral interlayer space, which is successfully demonstrated by using montmorillonite. The modified montmorillonite can be easily prepared via cation exchange reaction between material 2 and sodium ions of montmorillonite, dispersed in an aqueous solution at room temperature. The modified montmorillonite formed a precipitate within a few seconds. A single layer of material 2 found to be intercalated in the modified montmorillonite with a maximum interlayer space (d-value) of 18 Å (1.8 nm) from 13 Å (1.3 nm) of the unmodified one was confirmed by transmission electron microscopy (TEM) and X-rays diffraction (XRD). Moreover, the percentage uptake and nature of incorporation of material 2 into montmorillonite layers were investigated by thermal gravimetric analyses (TGA), ²⁹Si NMR and FT-IR spectroscopies.



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Syntheses and photophysical properties of pyrene functionalized-cyclic siloxane (D₄)

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Abstract: Cyclic siloxanes compose of Si-O backbone and organic functions, which their functionalizations could lead to increase more properties of this material including optical properties, isomeric properties, and adsorption properties. For example, small cyclic siloxanes such as hexamethylcyclotrisiloxane (D₃), octamethylcyclotetrasiloxane (D₄) and decamethylcyclopentasiloxane (D₅) were used as a monomer to prepare a polydimethylsiloxane (PDMS) in silicone industrial. But none of them can be further modified in organic functions. Herein, tetramethyl-vinylcyclotetrasiloxane (TMVS) can be functionalized with 1-bromopyrene through Heck reactions to obtain pyrene functionalized-cyclic siloxane. The chemical structures of desired products were characterized by IR, NMR and MS, while their photophysical properties can be studied by UV-Vis and fluorescent spectroscopies.

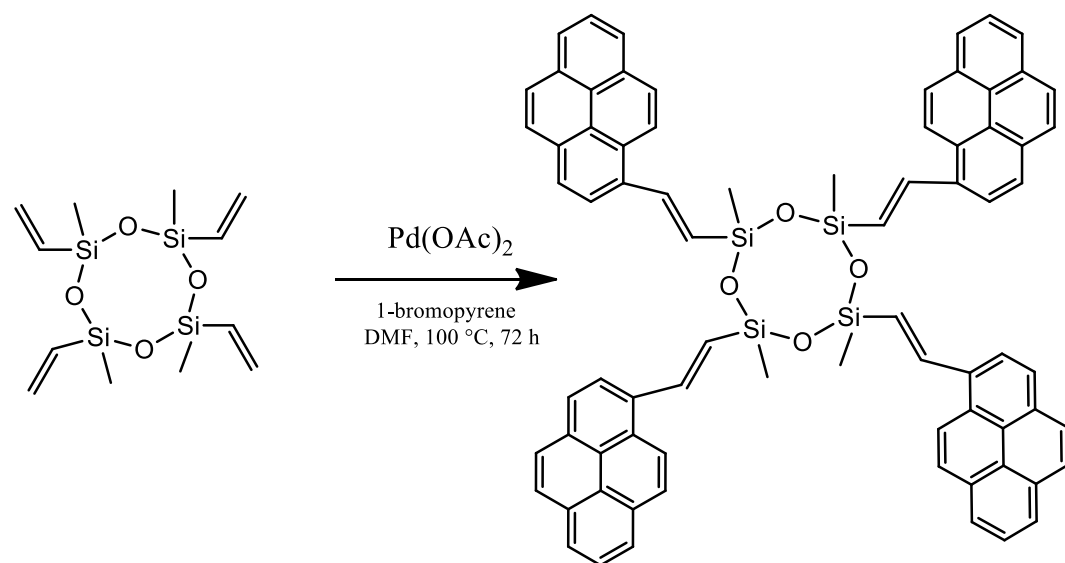


Figure 1. Synthesis of pyrene-functionalized cyclotetrasiloxane by heck reaction

Heterocoagulation and (homo)coagulation processes in bicomponent nanodisperse systems containing promising for use in sol – gel technology cerium and aluminum oxides

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Abstract: The process of heterocoagulation is vital in industry and scientific research. For instance, some core-shell structures are obtained using heterocoagulation as a driving force in the synthesis, Pickering emulsions are based on heterocoagulation phenomenon as well as sol-gel synthesis of ceramics.

Heteroaggregation in mixed CeO₂-Al₂O₃ hydrosols (commercial CeO₂ "Sigma Aldrich", primary particle size d₀ < 25 nm and γ-Al₂O₃ AEROXIDE Alu C "Degussa", 13 nm) with different numerical particle concentrations was studied at natural pH 5.6 and various NaCl concentrations. However, in order to investigate heterointeractions in mixed dispersions one should study the aggregate stability of monocomponent sols. Hence, the mono- and bicomponent hydrosols were both studied using the combination of spectroturbidimetry, dynamic light scattering and laser Doppler's electrophoresis. The coagulation thresholds, the corresponding hydrodynamic radii and electrophoretic mobility (zeta potential) were found for all systems under investigation at chosen conditions.

In bicomponent mixture three processes may occur: particle 1 interacts with the same particle 1, particle 2 interacts with 2 and particle 1 interacts with particle 2. In order to estimate the impact of hetero interactions in stability of the system, the approach of comparison of real and idealized optical density dependence on time was developed. Also, calculations in the framework of classical DLVO, extended DLVO (EDLVO) theories and the theory of heterocoagulation were carried out and the parameters of boundary layers near the surface of particles were estimated.

The reported study was funded by RFBR, research project № 17-03-01228a.

Temperature-responsive behavior of POSSs containing ammonium side-chain groups

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Abstract: Most of temperature-responsive materials are organic polymers, e.g., poly(N-isopropylacrylamide) (PNIPAM), whereas temperature-responsive oligomers are not common. In particular, to the best of our knowledge, temperature-responsive materials consisting of inorganic oligomers have not been reported. Polyhedral oligomeric silsesquioxanes (POSSs) are cage-like inorganic (siloxane) oligomers, which have thermal and chemical stabilities as inorganic compounds, as well as solubilities as organic compounds. So far, we have reported that ammonium-functionalized POSSs could be prepared by the hydrolytic condensation of amino-group-containing organotrialkoxysilanes using a superacid trifluoromethanesulfonic acid (HOTf) in higher yield with shorter reaction time.^{1,2} Furthermore, the effect of the reaction solvents on the preferential formation of crystalline cage-like octamer (T₈-POSS) and amorphous cage-like decamer (T₁₀-POSS) was also investigated.^{3,4}

In this study, we found that ammonium-functionalized T₈POSS with triflate anion (OTf⁻) as a counterion (Am-T₈-POSSOTf, Figure 1a) in water indicated temperature responsiveness. When aqueous suspension of Am-T₈-POSS-OTf was heated to 65 °C, it became transparent. Then, when this transparent aqueous solution was cooled to 40 °C, it became turbid (Figure 2). Since these behaviors were observed even after heating and cooling repeatedly, we consider that Am-T₈-POSS-OTf is regarded as a temperature responsive material.

For comparison, the temperature-responsive properties of ammonium-functionalized T₈-POSS with chloride anion (Cl⁻) as a counterion (Am-T₈-POSS-Cl, Figure 1b) and T₈-POSS (with OTf⁻ counterion) containing two ammonium groups in the repeating unit (2Am-T₈-POSS-2OTf, Figure 1c) were also investigated in water by heating and cooling. Consequently, they were transparent at 5–90 °C (Figure 3,4), indicating no temperature responsiveness. Furthermore, when ammonium-functionalized T₁₀POSS with OTf⁻ as a counterion (Am-T₁₀-POSS-OTf, Figure 1d) was heated and cooled in water, it did not indicate temperature responsiveness (Figure 5).

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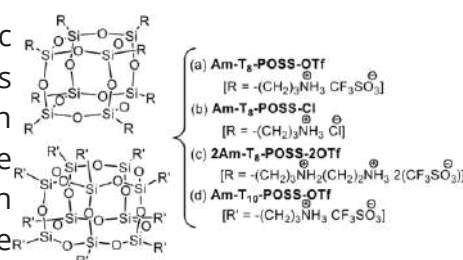


Figure 1. Structures of ammonium-functionalized POSSs.

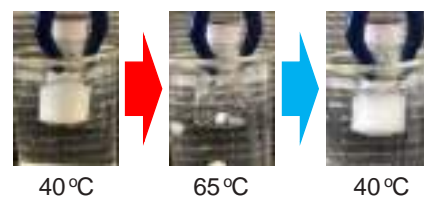


Figure 2. States of Am-T₈-POSS-OTf in water

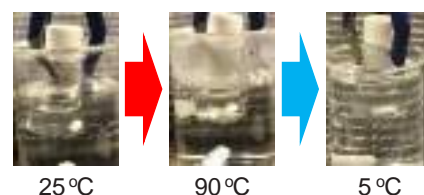


Figure 3. States of Am-T₈-POSS-Cl in water

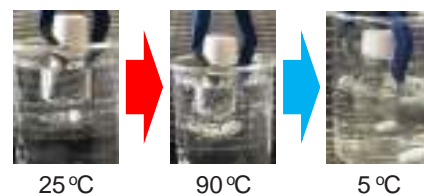


Figure 4. States of 2Am-T₈-POSS-2OTf in water

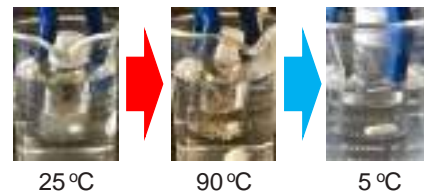


Figure 5. States of Am-T₁₀-POSS-OTf in water

Synthesis of new hierarchical flower-like structures

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Abstract: Hierarchical composite materials have a wide range of useful functions that can be adjusted by varying the composition, ratio of components and synthesis conditions. The most promising are materials with core-shell structure. In the present work we describe synthesis of magnetic composite composed of 3 components – magnetic core Fe₃O₄ with double cover of SiO₂ and layered double hydroxide (LDH). LDH are hydroxosalts with general formula $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]^{x+}[(A^n)_{x/n} \cdot m\text{H}_2\text{O}]$ where M²⁺ and M³⁺ are cations of metals, Aⁿ⁻ represents inorganic or organic anions. LDH are widely used as sorbents and catalysts, Fe₃O₄ core provides separating material by magnet, SiO₂ shell allows to co-precipitate LDH to Fe₃O₄ surface.

Magnetic nanoparticles were synthesized by co-precipitation from an aqueous solution of iron (II) chloride and iron (III) sulfate with a 1:2 molar ratio in an alkaline medium.

The shell of silicon dioxide on the surface of Fe₃O₄ particles was obtained using the modified Stober method [1]. The molar ratio of the components was as follows: Fe₃O₄: TEOS: C₂H₅OH: H₂O: NH₄OH = 1: 2: 50: 125: 35.

Resulting particles of Fe₃O₄@SiO₂@LDH were synthesized *insitu* by co-precipitation using the modified procedure described in [2]. The molar ratio of Mg:Al:Fe was 3:0.75:0.25.

Morphology of the samples was investigated using Transmission Electron Microscopy (TEM) analysis performed on a JEOL JEM 2100 microscope. The micrographs confirm the formation of flower-like structures (fig.1B). Powder X-ray diffraction (XRD) data were collected on a Rigaku Ultima IV diffractometer using CuKα radiation. The reflections correspond to mixed iron oxide and LDH of hydrotalcite type. Thermogravimetric analysis (TGA) was carried out, measurements were collected using a Q600 from TA Instruments. Magnetic susceptibility was determined using a magnetic susceptibility meter KLF-4 (AGICO). Sorption capacity of the synthesized material was determined towards anionic organic dye Congo red.

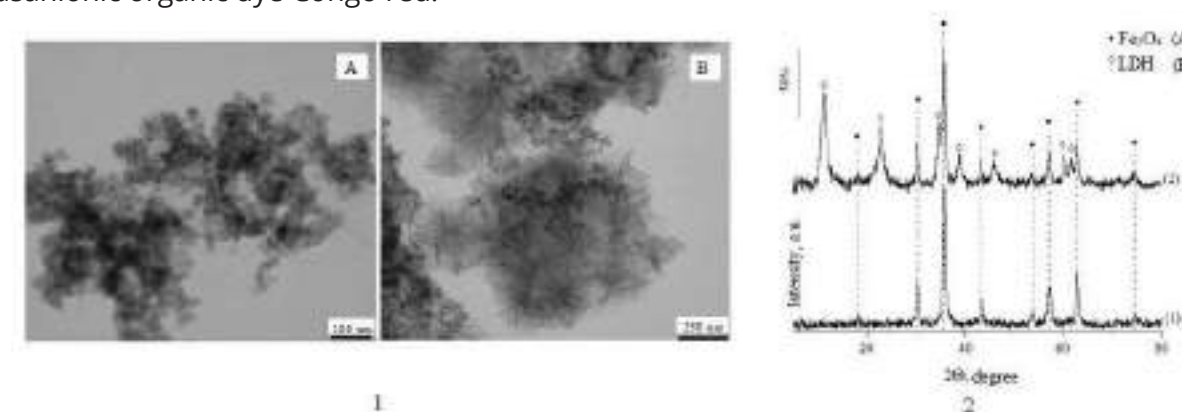


Figure 1. Characterization of the synthesized samples:

1 - TEM microphotographs of: (A) SiO₂@Fe₃O₄; (B) Mg/AlFe@SiO₂@Fe₃O₄; 2 - Powder X-ray diffraction patterns of: (1) SiO₂@Fe₃O₄; (2) Mg/AlFe@SiO₂@Fe₃O₄

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Fluorescent materials conjugated with Silsesquioxane cages as fluoride sensors

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Abstract: Silsesquioxanes (SQ) cages are classified as hybrid inorganic-organic materials, which consist of inorganic Si-O-Si framework surrounded with organic functions. Recently, those materials found to be used as a host material for anionic recognition. By uses the chemical benefits of thermodynamically stable Si-F, fluorescent polycyclic aromatic hydrocarbons (naphthalene, anthracene, phenanthrene, and pyrene) conjugated octameric silsesquioxane cages can be prepared and used as a fluoride sensor. The desired products can be characterized by FTIR, ¹H, ¹³C, ²⁹Si NMR, while their photophysical properties can be studied by UV-Vis and fluorescent spectroscopies. Furthermore, the screen of fluoride chemosensor and its sensing mechanism will be investigated later on.

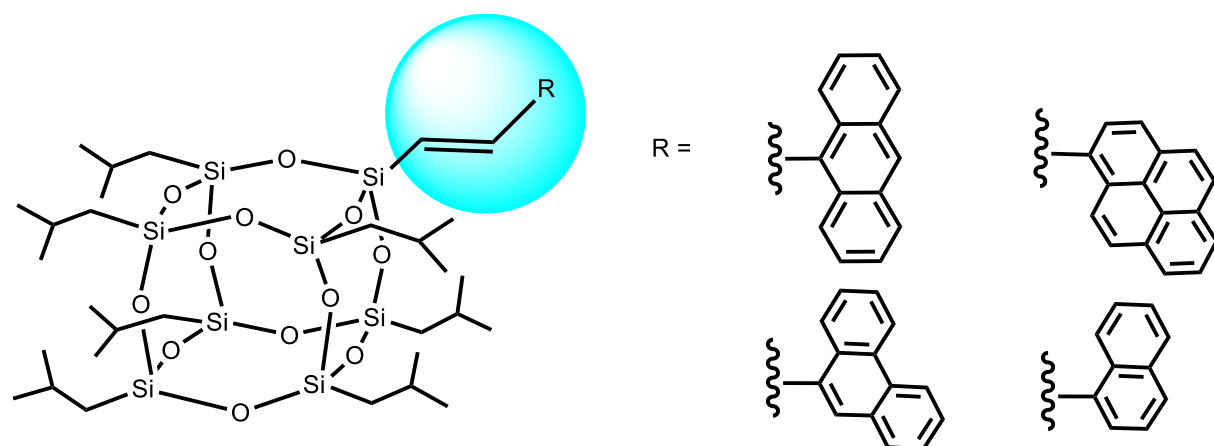


Figure 1. Molecular structures of fluorescent polycyclic aromatic hydrocarbons conjugated with silsesquioxane cages

Anthracene functionalized-triethylvinylsilane for anion detection

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Abstract: Recently, the development of anion sensing has received significant attention in chemo sensor. To take the benefit of strong bonds (Si-F, Si-O, Si-N etc.), silicon based materials may be applicable to be used in one of those sensing applications. In this work, anthracene functionalized-triethylvinylsilane can be prepared by Heck reaction between 9-bromoanthracene and triethyl vinyl silane. The desired product can be purified by column chromatography, which will be further characterized by ¹H NMR, ²⁹Si NMR, and mass spectrometry. Upon the addition of various anions such as fluoride, bromide, cyanide, chloride, and hydroxide ions, its photophysical properties will be investigated by UV-Vis and fluorescent spectroscopies.

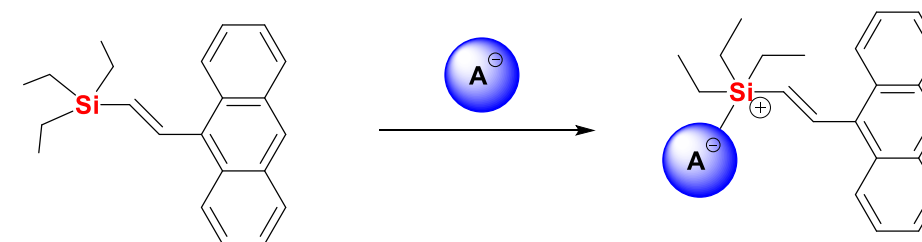


Figure 1. Anionic recognition of anthracene functionalized-triethylvinylsilane

Sol-gel bioprinting

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Abstract: 3D printing is raising high hopes in regenerative medicine. It allows the design of on demand structurally complex scaffolds for tissue engineering.[1] Hydrogels are highly attractive biomaterials for 3D printing as extracellular matrix surrogates.[2] Our team previously reported the 3D printing of biocompatible hydrogels from silylated PEG derivatives.[3] Nonetheless, PEG is biocompatible but bioinert, and is a poor mimic of extracellular matrix. As an alternative, we considered polysaccharides which are extensively used in bioprinting and showed a good interaction with cells.[4]

Physical hydrogels are the most of the time use for 3D printing (i.e hydrogel from alginate [4]), but chemical hydrogels are also very interesting since they display better tunability, mechanical properties, and higher stability than physical hydrogels. In our approach, we describe the design of the first modified oligosaccharide-based hydrogel that can be cross-linked at pH 7, by inorganic polymerization (sol-gel process) in the presence of cells.

The sol-gel process involves metal-containing molecular precursors, which react together to form a metal oxide as an inorganic network. This polymerization can be performed under mild experimental conditions, i.e. neutral pH, in water and at low temperature.

We demonstrated that this bioink could be used for the 3D printing of human mesenchymal stem cells (hMSC)-embedded cellulose hydrogel scaffold. Interestingly, this hydrogel can be easily functionalized in a covalent way using other alkoxysilylated molecules mixed with the silylated polymer during sol-gel process.

This strategy is generic enough to be applied to any type of biopolymer and bioactive molecules such as peptide ligands, drugs, growth factors or imaging agents to prepare a wide range of tunable bioinks to address many applications and other 3D printing techniques.

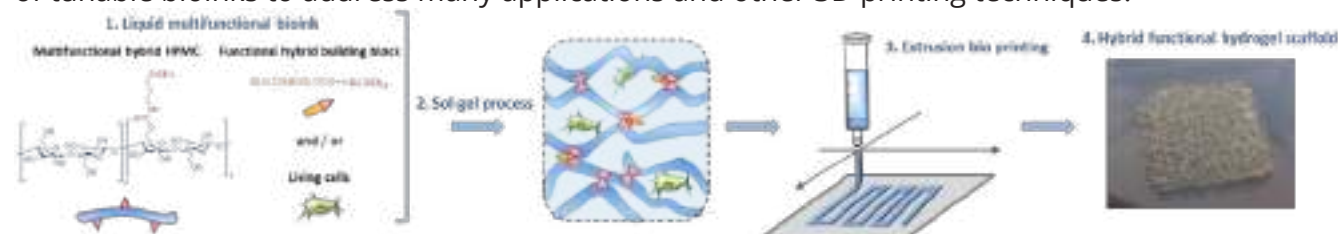


Figure 1. Hybrid cells containing hydrogels from HPMC-Si and sol-gel 3D printing.

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Influences of SF characteristics on properties of sequential SF/HA hydrogels for applications in regenerative of nucleus pulposus

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Abstract: Varying strains of silk fibroin (SF) polymers (e.g., tyrosine contents) and hyaluronic acid (HA) were sequentially crosslinked by BDDE and HRP/H₂O₂ crosslinking reagents, respectively, to produce rheological properties of inter-penetration network hydrogels (e.g., SH-IPN hydrogels) for biomedical applications. The strain of high amounts of tyrosine (Tyr) in SF increased the intensity of UV-excitable blue fluorescence, and revealed higher values of the viscoelastic properties (e.g., G', G'' and δ) of SH-IPN hydrogels than those of the strain of low amounts of tyrosine in SF in the hydrogels since SF-IPN hydrogels were produced by formations of di-tyrosine bonds in SF polymers by enzymatic HRP/H₂O₂ crosslinking reactions. In additions, increasing the weight ratios of SF to HA in fabricating HS-IPN hydrogels increased the values of viscoelastic properties of the hydrogels. For evaluations the bioactivities of the hydrogels, the seq. SH7-IPN hydrogels were used to regenerative of nucleus pulposus (NP) by inducing chondrogenic differentiations of human bone marrow-derived mesenchymal stem cells (hBMSC) *in-vitro*. Notably, 3D hBMSC micro-aggregates were first formed in proliferation, and after they were induced by using TGF- β for 7 days, their gene expressions of collagen type II were enhanced but collagen type I reduced. Moreover, histochemical staining revealed that the gels highly supported the chondrogenic differentiations of hBMSC microaggregates with promoting the expressions of glycosaminoglycan and collagen type II. In summary, novel SH-IPN hydrogels were fabricated, characterized and evaluated by possible applications of regenerative medicine such as regenerative of NP.

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Hierarchically porous zirconia through precursor-directed large-scale synthesis

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Abstract: Two new precursors, produced by modification of zirconium t-butoxide with 1-dimethylamino-propanol-2 (HDMAP), solid $Zr_2(DMAP)_3(O^tBu)_5$ (1) and liquid $Zr_2(DMAP)_4(O^tBu)_4$ (2), were obtained by reaction of 1.5 and 2 equivalents of HDMAP respectively in toluene on $Zr(O^tBu)_4$. The produced compounds were characterized by FTIR, 1H and ^{13}C NMR and TGA to estimate their stability and volatility. Action of traces of water in solvents or contact with humid air transform 1 and 2 into less soluble crystalline $Zr_2(DMAP)_3(O^tBu)_4(OH)$ (3). Molecular structures of compounds 1 and 3 were established using single crystal X-ray studies and for 2 was elucidated applying 2D 1H - ^{13}C correlated NMR spectra. The crystals of 1 were subjected to hydrolysis via either storage in ambient atmosphere or immersion into boiling water and resulting products were characterized by XPD, TGA, SEM and AFM techniques. The product of hydrolysis in air, ZrO_2 -1, is essentially non-porous, while hydrolysis in boiling water results in ZrO_2 -2 with hierarchical macro, meso and microporosity. Both materials are essentially X-ray amorphous with diffraction patterns appearing as oblique curves, resembling unresolved profiles of the monoclinic baddeleyite structure of ZrO_2 . Heat treatment at 200 and 400°C does not affect essentially the morphology or porosity and leaves phase composition unchanged, while that at 600°C converts both samples into tetragonal ZrO_2 phase. The ZrO_2 -2 material is via this treatment losing microporosity and becoming macro-mesoporous with well-defined pore size about 3 nm. Heat treatment at 900°C results in collapse of pores and transformation into a well-defined monoclinic baddeleyite structure for both materials [1].

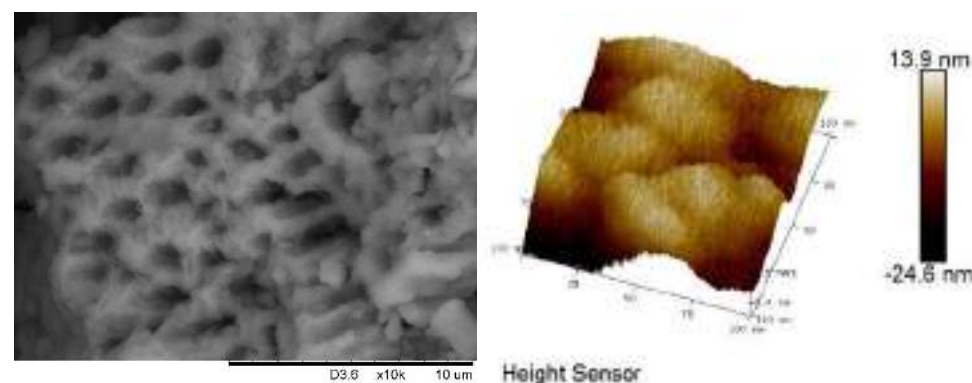


Figure 1. Porous ZrO_2 structure produced from 1 by hydrolysis in boiling water.

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Peroxo-methods for the synthesis of mixed metal-oxide materials

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Abstract: Mixed oxides of Group IV metals and alkaline-earth metals find application as ceramic semiconductors, biocompatible materials, adsorbents and catalysts. A significant problem arising in the preparation of mixed metal oxides is the difference in the hydrolysis rates of different metals. One of the best approaches is the use of an intermediate stage with H_2O_2 . In this case, peroxo-hydroxo complexes with the composition $[M(O-O)(OH)_x]_y$ are formed. We have developed several methods for obtaining mixed MO_x/SiO_2 oxides by peroxo route.

1. The TiO_2/SiO_2 based hydrogel is prepared by precipitating TiO_2 and SiO_2 from aqueous solutions of sodium silicate and titanium oxysulfate. The hydrogel is washed with water and dissolved in hydrogen peroxide in the presence of tartaric acid. A clear, non-opalescent, bright orange solution is formed. It is slowly evaporated in a water bath until formation of a polymer gel, then dried in vacuo and calcined in air at 470°C. The obtained samples consist of a silicate matrix, into which TiO_2 granules are included. The granules have a size of about 5 nm and 100% anatase phase. The surface area is $<300 \text{ m}^2/\text{g}$ [1, 2].

2. The method is similar to the previous one, but organic ligands not are used. A bright orange solution is left to decompose hydrogen peroxide. An orange precipitate forms, which is aged and washed with water. Peroxo groups decompose above 250°C. The anatase-rutile transition in TiO_2 granules is observed at lower temperatures than in the samples obtained without the peroxo stage [3].

3. The method is similar to the previous one before the stage of obtaining a solution of the peroxo complex of titanium and silicic acid. HNO_3 is added until pH equals 2 in the resulting bright orange solution, which is then transferred to an autoclave and thermostatted. The precipitate is then washed with water and dried. In this process the silica is adsorbed on the pre-formed TiO_2 particles. This separates the particles of titania from each other and controls the crystals growth. This sample has very high photocatalytic activity [4].

4. In the first stage, the solutions of $MgSO_4$ and $ZrOCl_2$ are co-precipitated with alkali. The obtained hydrosol is washed with water and dissolved in H_2O_2 . Then the Pechini-type method is applied. On the surface the homogeneous distribution of acidic and basic sites is observed. The sample exhibits high activity and selectivity with respect to the mesitylene in the self-condensation reaction of acetone [5].

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The study of aggregation processes in mono- and bicomponent ZrO_2 and $\gamma\text{-Al}_2\text{O}_3$ hydrosols

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Abstract: Heterocoagulation process plays the major role in the sol-gel production of composite oxide materials including ceramics on the base of zirconia and alumina powders. In this process, interacting particles can differ by nature, size and form, degree of their hydrophilicity and electrosurface properties. The study of mixed disperse systems is important for progress in sol-gel technology area as well as for the solution of a number of theoretical questions of the general theory of disperse systems stability, in particular, for the mixed systems with components considerably differing with hydrophilicity, as in case of $\text{ZrO}_2\text{-Al}_2\text{O}_3$ mixture.

In the present work, electrosurface properties and aggregate stability both one - and two-component (at various ratio of numerical particle concentrations) hydrosols prepared on the base of $\gamma\text{-Al}_2\text{O}_3$ AEROXIDE Alu C "Degussa" (the average size of primary particles (d_0) is 13 nm) and ZrO_2 "Vekton" ($d_0 = 24$ nm) powders at various pH (4.2, 5.6, 9.5, 11) and concentration of background electrolyte (NaCl) were studied. We consider cases at different pH when the interacting diverse particles are the same as well as opposite charged.

The colloid-chemical behavior of monocomponent and mixed sols was studied using the methods of turbidimetry, dynamic light scattering, laser Doppler's electrophoresis, dynamic potentiometric titration. The thresholds of slow and fast coagulation, hydrodynamic radii and electrophoretic mobility (zeta-potential), surface charge, isoelectric points and points of zero charge were found for all investigated systems. Theoretical study of oxide hydrosols were carried out in the framework of the classical and extended DLVO theories and the extended theory of heterocoagulation (the theory of interaction of diverse particles taking into account the structural component of the particle interaction energy). The energy of pair interaction of identical and diverse particles, factors of sol stability, coefficients of the delay of heterocoagulation process, the Hamaker constants for composite particles and also for aggregates, taking into account their non-monolithic structure, are calculated.

Parameters of the structural components for the interaction of ZrO_2 and Al_2O_3 particles are determined. The necessity of taking into account three types of possible interactions between particles (at the initial stage) in mixed dispersions even in case of intensively proceeding process of mutual coagulation is shown. Influence of a ratio of numerical particles concentration on bicomponent sol stability is analyzed.

The reported study was funded by RFBR, research project № 17-03-01228a

N-doped carbon layer modified $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ particles anchored at carbon cloth as flexible electrode for sodium-ion batteries

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Abstract: The invention of rechargeable lithium ion batteries (LIBs) has dramatically changed our lives around the world. However, a growing research orientation on alternatives to LIBs is in full swing on account of the high cost and scarcity of lithium. The emergence of sodium ion batteries (SIBs) has achieved great attention with similar physicochemical properties to lithium and referential developed fundamental theories of LIBs. Achieving high-performance SIBs has the particular challenge of designing advanced electrode materials with judicious design/construction. In this work, we construct an integrated $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ particles with modified N-doped carbon layer anchored at conductive carbon cloth (NVP/NC@CC) as flexible electrode via a facile impregnation method and following annealing process. The NVP precursor sol wrapped the surface of carbon cloth and then formed particles after heating treatment. By this ingenious design, the performance of electroactive material is enabled to be enhanced significantly. It is discovered that such NVP/NC@CC membrane can render 80.7 mA h g^{-1} at high rate of 50 C and satisfactory cycling stability, which is due to the improved electrochemical kinetics resulting from the highly conductive N-doped carbon layer and carbon cloth substrate. A symmetric full cell based on NVP/NC@CC as both cathode and anode is further assembled. This full cells exhibit both encouraging rate performance and long cycle life with a capacity retention of 88% after 2500 cycles at 10 C. The results demonstrate a convincingly design strategy for constructing high-performance electrode materials for SIBs.



Figure 1. Schematic illustration for the formation of the NVP/NC@CC flexible electrode.

Efficient Adsorption and Sustainable Degradation of Gaseous Pollutants using rGO-TiO₂ Photocatalyst

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Abstract: Two types of volatile organic chemicals (VOCs), acetaldehyde and o-xylene, were selected to probe the different adsorption and photodegradation mechanism of gaseous photocatalysis. Reduced graphene oxide (rGO)-TiO₂ nanocomposites were prepared by facile solvothermal process to perform the photocatalytic reactions. In the experiments, the removal efficiencies of the acetaldehyde and o-xylene at 80 mL·min⁻¹ flow rate were only 15% and 12% when P25 was applied, while the efficiencies were sharply increased to 42% and 54% by using 0.5wt% rGO-TiO₂ as the photocatalyst, respectively. Interestingly, it is notable that the removal efficiency of o-xylene was higher than that of acetaldehyde with identical rGO-TiO₂ photocatalyst. Experiments suggested that there were possibly two reasons. Firstly, the adsorbance of o-xylene was more than that of acetaldehyde owing to the π - π conjugation between rGO and aromatic compounds, which was proved by adsorption equilibrium and TPD tests. ESR test proved that rGO can promote the generation of surface \cdot OH radicals and depress the \cdot O₂⁻ radicals formation. Compared with the dominant role played by \cdot O₂⁻ radicals in the degradation of acetaldehyde, an almost equal position of \cdot O₂⁻ and \cdot OH radicals was observed in the degradation of o-xylene according to the subsequent radical scavenger experiments. Moreover, the optimized rGO-TiO₂ exhibited sustainable photocatalytic activity at 40-120 mL·min⁻¹ flow rate through 160 minutes tests, while P25 was deactivate only after 25 minutes. This work demonstrated the different adsorption and degradation characteristics of two types of VOCs, which could propel the target orientation design of photocatalyst in VOCs removal applications.

Keywords:rGO-TiO₂; Photocatalysis; Acetaldehyde; O-xylene; VOCs removal

Preparation and characterization of methylsilsesquioxane (MSQ) aerogels by microwave drying

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Abstract: Methylsilsesquioxane (MSQ) aerogels were prepared via a sol-gel process followed by microwave drying with methyltrimethoxysilane (MTMS) as a precursor, hydrochloric acid (HCl) as a catalyst, water and methanol as solvents, hexadecyltrimethylammonium chloride (CTAC) as a surfactant and template, and propylene oxide (PO) as a gelation agent. The microstructure, chemical composition, and pore structures of the resultant MSQ aerogels were investigated in detail to achieve controllable preparation of MSQ aerogels, and the thermal stability of MSQ aerogels was also analyzed. The gelation agent, catalyst, solvent, and microwave power have important roles related to the pore structures of MSQ aerogels. The resulting MSQ aerogel microwave-dried at 500 W possessed a specific surface area up to 821 m²/g and a mesopore size of 20 nm, and displayed good thermal stability. It indicates that microwave drying not only has a remarkable effect on improving production efficiency, but also is conducive to avoiding collapse of the pore structure (especially micropores), resulting from thermal gradients during drying.

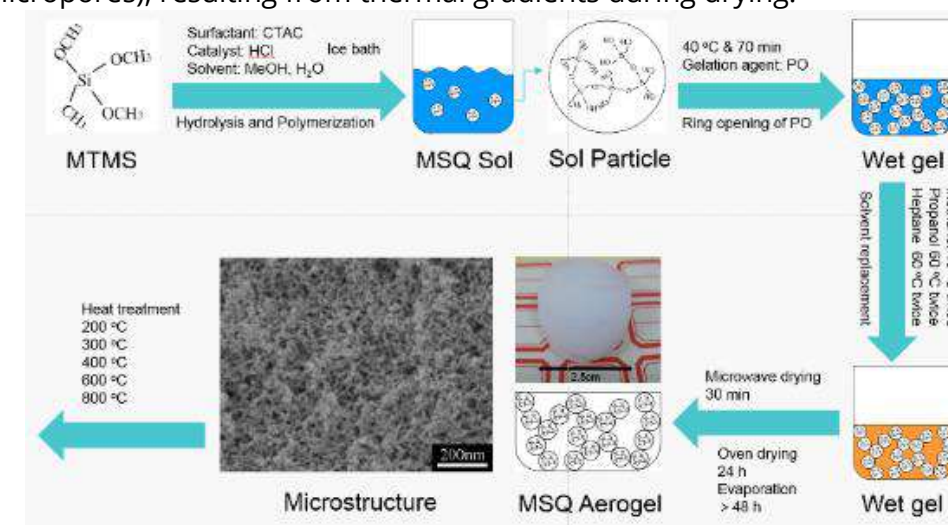


Figure 1. Reaction scheme and preparation process of methylsilsesquioxane (MSQ) aerogels

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The “Morse Code” between Solvent Polarity and Morphology Flexibility

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Abstract: LC physical gels are a new class of dynamically functional materials consisting of LCs and fibrous aggregates of molecules that are called “gelators”, exhibiting induced or enhanced electro-optical, photochemical, and electronic properties ^[1]. Phase-separated structures are formed in LC physical gels by the combination of two components, which can further affect its photoelectric performance due to the change of interface action on the boundary regions. Hence the regulation of various morphologies of LC gel is crucial.

Nevertheless, researches based on solvents-induced morphology are always focused on common solvents rather than the LCs, which may due to LCs’ unaware solvent parameters. Herein, by measuring solvent polarity of LCs and quantitatively comparing fiber flexibility, we connect solvent polarity with morphology flexibility by a fitting function, which can even be generalized to common solvents. Besides, additional coarse-grained molecular dynamics simulations unexceptionably support our theory that the solvent polarity is just like the “morse code”, and the “morse code” can be decoded as morphology flexibility by the fitting function we built. We hope it could be a quick way to judge morphology flexibility before troublesome electron microscope in supramolecular systems.

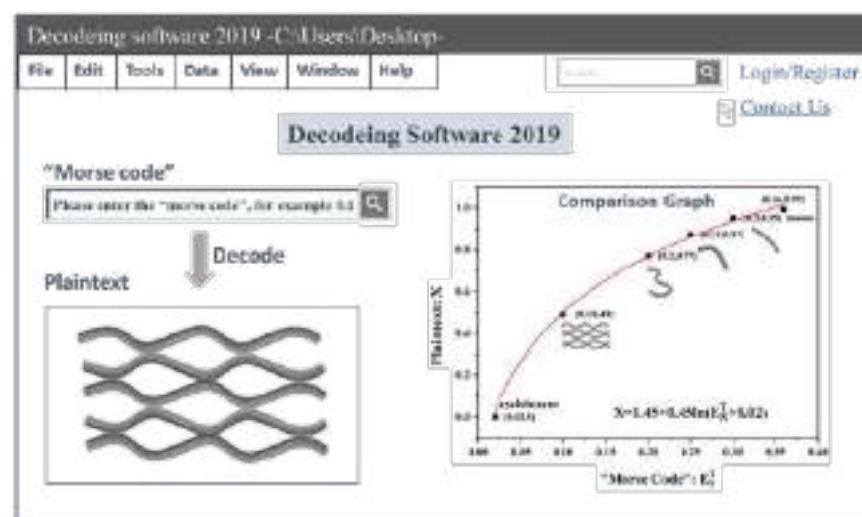


Figure 1. Schematic of the “Morse Code” between Solvent Polarity and Morphology Flexibility.

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Preparation of macroporous monoliths based on low valence transition metal (Cu, Mn, Co) oxides: gelation and phase separation

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Abstract: Hierarchically porous monoliths based on metal oxides, such as TiO₂, ZrO₂, Al₂O₃ and Fe₂O₃, with three-dimensionally interconnected macropores and mesopores in the skeletons have been reported via sol-gel process accompanied by phase separation. However, it is still a challenge in preparation of low valence metal oxides monoliths without an addition of organic molecule as structure supporter, since the hydrolysis and polycondensation are thermodynamically unfavorable for low valence metal aquo complexes. As a result, the complexes prefer to precipitate rather than to form three-dimensional networks via gelation and oxolation. It has therefore been difficult to obtain monolithic gels with a controlled pore structure.

Here, we propose a new method to prepare macroporous monolithic gels based on low valence metal oxides and hydroxides using three kinds of metals (Cu, Mn, Co) as examples. The epoxide-mediated sol-gel process starting from CuBr₂ reported by Hope-Weeks et al. [1] has been employed. Based on the process, we propose a universal method to prepare monolithic gels for three kinds of metal oxides. As shown in the figure below, all the samples were obtained through simple evaporative drying after solvent exchange. The three-dimensionally interconnected macroporous structures in the Cu-based monolith and Mn-based monolith were formed in the presence of appropriate organic polymers, which play a role of inducing the phase separation rather than supporting the network in the skeletons. The Co-based monolith with interconnected macroporous structure is currently under development.

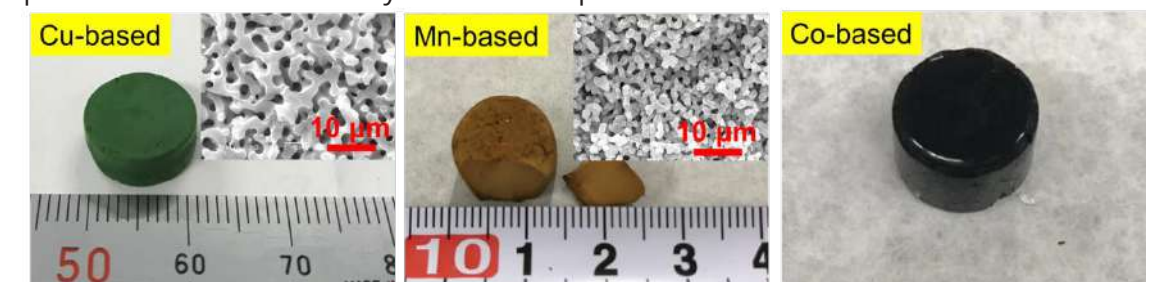


Figure 1. Photographs and SEM images (inset) of Cu-based, Mn-based, and Co-based monoliths (from left to right).

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Corrosion protection of light alloys by smart innovation sol-gel systems

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Abstract: The aluminum and magnesium alloys are designated as “light alloys” due to be their favorable strength to weight ratio making a good candidate for applications very different industries such as aerospace, sports equipment, biomedical devices, etc. Especially, Mg alloys have increased notably the volume produced in recent years. However, the most important limitation to use is their susceptibility to localized corrosion, closely related to their heterogeneous composition and microstructure. In particular, this is the major limitation for the introduction of Mg alloys in the transportation field. The control of the corrosion is a milestone in the whole world.

Different alternatives can be considered to increase the corrosion resistance, the most suitable being the surface modification by deposition of coatings and especially by using the Sol-gel process. This process is one of the key technologies to prepare efficient anti-corrosive coatings and has well known advantages, including relative low processing temperatures, homogeneity and purity of the resultant materials, a wide range of compositions and properties, etc.

Hybrid inorganic-organic SiO₂ sol-gel coatings have been proposed as good barrier protective system because they combine the properties of organic components with those of the inorganic components. However, corrosive ions still can diffuse through micro-pores and attack the metallic substrates, producing their degradation when they are exposed to aggressive medium for a long time. Thereby, the combination of hybrid silica coatings with systems based on cerium or other rare earths, and organic inhibitors are regarded as promising candidates to combine passive and active corrosion protection and self-healing ability. However, although significant progress is reported in literature and important limitation is observed.

For this reason, this work describes the preparation of smart innovative multilayer systems combining the anodizing process with deposition of cerium coating and hybrid silica coatings by sol-gel as alternative to hexavalent chromium system. The anodizing coating acts as carrier for the corrosion inhibitors, so if the system is damaged, these substances should be released in a controlled way to inhibit corrosion. All the coatings are generated without the application of hazardous substances.

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Acetic anhydride as oxygen donor in the non-hydrolytic sol-gel synthesis of mesoporous TiO₂ with high electrochemical lithium storage performances

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Abstract: Non-hydrolytic (or non-aqueous) sol-gel chemistry has been shown to provide simple and powerful routes for the synthesis of nanoparticles and mesoporous oxides. However, the main pathway to mesoporous oxides is based on the reaction of metal chloride precursors with organic oxygen donors such as alkoxides, ethers or alcohols. Metal chlorides such as TiCl₄ can be difficult to handle, and may lead to chlorine contamination of the oxide. Previous attempts to develop halide-free routes to mesoporous metal oxides have met a very limited success, either because of poor yields or because they employ precursors that are not commercially available.

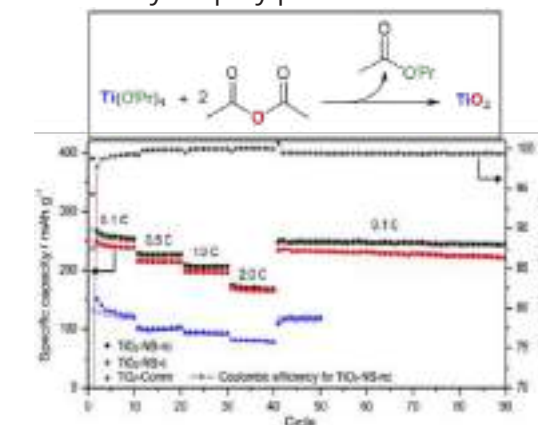


Figure 1: Synthesis of mesoporous TiO₂ and rate capability and long term cyclability test.

Due to its remarkable properties and low cost, TiO₂ is certainly the most studied metal oxide for applications such as photocatalysis, energy conversion, or energy storage. In this work^[1], we show that the reaction of titanium isopropoxide (a common titanium precursor) with acetic anhydride at 200 °C provides a simple and versatile halide-free route to mesoporous anatase TiO₂ with outstanding specific surface area. We investigated the mechanism and confirmed that this route was truly non-hydrolytic. The lithium storage performances of the resulting TiO₂ materials have also been evaluated, showing excellent reversible specific capacity, particularly for the non-calcined sample with the highest specific surface area.

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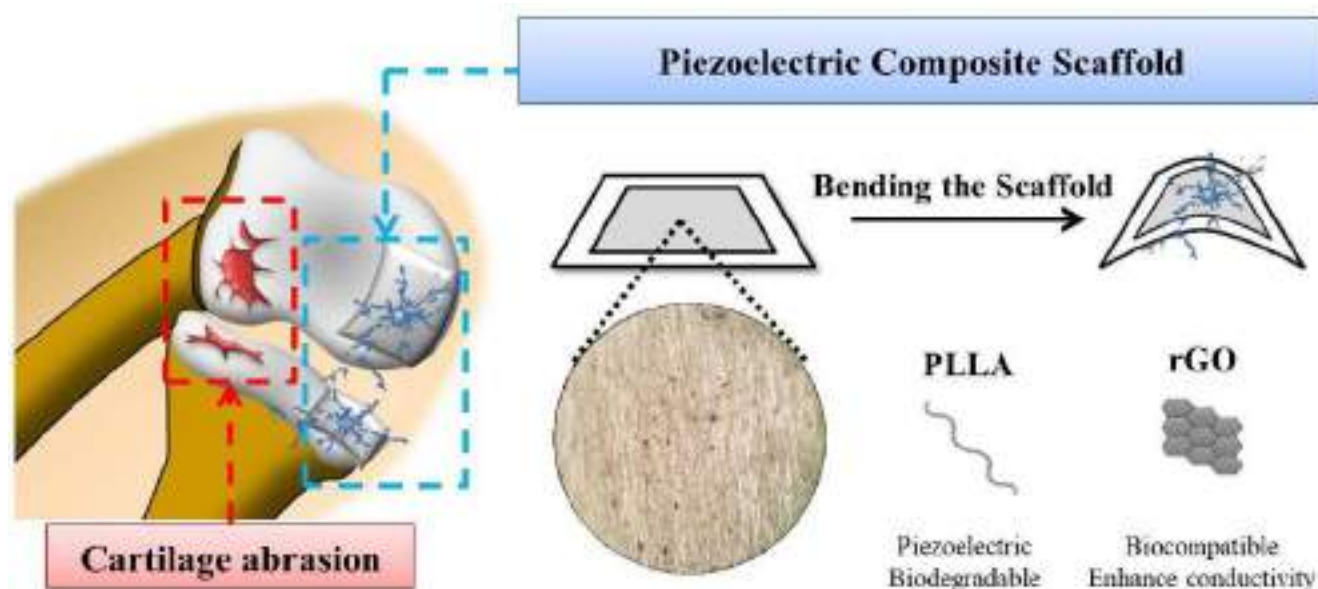
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Biodegradable Piezoelectric Composite Scaffold Applied to Modulate Chondrocytes Proliferation and Enhance Cartilage Repair

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Abstract: The articular cartilage disorder most commonly occurs at the conjunction between the bones because of lacking intrinsic ability to repair defects, often leading to more serious joint disease. Piezoelectric materials can generate electrical signals in response to the applied stress to stimulate the signaling pathways for enhancing the tissue regeneration at the impaired site but they face a tremendous challenge with biocompatibility and degradation. In this study, we developed a novel biocompatible and degradable piezoelectric composite scaffold to act as piezoelectric mechano-electrical transduction systems for cartilage tissue engineering. The rGO-loaded poly-L-Lactic Acid (PLLA) with biodegradable and piezoelectric properties was used to fabricate nanofiber membrane with different orientations (0°, 90°) and surface morphology (wrinkle and porous) by electrospinning and roller. The results demonstrated that the biodegradable rGO-PLLA displayed electrical output with 5V and 30nA, higher than other polymer-based, which can be used to control and simulate chondrocytes proliferation. The piezoelectric response between the mechanical and electrical state of the biocompatible graphene-loaded PLLA changed with orientation, porous morphology and electrical output, which is further affected by degradation time period. The animal experiments have proved that the piezoelectric scaffold not only stimulate proliferation, but also can be used for rapid cartilage repair. The mechanism related to the electrical stimulation on the proliferation of the biodegradable piezoelectric composite scaffold is further reported.



SiO₂@Al₂O₃ core shell nanoparticles prepared by sol-gel emulsion method

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Abstract: Sintering ability of alumina can be enhanced by incorporation of sintering additives such as SiO₂ to lower the sintering temperature. However, local inhomogeneity is frequently found in the sintered products due to the agglomeration of the powders. This problem may be overcome by using the powders with core-shell structure. In this study, the core-shell structure of Al₂O₃ nanoparticles coated with SiO₂ layer was prepared by sol-gel emulsion method. Al₂O₃ nanoparticles of about 50 nm in average size and Tetraethyl orthosilicate (TEOS) were used for the formation of SiO₂ layers on the surface of Al₂O₃ nanoparticles. The reaction of TEOS via NaOH and water was conducted in the soybean oil under vigorous stirring at 100°C. The TEOS to NaOH ratio has been varied to control the thickness of the SiO₂ shell. Formation of SiO₂@Al₂O₃ core-shell nanostructure has been confirmed by Transmission electron microscope (TEM) and energy dispersive X-ray spectroscopy (EDS) analysis. The results obtained from TEM images showed that the shell materials were smoothly and tightly adhered on Al₂O₃ nanoparticles. The core-shell material was composed of crystalline Al₂O₃ core covered by an about 5~10nm amorphous SiO₂ shell through X-ray diffraction (XRD) and TEM electron diffraction analysis. The core-shell powders also showed a good result in homogeneous microstructure under modification of the mechanical properties of laser sintered ceramic products. The core-shell nanoparticles in comparison with the simple mixed powders resulted in a modification of the mechanical properties of laser sintered ceramic products.

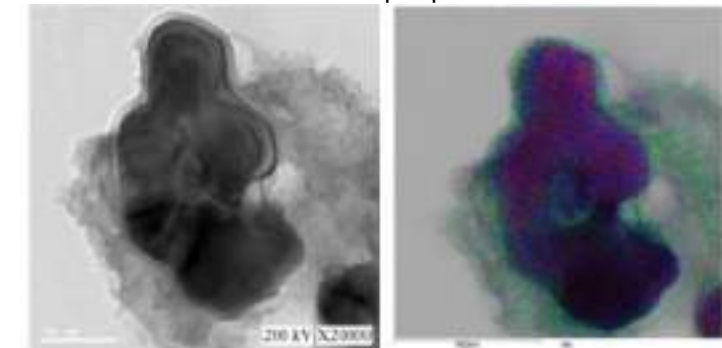


Figure 1. TEM microstructure (left) and TEM-EDS mapping image (right) of the SiO₂@Al₂O₃ core-shell nanoparticles. (The green color indicates the Si element.)

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Sol-gel derived metal oxide thin films as electron transport layer for efficient perovskite solar cells

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Abstract: Organic-inorganic metal halide perovskite solar cells (PSCs) have made significant breakthrough and achieved power conversion efficiencies (PCEs) over 23%. In an efficient PSC, the electron transport layer (ETL) is generally made from semiconductor metal oxides such as TiO_2 , SnO_2 , Nb_2O_5 etc. and it is a key component of the device. Thin film ETLs are required to be fully dense without pin-holes in order to protect the bottom electrode from direct contacting with the perovskite light absorber. Otherwise, the current leakage would occur. Sol-gel process is a powerful and economical technique to fabricate dense metal oxide films. Here, we employ the sol-gel method to prepare TiO_2 , SnO_2 , Nb_2O_5 thin films for perovskite solar cells and investigated the effects of environmental humidity on the quality of the prepared metal oxide thin films. Various characterization techniques including SEM, XRD and XPS are taken to reveal the relationship between the humidity and the properties of the thin films. By optimizing the level of humidity or eliminating the effect of the humidity, high quality metal oxide thin films are obtained and made into perovskite solar cells, achieving efficiency up to 19%. Correlations between the solar cells' performance and the microstructures and properties of the metal oxide thin films are investigated and a strategy for further improvement of the perovskite solar cells' performance is discussed.

Preparation of brochosomes tungsten oxide with enhanced electrochromic performance

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Abstract: Bio-inspired WO_3 electrochromic films featuring periodical brochosomes structure with high surface ratio were prepared in the framework of sol-gel method using double-layer polystyrene (PS) colloidal crystal templates. Compared with dense films prepared without template, the unique structure of the WO_3 brochosomes endowed them outstanding electrochromic performance, including the fast color switching, strong color contrast between the bleached and the colored state, and the good cyclability. These outstanding electrochromic performances are comparable to the color-changing capability of natural species, making the WO_3 brochosomes have promising applications in those fields where thermal and optical management are desirable.

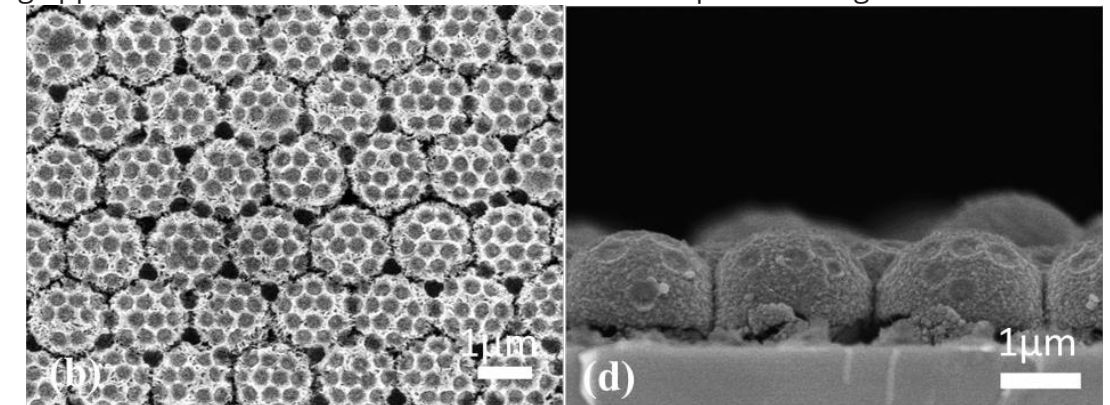


Figure 1. The surface and cross-sectional SEM images of as-prepared dense and brochosomal WO_3 films

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The work was financially supported by National Natural Science Foundation of China (No.51572236) and the Fundamental Research Funds for the Central Universities.

Preparation of the self-standing electroconductive metal oxide with controlled multiscale porosity

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Abstract: Hierarchical porous materials have considerable attention due to their specific functionalities depending on the combination of discrete pore structures. Multiple length-scales porosity provide better mass transportation, high surface area, and size and shape selectivity. In particular, when they are electroconductive materials, various application can be found such as electrode, electro catalyst, catalyst support, and so on. However, focusing on metal oxide group, there are few reports about self-standing electroconductive metal oxide materials with controlled multiscale porosity. Here, we report multiscale controlled antimony-doped tin oxides via the simple template-free process. By combining the polymerization induced phase separation process and appropriate heat-treatment process, the multiscale porosity was successfully controlled. As similar crystallinity, the main porous structures defined by the 3D network skeletons, which were derived from phase separation, could be controlled from about 1 μm to 5 μm . In addition, the secondly porous structures in the skeletons could be controlled from 30 nm to 180 nm by choosing the appropriate heat-treatment. The obtained samples have low bulk electrical resistivity about $1 \times 10^{-2} \Omega \text{ cm}$. These hierarchical porous electroconductive materials are expected to be used as chemical stable electrocatalyst support, oxidation resistant electrodes, and so on.

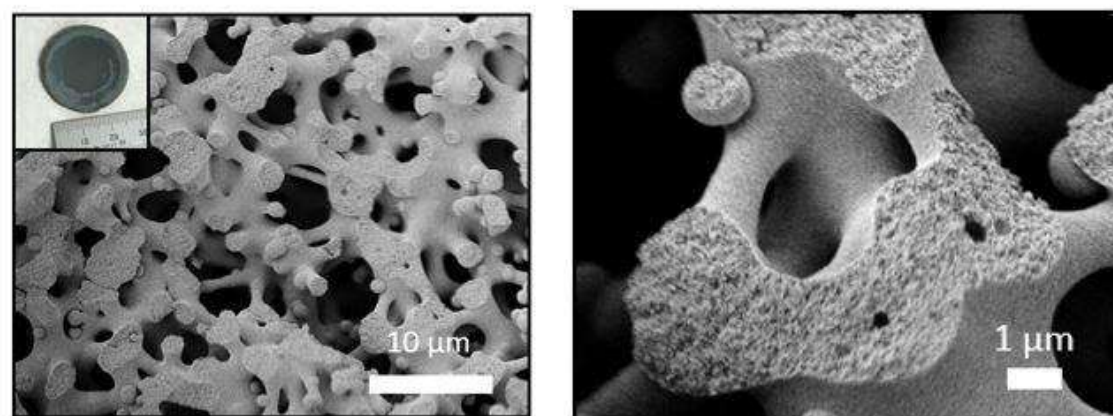


Figure 1. The appearance and FESEM images of the obtained antimony doped tin oxide heat-treated at 800 °C for 4 h

Synthesis and high SERS Sensitivity of Non-stoichiometric $\text{W}_{18}\text{O}_{49}$ nanowires for the detection of rhodamine B

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Abstract: The Surface-enhanced Raman scattering (SERS) has become a mature vibrational spectroscopic technique during the last decades and its applications in the field of chemical, material, and especially in life sciences are rapidly increasing [1]. As cheap and stable materials, semiconductor SERS substrates have undergone a remarkable development in SERS detection field [2]. The $\text{W}_{18}\text{O}_{49}$ possesses the maximum oxygen vacancies and contains tungsten ions of mixed valence, used as the SERS substrate is very significant for exploring its new application.

The non-stoichiometric $\text{W}_{18}\text{O}_{49}$ nanowires were prepared by sol-gel method combined with solvothermal technique using WCl_6 as the raw material, polyvinyl pyrrolidone as the regulating agent and ethanol as the solvent. The prepared $\text{W}_{18}\text{O}_{49}$ nanowires possess relatively uniform morphologies with the diameter of about 12 nm. After calcination in Ar/H_2 , these nanowires possessed higher crystallinity and more abundant oxygen vacancies without obvious morphology change. When used as the SERS substrate for the detection of rhodamine B (RB), the detection limit was as low as $1.3 \times 10^{-7} \text{ M}$, showing enhanced SERS sensitivity compared with uncalcinated $\text{W}_{18}\text{O}_{49}$ nanowires. The above results are due to that the existence of oxygen vacancy could enrich the surface states of substrate and making more rhodamine B molecules adsorbed on the substrate. Therefore, as a new non-noble metal SERS substrate, the $\text{W}_{18}\text{O}_{49}$ nanowires provide an important inspiration for their application in the detection of pollutants..

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Preparation of hierarchically controlled melamine-formaldehyde polymer monoliths via sol-gel process

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Abstract: Melamine-formaldehyde (MF) polymer monoliths attract interests for a wide variety of applications such as separation media, catalysts, and electrode materials, because MF polymer has a good chemical stability and has abundant functional amino groups. Although a lot of porous MF gels have been reported so far, MF polymer monoliths which have hierarchically controlled porous structure have been merely reported. As monolithic materials, silica and various metal oxides with hierarchical porous structure have been reported via sol-gel process accompanied by phase separation. For effective applications of the monolithic hierarchically porous materials, it is important that macro-meso porous structures are individually controlled in order for macropores serving as the fluid transport channels and for mesopores giving high specific surface area and accessible active sites. In this study, by introducing sol-gel process accompanied by phase separation followed by hydrothermal treatment, we tried to prepare MF polymer monoliths which have hierarchically controlled macro-meso structures.

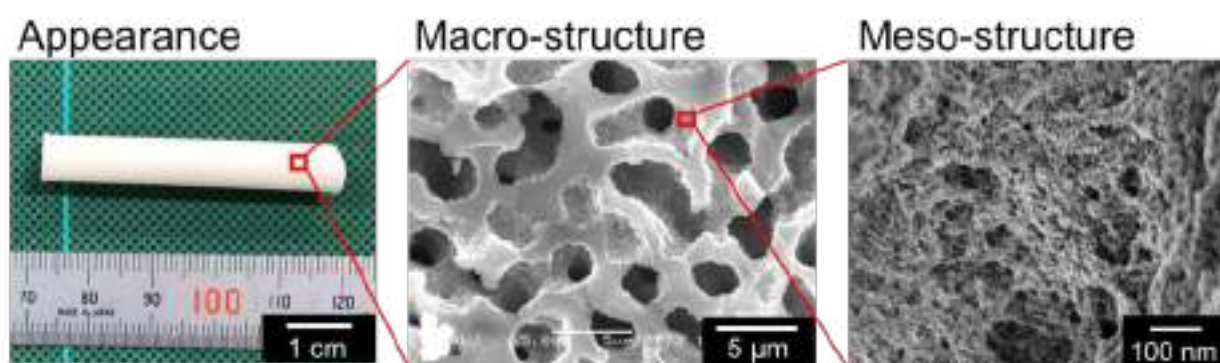


Figure 1. Appearance of a typical MF polymer monolith and SEM image, FE-SEM image of the same MF polymer monolith.

Photo-patternable QD/siloxane composite with high thermal stability for color filters

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Abstract: The Quantum dot-color filters (QD-CF) have gained enormous interests for color-converting layers due to their fascinating properties, like narrow emission spectra, high photoluminescence quantum yield (PLQY), and tunable emission owing to size dependence. Despite of the innovative optical properties, QDs have various limitations for practical applications because of vulnerability, against heat and moisture. In addition, it is difficult to fabricate an individual RGB pattern onto a pixelated display with solution process. To solve these problems, dispersion of QDs in photo-patternable polymers have been studied, but several issues are remained such as compatibility between QDs and polymer, poor thermal stability, and necessary of barrier film on QD-polymer films.[1]

Recently, we reported a siloxane encapsulated QD (CdSe/CdZnS, ligand: oleic acid, from POWERLOGICS) resin through in-situ sol-gel condensation reaction of methacrylate and phenyl silanes in the QD existence.[2] The QDs were uniformly dispersed in the photo-cured QD/siloxane film, and the QD/siloxane film showed long-term stability in harsh environment (85°C in air and 85°C/85% RH conditions). However, the oleic acid-capped QDs showed poor dispersion stability when the concentration of QDs was over 1 wt%.

To apply our QD/siloxane composite into practical QD-CF, we modified the oleic acid-capped with mercapto-contained monomer and chemically reacted with methacrylate and phenyl silanes during sol-gel condensation. The mercapto-modified QD (MerQD) was stably dispersed in the methacrylate-phenyl oligo-siloxane resin with even QD concentration of 5 wt% by remaining the superior thermal stabilities without additional barrier films. After synthesis of the MerQD/oligo-siloxane resin, we added thiol monomer, could fabricate patterned QD-CF under ambient atmosphere, as depicted in Figure 1. Moreover, we will study printable ink by adding thiol and methacrylate monomers, and solvent to fabricate thin QD-CF with inkjet printing, which is the best candidate for RGB pattern at low materials consumption.

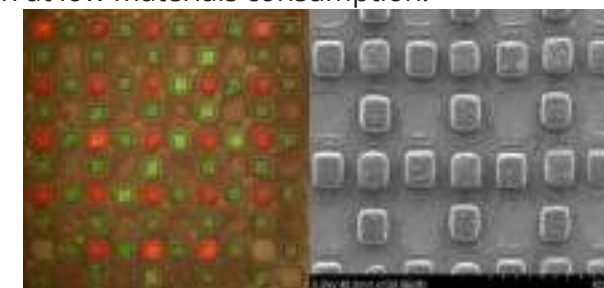


Figure 1. Photo-patterned red and green QD/siloxane composite for QD-color filters.

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Hierarchical Y zeolite obtained by NH_4HF_2 dealuminization: Porosity, and toluene adsorption property

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Abstract: Toluene is one of the most common volatile organic compounds (VOCs), which is harmful to natural environment and human health. Zeolite is a kind of excellent molecular pollutant adsorbent material, and its pore structure is an important factor for molecular adsorption performance. The microporous dimension of microporous zeolite is normally between 0.25 nm and 1 nm, which limits the diffusion of reactants and products. The hierarchical zeolites formed by introducing mesoporous into the framework of microporous zeolite facilitate the transportation of reactants and products in narrow channels. In this work, the hierarchical Y zeolite is first obtained by etching the parent NaY with different NH_4HF_2 solutions in the absence of buffer solutions. The morphology and microstructure, toluene adsorption property of as-prepared hierarchical Y zeolite are characterized. The results demonstrate that the $n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)$ of hierarchical Y zeolite and the number and size of mesoporous in modified Y samples increase as the increase of the NH_4HF_2 solution concentration. Furthermore, the synthesis mechanism of hierarchical Y is elaborately demonstrated and the possible reaction equations between NaY zeolites and NH_4HF_2 are generalized. The synergistic effect of H^+ and F^- is more beneficial to dealumination as well as the introduction of mesoporous. The NH_4HF_2 ionizes into positive H^+ and negative F^- at a very slow rate, which does not cause the concentration of H^+ and F^- ions to rise suddenly. The dealuminization reaction between NH_4HF_2 and NaY zeolites is more sustained and mild, and the crystallinity of hierarchical Y zeolite is higher than that of the $\text{HCl}/\text{NH}_4\text{F}$ -etched NaY. The toluene adsorption performance of different hierarchical NH_4HF_2 -etched NaY samples were also studied. The 0.3 M NH_4HF_2 -etched NaY with the high crystallinity and suitable mesoporous content shows the best toluene adsorption performance, and the NH_4HF_2 -etched NaY is an excellent material for pressure swing adsorption. This work presents an effective method to synthesize the hierarchical Y zeolite.

Colored sol-gel derived coatings for solar collectors and photovoltaic modules

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Abstract: With the recent entering of the Paris Climate Pact, Europe has to increase its efforts to achieve its goals on energy savings and renewable energy production. The built environment contributes 46% to the final energy consumption in Europe. To obtain the goals of the Paris Climate Pact, the building envelope will contain integrated energy producing products, like PV and solar collectors in 2030. On this moment most solar collectors and PV modules are still black or blue (non-colored). The acceptance of solar cells and solar collectors in the built environment is partly dependent on the appearance (color) of the solar modules. For application in the building envelope, like roofs and facades it is important to obtain colored solar collectors and PV modules.

TNO proposed a front-sheet covered with a stack of thin layers consisting of high and low refractive index materials deposited from sol-gel onto PET foil and glass such that only a particular wavelength range is reflected. We show through modeling that by alternating layers consisting of low refractive index layer (silica (SiO_2)) and high reflection layer (TiO_2) onto PET foil and glass such color reflection can be achieved. In modeling exercises the influence of the number of layers, thickness variations and angle of incidence on the reflected color are predicted as well as an estimated influence on the module efficiency. We show that with a four and six layer stack systems we can reach esthetical yellow green, red and signal blue PV panels and solar collectors, that remain a high efficiency

The yellow green sol-gel derived colored coating system was scaled up to a size of 80x100 cm² for application in PV modules and placed for three years at a roof in Heerlen in The Netherlands. The reliability of these colored coatings remain good after three years. On this moment we are scaling up the system for colored solar collectors.

Photoelectrochemical performances of ZnO nano-composites with double enhanced effects by morphology regulation and graphene-coated modification

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Abstract: ZnO is proper photocatalytic material for its suitable band gap, high electron mobility, low cost, and pollution-free. However, the high recombination efficiency of photo-generated electron-hole pairs and relative wide bandgap restrict the further application in solar light. Three kinds of ZnO nanoparticles with hexagram-like patterns, 1D slab-like, and nanorod arrays were synthesized by one-step solution method and hydrothermal method, respectively. Then graphene was coated on each kind of ZnO surface by electrostatic force-induced self-assembled with an amine-functionalized process. The morphology of ZnO nanoparticles and Graphene-coated ZnO nanocomposites were studied by scanning electron microscopy (SEM), field emission SEM (FESEM) and high resolution transmission electron microscopy (HRTEM). The photoluminescence (PL) spectra and UV-visible spectra were measured to study the recombination of electron-hole pairs and absorption of UV-visible light. The photocatalytic properties and photoelectrochemical performances of these composites were evaluated to determine the effect of the morphology. The results showed that ZnO nano-composites greatly enhanced the efficiency of photodegradation of organic dyes and photoelectrochemical (PEC) performance by morphology controlling and surface modification of graphene. The 1D slab-like ZnO/graphene composite has the best catalytic performance and PEC performance because its special structure could provide a larger internal electric field, and is beneficial to the separation of photo electron-hole pairs and migration of photo charger, which exhibits a good potential for application.

A new method based on CO₂-switchable wormlike micelles for controlling CO₂ breakthrough in tight fractured oil reservoir

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Abstract: CO₂ is widely utilized for enhancing oil recovery (EOR) due to its high ability of washing oil and favorable injectivity, especially for tight oil reservoir. During EOR process, the oil recovery is significantly affected by gas channeling and the sweep efficiency of CO₂ is limited. Herein, we report a CO₂-switchable smart wormlike micelles (WLMs) based on sodium dodecyl sulfate (SDS) and diethylenetriamine (DETA) to prevent gas channeling of CO₂ in tight fractured oil reservoir.

The proof to the microstructure, formation mechanism and plugging performance of CO₂-switchable WLMs were studied by cryo-TEM, DLS, NMR, rheology and plugging property measurement. The results indicated the system can be reversibly circulated between spherical micelles and wormlike micelles by repeatedly bubbling and removing CO₂. When CO₂ is introduced to the solution, part of DETA molecules are protonated, and "bridge" two SDS molecules to form pseudo-gemini surfactant by noncovalent electrostatic attraction, behaving a high viscosity fluid. Upon removal of CO₂, the protonated DETA molecules return to original state, causing the pseudo-gemini structure being destroyed and the viscosity of the fluid is recovered. Moreover, based on the results of plugging property measurement, the solution presents conspicuous injection and plugging performance. This WLMs viscoelastic fluid might have potential application in the enhancement of CO₂ flooding in tight fracture reservoir.

Preparation of AM/PF microspheres and investigation of temperature resistance mechanism

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Abstract: To solve the problem of rapid decline in crude oil production, polymer microspheres have been applied for petroleum reservoir enhanced oil recovery (EOR). However, the temperature resistance of polymer microspheres is not satisfied for high-temperature reservoirs. In this work, microspheres with preferable temperature resistance were synthesized using water soluble phenolic resin (PF) and acrylamide (AM) as monomers, N, N-methylene bis acrylamide (Bis-A) as crosslinking agent, Span-80 as emulsifier and potassium persulfate as initiator. The inverse suspension polymerization method was adopted. The effects of crosslinking ratio and monomer ratio on the particle size are investigated and the swelling behavior of microsphere is studied. The temperature resistance of AM/PF microspheres is investigated by thermogravimetric analysis (TG-DSC), IR, microscopy and scanning electron microscopy (SEM). The results show that the temperature resistance of the microspheres is significantly improved by the addition of phenolic resin. The AM/PF microspheres can be placed 180 days at 120 °C and 150 days at 140 °C. The degradation process of microspheres is discussed preliminarily.

Deposition of polyelectrolytes on GaP for solar water splitting

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Abstract: Hydrogen is an important energy carrier for renewable energies. It is mainly produced from hydrocarbons through chemical reforming processes. [1] The use of a semiconductor absorber as photoelectrode immersed in an electrolyte for direct solar water splitting is an attractive renewable alternative to produce hydrogen (photoelectrochemical water splitting (PEC)). [2] It was shown that polyelectrolytes layer structures have an influence on the photoactivity of TiO₂ for the solar water splitting. [3] And with III-V semiconductors it is possible to get a high efficiency of 19 % for solar water splitting. [4] In this work gallium phosphide (GaP) and polyelectrolyte layer by layer deposition are studied here as a reference material for GaP-based III-V top-absorbers, such as GaAsP or GaPNAs, to be used in tandem absorber PEC devices promising high conversion efficiencies and corrosion protection.

The impact of the surface behaviour of p-type GaP and polyelectrolyte layers were analysed with regard to the water splitting performance and stability. As polyelectrolyte were used polyethyleneimine (PEI) and polystyrenesulfonate (PSS). Prepared surfaces for solar water splitting were measured in 1M KCl with a three electrode set up (working electrode: GaP, reference electrode: Ag/AgCl and counter electrode: Pt-wire) and a white light source. It will present the influence of polyelectrolytes on GaP surfaces for long time stability. The in-situ formation of such layer-by-layer polyelectrolytes is particularly interesting to tune the semiconductor-liquid interface with regard to stability properties.

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Radio controlled enzymatic composites based on sol-gel magnetite

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Abstract: Hybrid enzymatic nanocomposites are perspective class of materials that are used to catalyze biological processes and can be used in different fields of industry and medicine. Such materials are combining both high catalytic rates and selectivity inherent to enzymatic systems with a stability and responsiveness to physical stimuli due to presence of nanoparticles. These properties allows to use such materials in extreme conditions inaccessible to free enzymes, such high temperatures, extreme pH values or presence of oxidizing agents [1,2]. Responsiveness to physical stimuli allows to manipulate hybrid enzymatic composites in order to increase their local concentration, to perform magnetic separation or modulate their catalytic activity under the influence of electromagnetic irradiation of different nature, such as UV/VIS light, electric fields or alternating magnetic field [3,4]. While light- and electric-responsive enzymatic composites are known and are described in the literature, magnetic modulation of enzymatic activity is much less described and holds up a great potential, as it can allow to manipulate the bioactivity of a material in a non-invasive manner with a good penetration depth.

Here we are demonstrating acceleration of the reaction rate under the influence of RF-field carried out by carbonic anhydrase (CAB) entrapped within sol-gel magnetite matrix. Observed phenomena is occurring in a process of heating of superparamagnetic magnetite nanoparticles due to Neel relaxation processes and possible due to high thermal stability of entrapped CAB. The reaction rate of CAB@magnetite composites can be increased up to 457% of its initial value at the AC field frequency 210 kHz and amplitude 937 A/m. Reaction rate acceleration is fully reversible and demonstrates fast response to applied field. Such hybrid materials can find their application for drug delivery systems with controlled activity design, creation of magnetically-responsive biosystems and nano-biorobotics.

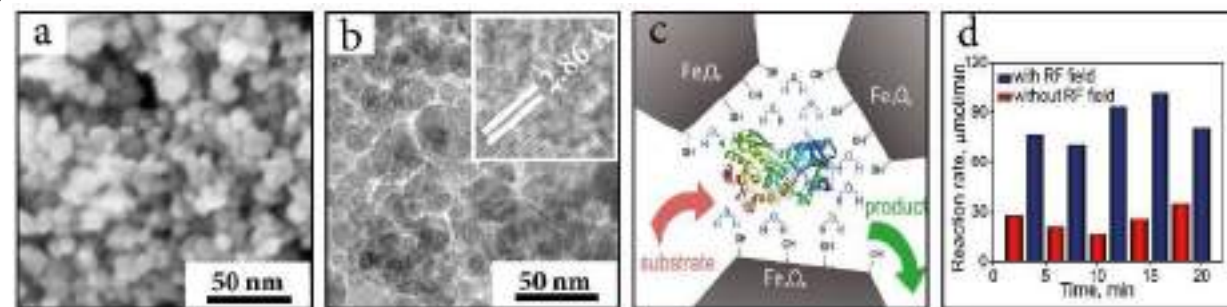


Figure 1. SEM image of CAB@magnetite hybrid (a); TEM image of CAB@magnetite hybrid (b); schematic representation of entrapped CAB in magnetite mesopore (c); catalytic activity of CAB@magnetite in presence and in absence of RF-field (210 kHz, 937 A/m) (d).

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Modification of nanostructured metal catalysts for carbon dioxide reduction

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Abstract: Nowadays there is the challenge of carbon dioxide (CO₂) utilisation. The first step of CO₂ recycling is the reaction of CO₂ recovery. Unfortunately, this reaction has slow kinetics. That issue can be addressed with a nanosized metal catalyst. These catalysts were usually fast poisoned. In the research, these catalysts were modified by the chemical vapor deposition method.

Functional hybrid materials based on carbon and metal oxide nanoparticles

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Abstract: Creation of the hybrid materials based on nanostructured carbon is an excellent investment in development of the future functional materials. There are several types of carbon-based nanomaterials that have different structure and properties. First of them are nanocomposites, which contain filler (carbon) and matrix or base (for example, ceramic or polymer) and which usually combine the individual properties of both compounds [1]. Unlike nanocomposites, carbon hybrid nanomaterials provide access to a large specific surface area and an extended interface. Due to this morphology, charge and energy transfer processes create synergistic effects that lead to unique physicochemical properties and increased productivity [2, 3].

Hybrid carbon nanomaterials are intensively researched and applied in various areas of nanotechnology, such as environmental catalysis, photocatalysis, sensors, batteries, photovoltaics [2, 3]. One of the most promising areas for these materials application of is adsorption of harmful pollutants from air or water.

In this work hybrid CNF/Fe₂O₃ and CNF/TiO₂ materials were synthesized by ex situ method and characterized by a number of techniques. Sorption of Sr²⁺, Ba²⁺, and Cs⁺ on the hybrid materials is considered. The TiO₂ and Fe₂O₃ nanoparticles were synthesized via a sol-gel technique. TEM images (Fig 1) shows coaxial coating and uniform distribution of MeOx NPs on the CNFs (carbon nanofibers) surface.

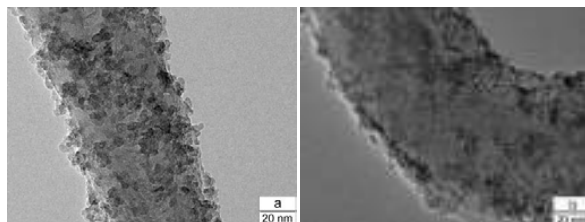


Figure 1. HRTEM images of: a) CNF/TiO₂ (mass ratio 10:1); b) CNF/Fe₂O₃ (mass ratio 10:1) hybrid systems.

Raman spectroscopy results demonstrated the electrostatic attraction between components without the formation of covalent bonds. Sorption properties results revealed the synergistic effect of the hybrid CNF/TiO₂ (10:1) in relation to Cs⁺ and Sr²⁺, which demonstrates its prospects to be used as an effective adsorbent.

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Functionalization of Hafnium Oxide Nanoparticles

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Abstract: In recent years nanoparticles (NPs) of high-Z elements have drawn scientists' attention, as they can be used for the radiotherapy [1]. Moreover, the usage of NPs can help to overcome the common drawbacks of this treatment including cardiac toxicity, secondary malignancy, radiation pneumonitis, and lymphedema due to the specific distribution in cells and the enhancement of radiotherapy through radio sensitization [2].

Sol-gel methods of synthesis provide an easy and effective way to get NPs with controlled composition, size, and morphology. Even greater advances are accomplished if aerogels are obtained as these materials possess high specific surface area and porosity. Nowadays, they are used as catalysts, thermal insulation, particle detectors, supercapacitors and in many other applications [3].

During this work nanoparticles of hafnium oxide with fluorescent mark and polymeric shell were designed. In order to obtain hafnium oxide nanoparticles a controlled hydrolysis of hafnium n-butoxide was performed (Figure 1). A simple sol-gel reaction allowed to obtain a stable gel that was further exposed to the supercritical drying in CO₂. Fluorescent mark was added during sol stage to provide visualization of nanoparticles for the biological tests.

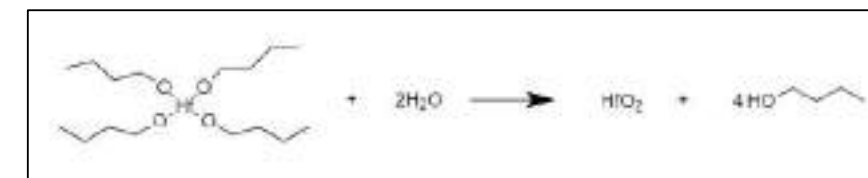


Figure 1. Hydrolysis of Hf n-butoxide.

Furthermore, to improve stability of nanoparticles in water and biological media a polymer layer was introduced. Nowadays, one of the most popular polymers for the surface modification of metal and metal oxide nanoparticles is amphiphilic block co-polymer PEG-PCL. Choice of this polymer was also founded on the FDA approval to use it in the biological systems in order to prevent protein corona formation [4]. Polymers with different ratios of hydrophobic/hydrophilic parts were synthesized and tested to find the best composition to provide stable water sols.

The nanoparticles were characterized by TEM, IR-spectroscopy, Nitrogen adsorption, DLS measurements. Polymer was characterized through IR-, NMR-spectroscopy, DSC, GPC. Cell viability tests were conducted to state the biocompatibility of the nanoplatform.

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Producing an enzymatic biofuel cells based on carbon nanomaterials

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Abstract: Biofuel cells (BFCs) are bioelectrochemical devices operating from the energy released during biochemical reactions, such as oxidation of biofuels (for example, glucose) at the anode, and oxygen reduction at the cathode [1]. BFCs which catalysts of redox processes are enzymes are called enzymatic [2].

The majority of created enzymatic BFCs have a low power of the electric energy produced by them, which makes their practical application very doubtful. In theory, they can be used to provide energy and recharge micro-devices implanted into the human body (hearing AIDS, pacemakers, insulin pumps, etc.) [1]. Studies have been conducted [1, 3], proving that bioelectrochemical devices, including enzymatic biofuel cells, are able to work in the body of a living organism. Most often experiments were carried out on molluscs and crustaceans, as well as mammals [3].

Carbon nanomaterials, such as carbon nanotubes and nanofibers (CNT and UNV respectively) serve as a good substrate for immobilization of enzymes for efficient operation of the biofuel cell, as they have the key characteristics for this – a large area of the specific surface area and low electrical resistance [2]. Also, for many redox reactions CNTs have the property of direct electron transfer, which increases the efficiency of electron transfer from the enzyme active centers to the electrode surface [4].

Improvement of the performance of BFCs is also associated with the use of hybrid bioelectrodes based on nanocarbon materials. The application of metal or ceramic nanoparticles to the carbon surface increases the catalysis rate and the electron transfer process.

For example, the increased stability of the enzymes can be achieved by attachment of the protein to Au nanoparticles entrapped inside. This immobilization will result not only in the increasing stability of the enzymes but will also improve the electron transfer process between the enzyme and the conducting electrode support. Immobilization of the enzyme and Au nanoparticles in the nanostructured surface of electrode will increase the fraction of the electrically active enzymes, thus resulting in the increasing current density.

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Sol-gel synthesis of tantalum oxide (V) nanoparticles

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Abstract: Due to physical-chemical properties, high-Z elements are applied in a variety of areas, especially in the theranostics. Tantalum oxide ($Z_{Ta} = 73$) is a strong candidate for this approach, which possesses characteristics of both contrast agent for computed tomography (CT) for bioimaging of tumors and radiosensitizing agent for therapy. The ability of CT to distinguish tissues is based on the fact that different tissues provide distinct degrees of X-ray attenuation, where the attenuation coefficient depends on the atomic number and electron density of the tissues. Closely monitored doses of ionizing radiation cause damaged to the DNA in cancer cells. Even so, these doses must be accurately delivered to the lump because of its effects both malignant tumor and normal tissues. Radiosensitizers, which increase the sensitivity of unhealthy cells to irradiation, are promising agents that damage tumor tissue by production free radicals (this process is known as radiolysis). Formation of free radicals is a result of the emission of secondary radiation by NPs during radio therapy (RT). The interaction of free radicals with DNA and cellular structures induces radical destruction of malignant cells, further apoptosis. During the recent years, tumor-selective radiosensitizers based on noble metal NPs have attracted increasing attention due to their unique physical and chemical properties for usage in RT. Corrosion resistance, low toxicity, and high biocompatibility with body tissues provide nanoparticles of tantalum oxide (Ta_2O_5) with a wide range of applications from thin films for a capacitor insulator in random access memory devices to biomedical and clinical applications (implants in orthopedics and dentistry, biosensors, radiographic markers, vascular clips).

The aim of the present work is to obtain Ta_2O_5 NPs, to study properties of hydrosols. In this regard, the following objects are the development of a technique of sol-gel synthesis of tantalum oxide NPs; investigation of the physical-chemical characteristics of the produced systems. The production was performed by the sol-gel method from inorganic precursor (Ta_2Cl_5). The impact of different process parameters (a constituent of the dispersion medium, drying process) on the preparation of nanoparticles was investigated in order to reach the optimal conditions of synthesis. Tantalum hydrosols were studied by the dynamic light scattering (DLS). Shape and morphology of nanoparticles were investigated by scanning electron microscopy (SEM).

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Upconversion natural spider silk-based hybrids

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Abstract: Optimizing molecular interactions between structural proteins and inorganic nanoparticles, innovative composite materials can be made. In this work, we show upconversion modification of natural spider silk fibers with inorganic nanoparticles. The physicochemical properties of the resulting material are analyzed, as well as antimicrobial and regenerative properties.

The production of new scleroprotein-based hybrid materials is very promising, since these objects are natural efficient and functional models of durable and lightweight systems that can work in virtually any environment [1]. The design of silk proteins based hybrids using the inorganic phase induction allows introduce new material properties. Due to their biocompatibility, these nanocomposites are promising in the field of tissue regeneration, targeted drug delivery, biosensors and bio-imaging [2]. Such innovative composite materials provide analogies to more conventional synthetic polymers, but with enhanced utility due to superior mechanical properties, biodegradability and functionalization. In the present work, the use of colloidal systems of optically active HfO_2 and ZrO_2 nanoparticles for spider silk based materials is highlighted.

Curtain-web spiders (genus *Linothele Fallax*) supplied the scleroproteins of the spider silk fibers. HfO_2 and ZrO_2 nanoparticles were obtained by sol-gel method using controlled hydrolysis. The obtained nanoparticles were characterized using the complex of physical-chemical methods. The morphology and optical activity of composite materials were analyzed (Fig. 1).

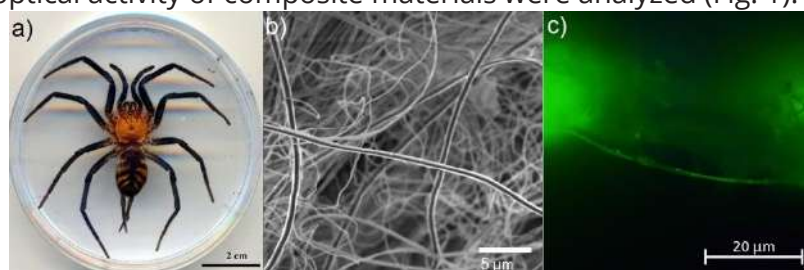


Figure 1. a) *Linothele Fallax* image; b) SEM image of hybrid material; c) Photoluminescence image of hybrid material.

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Spider web as a natural nanocomposite material for eco-friendly applications

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Silks are conspicuous examples of natural biopolymers, receiving attention due to their structural complexity¹ and variability of properties². In nature these organic composites are generated by several types of insects among which silkworms and spiders are considered to be the most studied. Multiple investigations on natural and artificial silk are mostly focused on that produced by silkworms³, although spider silk seems to outperform most of natural or synthetic fibers due to extremely high mechanical stability⁴, flexibility, biocompatibility and biodegradability⁵. These features make spider a promising material for environmental, energy, optical and biomedical applications⁶. One of major challenges of producing spidroin-based materials involves a comprehensive understanding of spider silk proteins and their assembly into fibers.

Natural spider silk was obtained from a curtain-web spider *Linothele Fallax* through an insectarium on the base of the laboratory. In this work organic and water solutions of spider silk were discussed. As curtain type of web appears to be difficult to dissolve using typical solvents as formic acid or chaotropic salts, stepwise approach was used to provide a better dissolution of the spider silk. The obtained substances were characterized using the complex of physical-chemical methods. The morphology of composite materials produced from spider silk solutions was analyzed (Fig.1).

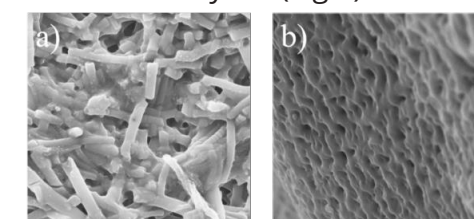


Figure 1. SEM images of silk-based films obtained in (a) water solution and (b) organic solution (99% HFIP).

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Hafnium oxide nanoparticles as radiosensitizers

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Abstract: The effectiveness of radiotherapy is linked to the ability to absorb/interact with x-rays, which depends on electron density and the energy used. Introduction of hafnium oxide nanoparticles with high electron density into the x-ray pathway can increase the absorption. By means of upconversion it is possible to visualize tumors and detect them.

Radiation therapy is one of the classic methods of treating oncological diseases along with surgery, chemotherapy and immunotherapy. Up to 60% of patients receive radiation therapy at various stages of treatment. Despite its widespread use, this method has limitations, in particular undesirable reactions of perifocal (non-tumoral) tissues [1]. The development of agents that increase the sensitivity of tumor tissues to ionizing radiation is one of the methods for increasing the effectiveness of radiation therapy [2]. This paper proposes the use of nanoparticles of hafnium oxide (HfO_2) as radio-sensitizers. Such nanoparticles with high electron density, possessing biocompatibility and selective accumulation in cancer cells make it possible to enhance the radiation dose [3]. The aqueous dispersions of HfO_2 nanoparticles were obtained and investigated. Phase composition, morphology and distribution of elements in aero- and xerogels were studied (Fig. 1). The cytotoxicity of the nanoparticles on cell cultures was evaluated.

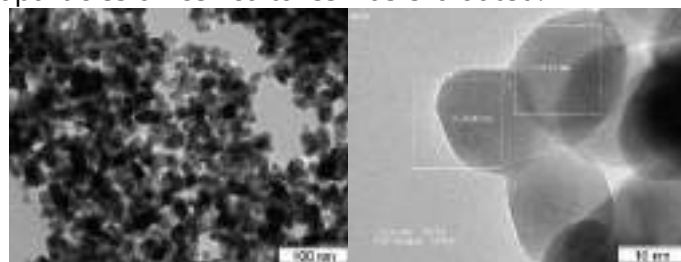


Figure 1. HR-TEM images of HfO_2 nanoparticles.

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Simple test-system for bacteria sensing based on peroxidase-like activity inject printed magnetite nanoparticles

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Abstract: Research has been focused on development simple test-system for bacteria sensing by inject printing of magnetite nanoparticles. Iron oxide nanoparticles are known as cheap, but effective and biocompatible peroxidase mimetics, which exhibit high stability and easy to storage. The enzymatic activity of the nanoparticles is inhibited in the presence of bacteria. Magnetite nanoparticles obtained by US treatment without any surfactants seems to exhibit high peroxidase-like activity which is not only useful in obtaining sensors, but also answers theoretical questions on the behavior of magnetite-based peroxidase mimetics in the absence of a surface organic layer. The development of ink based on magnetite nanoparticles allowed the use of inkjet technology to create sensors, without the need to create pre-patterns such as templates. The application of nanoparticles in the detection of bacteria will not only potentially allow the use of more accurate methods, but also would decrease the cost of sensors and medicine respectively.

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Application of ceramic membranes with immobilized enzymes in food industry

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Abstract: Enzymes are widely used in many industrial fields such as microbiological, biotechnological, pharmaceutical, medicine and others. In food industry they also play a great role. For instance, amylase is used in starch hydrolysis to produce oligosaccharides which application includes coating agents, viscosity producers, and flavor carriers. Another example is lactase catalyzed lactose hydrolysis that is applied in lactose free milk production. The latter is especially important process because about 30 percent of people in Russia have lactose intolerance [1]. However, used technologies have some disadvantages because enzymes can not be recovered from the reaction mixture and they are used only once. It makes the process economically unprofitable. Therefore, this problem can be solved by using immobilized enzymes.

Immobilized enzymes have advantages over native enzymes including their higher stability, ability to enzyme recovery from the reaction mixture at the end of the reaction, a possibility of repeated and continuous using [2]. On the other hand, there are many materials that may be used as a surface for enzyme immobilization. Among them ceramic membranes are perspective systems for this application. They perform contemporaneously such functions as biocatalytic, stabilizing, and a function of product separation. Ceramic membranes possess high thermal stability, provide short time of substrate and enzyme interaction, they also can be easily regenerated from bacterial films that makes their applying as a surface for enzyme immobilization more preferred. Application of such enzymes ceramic membranes in membrane reactors will allow getting pure products with low production cost.

Thus, the main purpose of our study is to develop a method of enzyme immobilization on mesoporous layer, obtained by sol-gel method, of silica based ceramic membranes. In this research main filtration characteristics of membranes were studied, the material was analyzed using XRD technique. Properties of enzyme ceramic system were studied by Scanning electron microscopy; functional composition was analyzed by IR-spectroscopy.

In order to define enzyme activity lactose was chosen as a substrate and lactase as the enzyme catalyzed its hydrolysis. The influence of time, number of cycles and temperature in case of lactose hydrolysis was investigated. Although, enzymes have slightly lost their activity, they continued to work for at least 4 cycles.

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Synthesis and characterization of biocompatible protein nanocontainers (NCs) with the ability of magneto-controllable delivery and short-term release of hemostatic agent ϵ -aminocaproic acid (EACA).

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Abstract: One of the most acute problems in surgical practice for many years has been the problem of reducing blood loss during operations. The main difficulties in the development of new drugs designed to stop bleeding are associated with the need for local application of hemostatic agents, their low toxicity to surrounding tissues and the absence of side effects. Work on the creation of local hemostatic agents has been going on for quite some time, and now there are several types of medicinal substances that are used as local hemostatic drugs. These include hemostatic sponges, wound dressings with various substances and surface-applied substances such as thrombin.

Among intravenous delivery hemostatics, there is only a small group of antifibrinolytic drugs, including α -aminocaproic and tranexamic acid. The severe side effects of these drugs, when administered intravenously, is a significantly increased possibility of thrombosis, so their use is limited to such serious conditions as a hemorrhagic syndrome, complicated abortion, surgery on organs with high vascularization.

In this work, for the first time, we propose an approach for creating a nano-formulated ϵ -aminocaproic acid with the ability to control by a magnetic field based on albumin nanocontainers (NCs) with embedded magnetite nanoparticles (MG). In this form, the hemostatic drug can be applied locally, without affecting the entire body.

The method of synthesis developed by us is relatively simple and allows to obtain magnetically controlled nanocontainers that ensure the release of the drug substance within 48 hours.

Albumin NCs were synthesized by desolvation bovine serum albumin (BSA) using methanol without any additional crosslinking. Polyethylene glycol (PEG) was used as a stabilizing agent and for size control. Characterization of nanocontainers was carried out using transmission and scanning electron microscopy, dynamic light scattering, X-ray diffraction, and FTIR spectroscopy. Cytotoxicity of the nanoformulation was assessed using the MTT assay. The release of the loaded substance from NCs was measured spectrophotometrically using rhodamine B as a marker molecule. The hemostatic activity was assessed by analyzing the curve of lysis and thrombus formation (CloFAL), and the ability to magnetically control was evaluated using a fluidic installation.

The NCs obtained during the research work had an average size of 186 ± 24 nm, and in turn, consisted of smaller structural units — nanoparticles – with an average size in the range from 10 to 20 nm. The nanocontainers were stabilized with a PEG shell with a size of 6-10 nm. It was shown, that NCs is not cytotoxic at concentrations up to 8 mg BSA/ml. Absorption capacity was about 36%, while drug release during the first day was 17%. An analysis of the CloFAL curve showed the ability of NCs to successfully inhibit thrombus lysis, and the ability to magnetically control was confirmed in flow system conditions.

Thus, the nanocontainers obtained were distinguished by their small size and high aggregation stability. At the same time, their structural stability ensured the release of the loaded

substance within two days. NCs are easily and quickly controlled by a magnetic field and accumulate in a given place for 5 minutes, even under conditions of rapid fluid flow. We assume that this system can be successfully used to deliver other substances of the "small molecule" category.

Theoretical modelling of polyhalidebismuthates

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Abstract: In the last decade, chemistry of the polynuclear halides complexes, especially bismuth (III) and polyhalidebismuthates (PHBs), attracted great interest in scientific community [1, 2]. There are several reasons for this: first, semiconductor [3, 4] and photochromism [5] properties open ways for electronic industry; second, is a fundamental significance for inorganic chemistry. PHBs are very labile due to their favorable kinetics and low M - X binding energy. Were Assumed that they exist as $[\text{BiX}_6]^{3-}$ species and form multinuclear complexes in solid state only. So, the "building block concept" suitable for many other complex inorganic systems seems inapplicable in this case. Therefore, a fundamental question arises: is it possible to predict the structure or at least the composition of the complexes by varying the reaction conditions, stoichiometry and the nature of the cation used in the synthesis?

In this paper, ion pairs were studied $(\text{Cat})_x^+[\text{Bi}_y\text{Br}_z]^{1-}$. The calculations were carried out using different solvation models and methods to account for the influence of the cation on the PHB formation reaction. The energies of formation were calculated not only for ion pairs whose existence was confirmed experimentally, but also for those that apparently do not exist.

All calculations were performed in the program Gaussian16 (method: LC-wPBE, the basics: ma-def2tzvp) and COSMOTherm (solvation model: COSMO-RS).

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Tissue plasminogen activator loaded magnetite nanocontainers: a new way of magnetically controlled thrombolysis

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Abstract: Magnetic gels are fast developing areas in the material science. For biomedical application these materials should fit criteria such as large specific surface area, well-developed microstructure and biocompatibility [1]. Among all magnetic materials only two of them are considered biocompatible and regarded as safe to be applied for biomedical applications, namely magnetite and maghemite [3]. In the ideal situation, the magnetic carrier consists of only magnetic material, but due to the chemical nature and surface properties of these two oxides, difficulties in covalent condensation of iron oxide nanoparticles, they cannot be used directly for the creation of magnetic capsules.

Magnetite-based nanocontainers (designated as MNCs) were prepared by template-promoted formation of magnetite gel using the microemulsion technique. Using microemulsion technique helps to synthesize the magnetite-based nanocontainers with adjustable size. The diameter of NCs can be varied in a wide range by the regulation of microemulsion composition and emulsifying conditions. The MNCs exhibit a developed microstructure and textural properties with total surface area up to 135 m²/g, excellent magnetization up to 60 emu/g and low cytotoxicity against both HeLa and postnatal human fibroblast (up to 260 µg/mL). To evaluate the potency of magnetic NCs for the targeted drug delivery, magnetic thrombolytic composites (designated as tPA@MNCs) were prepared by the entrapment of tissue plasminogen activator within a magnetite cage and tested for their ability to destroy model thrombi made of human plasma clots. The applied magnetic field can concentrate such composite materials in the desired place, keeping for a certain period of time, until the encapsulated preparation is released, thereby minimizing the side effects caused by nonspecific distribution. The process of thrombolysis began in 60 minutes after the components contact under static conditions, while the full lysis of the clot was observed after 620 min of the experiment (Figure 1).

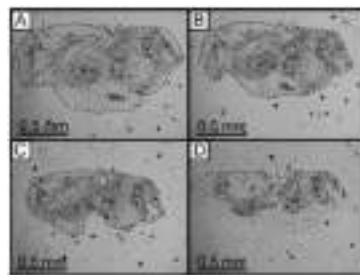


Figure 1. Thrombolysis provided by targeted tPA@MNCs. Changes in the thrombus periphery are clear seen after the containers were delivered by magnet (A), after 60 (B), 245 (C), 620 (D) min.

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The inkjet printing of the microlenses raster

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Abstract: Microlenses raster systems are one of the most popular microsystems used not only for optical imaging and focusing but also for the design and anti-counterfeiting purposes due to their enormous stereoscopic representation. The working principle of one microlens in an array and formation of a virtual image is shown in Fig. 1. Nowadays, such rasters are typically produced by the hot embossing or molding of polymers. Here, a negative of lens array arranged hexagonally are used. This methodology has a high filling and accuracy degree of array deposition which guaranty the fast and cost-effective fabrication of contrast images in the final product. However, on the other hand, these technologies are non-flexible for design changes and do not allow a selective deposition of the lens arrays. The inkjet printing of this type of structures can improve this disadvantage without sacrificing advantages of filling and accuracy. This work is devoted to fabrication of microlenses arrays by the inkjet printing approach.

The main challenges for this manufacturing method are its scaling to the micro sizes and selection of an appropriate ink material. The next parameters of printed pattern is the hexagonal arrangement of microlenses in an array. The focal distance of printed half spherical lenses is estimated by the Lippman expression depending on their radius and refractive index of ink material. The system is arranged in the way that the focal plane is situated on the back surface of raster film patterned with a text, resulting in its magnified virtual image as an ink material, the UV-curable resin was selected. It has refractive index in the visible spectral range of approx. 1.5 and rheological parameters suitable for printed head of the used inkjet printer Dimatix Fujifilm 2831: viscosity ≥ 10 cP, surface tension is 30-55 mN/m. The right balance of hydrophilic-lipophilic components allows forming a half-sphere drop on the substrate surface (PET foils, glass).

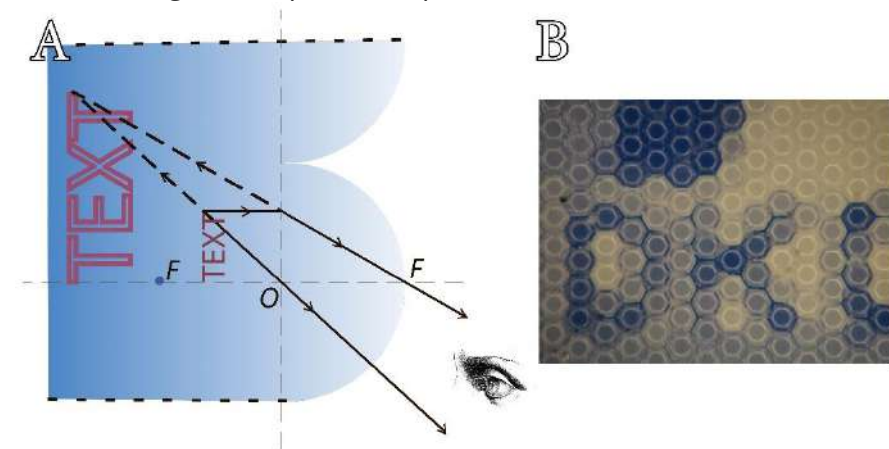


Figure 1. A - Schematics of virtual image formation by a polymer converging microlens
B - the optical microscope picture of printed microlenses arrays.

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Inkjet printed memristors

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Abstract: Neuromorphic engineering is one of the leading technological trends shaping the future of technical systems. Neuromorphic memristic systems can be implemented in a very compact form and can operate at high speed, low energy loss and well-distributed energy dissipation. A memristor is a resistive element of an electrical circuit whose resistance depends on the background of the current load. Memristic effect occurs in many organic and inorganic nanomaterials, including simple oxides, which allows to integrate memristors in micro- and nanoelectronics [1].

Memristive devices are implemented in a crossbar geometry, see Figure 1. Its topology was adapted for the study of cell populations.

Inkjet printing is a suggested technological approach for deposition of functional layers and specific patterns die to its flexibility. Colloidal solutions of TiO_2 , ZrO_2 and Fe_3O_4 obtained by low-temperature sol-gel synthesis are used as inks for printing of dielectric layers [2].

Research of memristor devices with different oxides dielectric layer and analysis of its electrical properties will significantly expand the possibilities of neuromorphic engineering interactions.

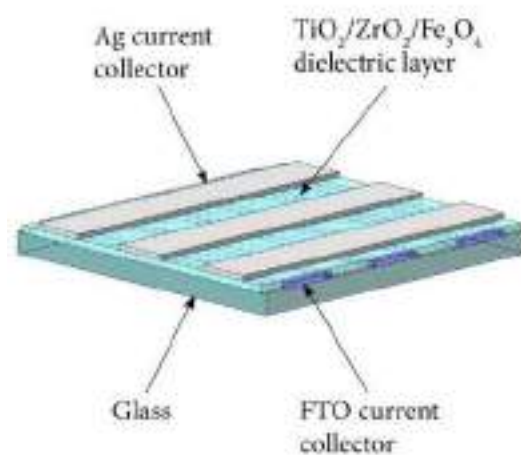


Figure 1. Crossbar architecture of a memristor.

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Comprehensive characterization of TiO_2 inks and their application for inkjet printing of microstructures

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Abstract: Nowadays, inkjet printing is one of the promising and widely used techniques for fabrication of various structures. The most popular are elements for flexible, wearable electronics and sensing, LEDs, optical waveguides, solar cells, and optic lenses. This method has obvious advantages comparing with other deposition techniques such as low cost, low consumption of materials, rapid production times, and high reproducibility. This research gives comprehensive characterization of inkjet printing as a deposition technique and optimal printing parameters with the focus on titanium dioxide based inks deposition. The parameters which can be optimized are drop spacing, sol concentration in synthesized ink compositions, drying temperature, the type of desired pattern. We described the best matching between designed patterns and inkjet printed samples. Also, an extensive description of ink drop coalescence on various substrates is provided.

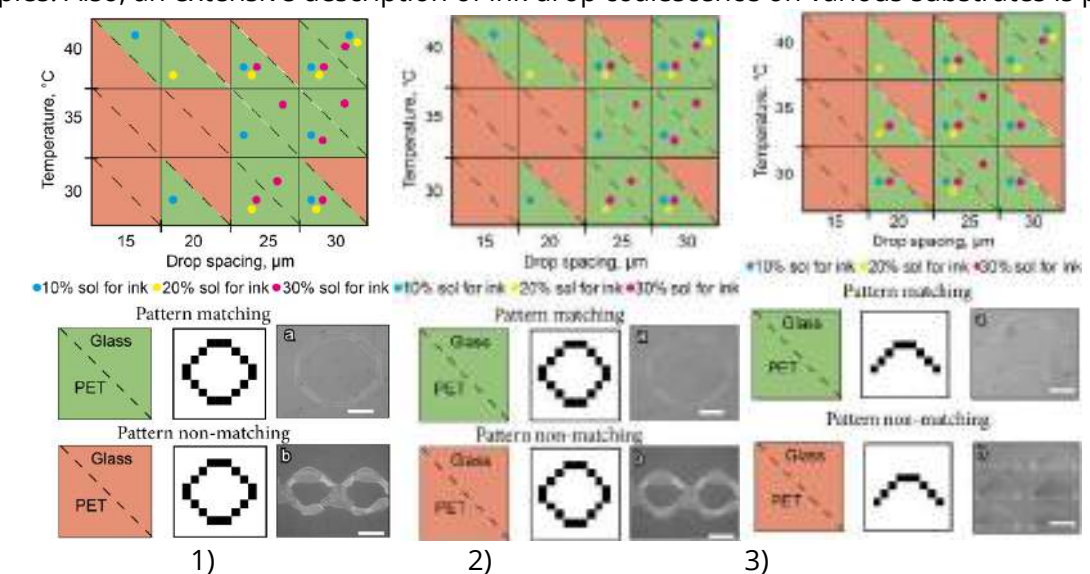


Figure 1 - Matching of printed structure with a basic pattern - blue point for 10% sol in inks, yellow for 20% and purple for 30%. Matching represented: a - optic image of matching structure; b - optic image with defective structure, i.e. coalescence inside printed structures. Colors represent the matching of inkjet printed structures to designed patterns: red - no structures matching, green - all structures are matching, grey - some structures are matching with the designed pattern. All right upper corners in each square indicate structures printed on glass substrate, bottom left corners - on PET substrate. Numbers 1, 2 and 3 indicate three different patterns: circle, arc and rhombus, respectively.

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Hybrid technology for fabrication of memristive Au/TiO₂/Au devices

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Abstract: This work is focused on the development of a hybrid fabrication method of low-power, horizontal structured memristive devices. Memristor is a two-terminal electric circuit element with adjustable resistance depending on the previous current history. In this way, memristors act electrically similar to synapses connecting neurons. Arrays of memristive elements found their application in fuzzy logic systems, non-volatile resistive memory, and artificial neural networks. Such memristive elements have faster and power-efficient parallel computing architecture, superior to conventional von Neumann architecture for certain computation tasks. Various fabrication technologies have been implemented to produce memristors with precise resistive switching. Here, we introduce a novel method that synergistically combines photolithography, material scratching using atomic force microscopy (AFM) cantilever, and inkjet printing.

The design of the proposed memristive element is shown in Fig. 1 a). This arrangement differs from traditional cross-bar memristive arrays by its planarity and reduction of necessary fabrication steps. The 30 nm thin gold layer with 3 nm of chromium adhesive layer nanoelectrodes on a glass substrate were patterned by a lift-off process. In the next step, narrow gaps in the gold layers were obtained by the direct scratching using a cantilever of an atomic force microscope Ntegra Aura (NT-MDT, Russia) operating in the contact mode. These resulted in reproducible cone-shaped trenches. Their shape and morphology was investigated by scanning electron microscopy (SEM Tescan Vega 3) and AFM. The final technological step was the deposition of thin titanium dioxide (TiO₂) layer on the top of the trenches by inkjet printing, so that the scratched gaps between the gold electrodes were filled with the memristive dielectric component. The inkjet printing was performed with Fujifilm Dimatix Materials Printer DMP-2831 with 10 pl drop cartridge. The sol-gel synthesis of TiO₂ ink, as well as parameters of optimal printing, drying, and annealing have been investigated in detail.

The memristive elements fabricated using the proposed technological approach have been subjected to electrical characterization using a sub-femtoampere source meter Keithley 6430 upon annealing. The obtained current-voltage dependencies of the fabricated memristor device are shown in Fig. 1 b). Incrementally decreasing resistance with hysteretic voltage-current dependencies was observed upon application of 10 consecutive voltage sweeps.

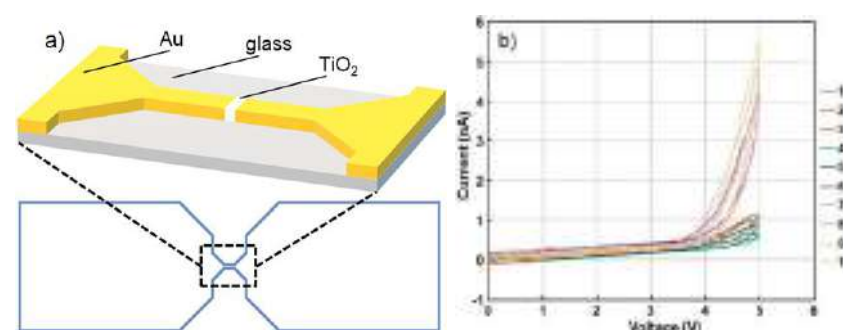


Figure 1. a) Schematic and b) Voltage-current characteristics of fabricated memristive devices

The research has been carried out with financial support from the Russian Science Foundation (project No 19-19-00433).

Study of the effectiveness of antimicrobial effects on biofilms of magnetically controlled composites with a biocidal component

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Abstract: The problem of effective therapeutic treatment of chronic and acute inflammation caused by the development and vital activity of microbial biofilms is still relevant because of the resistance of bacteria to the antibiotics most often used in medical practice. In recent years the use of nanocomposite materials which can easily penetrate into the biofilm internal environment has become the most promising. In particular, magnetic particles in the composition of antibacterial agents can increase its effectiveness. Thus, the purpose of this work was to develop a new composite material with magnetically controlled properties and high antimicrobial activity.

Amorphous calcium carbonate encapsulated with biocide was chosen as the main frame material. The composite matrix also consists of magnetite nanoparticles giving it magnetic properties. Targeting of the drug occurs due to its targeting to the inflammatory focus under the influence of a magnetic field; the target release of the active substance from the nanocomposite is accomplished by the magnetic-inductive recrystallization of calcium carbonate under the action of a high-frequency magnetic field (figure 1).

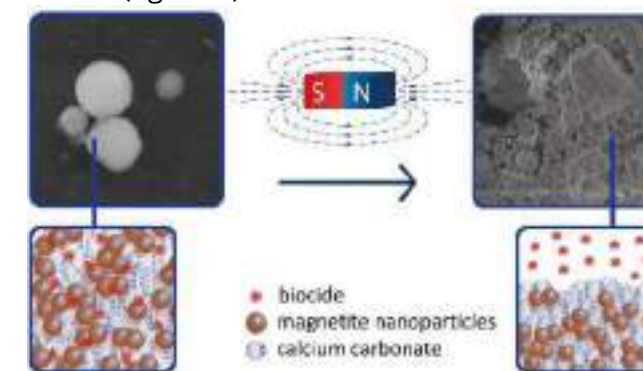


Figure 1. Schematic diagram of a magnetic ceramic nanocomposite material.

Experimental studies conducted on the biofilms of several types of bacteria proved the presence of a well-pronounced composite effect based on the synergistic antibacterial effects of calcium carbonate and magnetite. The antibiotic in its initial form showed less effect on bacteria compared with the preparation with immobilized antibiotic. The antibacterial effect was also manifested in the case of nanocomposite particles without an antibiotic which makes it possible to judge the possibility of providing a synergistic effect. Thus, the results are promising for further research and application development in particular in medical practice.

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Polyelectrolyte-based nanocontainers for switching fluorescence of biosystem

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Abstract: At present time, there has been increasing interest in the development of stimuli-responsive materials for effective delivery into the live system. The fabrication of functional hybrid materials comprised of nanoscale building blocks represents one way in which nanotechnology can contribute to biology and medicine.

Herein we present a simple approach of chemicobiological switching of bacteria fluorescence with IR light using nanoarchitecture container initiators and metabolic bacteria pathway. It based on feedback IR activation of the container with a loaded substance that can effect on bacteria metabolism switching its bioluminescence. Containers (A) are nanoarchitected for the response to IR. After irradiation of the containers at 980 nm active molecule (B, L-arabinose) was released. L-arabinose switches bacteria (C) metabolism in the needed direction, here to switch fluorescent gene and we can detect light at 510 nm.

In summary, the novel and simple strategy of controlled release of biomolecules from the containers work successfully in a biological system was shown. The developed materials can induce metabolic processes in both plankton cells and in biofilms (in the macrocolony model). The approach described herein can be used in many applications where the target and delayed switching and light upconversion are required, for example.

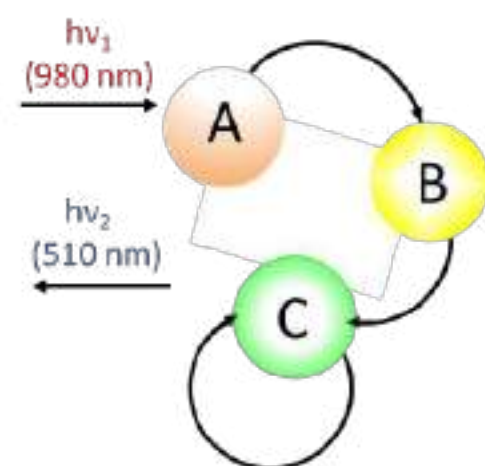


Figure 1. Scheme of signal processing in a biocompatible system that communicates with bacteria through small organic molecules and possesses delayed switching of bioluminescence

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Periodic silver based structures assembled in gel

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Abstract: This research aims to investigate the self-organization of stepwise-graded structure due to non-linear chemical phenomena with the formation of graduate SPR (Surface Plasmon Resonance) response.

Functional materials with gradients (FMG), i.e. the materials with a change over the volume properties [1], may achieve a set of specified non-linear functions [2]. Periodic precipitation is suitable for studying this, as they can be manipulated and will be between different morphogen-like structures. Light triggered processes in the gel are a multilevel system promising for the regulation of optical properties and effects localization in time and space for nanoparticles generation and assembly modulation.

To create gradient structures the following reagents were used Silver nitrate, 99%, and agar (A1296) which were purchased from Sigma Aldrich. When diffusion of silver salt into agar gel occurs, Ag⁺ ions react with galacturonic acid monomers in pectin to form white precipitation [3]. Then upon light irradiation salt decompose to form metal silver nanosized aggregations. The formation of nanoparticles was proved by UV-Vis spectra, where the characteristic SPR peak at 325 nm is observed: dark film absorbs the almost whole range of light except narrow zone where relatively high transmission occurs. It is the classical behavior of colored particles: within a high concentration of dye self-absorption of the light occurs, so the transparency signal became smaller. The hypothesis is that the size depends on the parameters of the light that we use to irradiated films rather than the concentration of silver salt.

Besides, for a given concentration AgNO₃, the bans of the periodic structures follow the spacing law of consecutive band distance, which is related to the spacing coefficient. This dependence correlates with the Matalon - Packter law [4] for the ionic system, which states that our samples have the possibility of self-organization.

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Hybrid sensor systems based on polyelectrolytes and semiconductor carbon material for analysis of biologically significant analytes

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Abstract: The medical diagnostic and professional sport are particularly interested in real-time, wearable, minimally invasive monitoring. Human sweat could enable non-invasive monitoring. Sweat mostly consists of water with small concentration of electrolytes, including sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), and magnesium (Mg^{2+}). Such parameters are noninvasively controlled in professional sport to athletic performance optimization.

Electrolyte ions in aqueous solutions are usually measured using a potentiometric method with ion-selective membranes. Typical ion-selective electrodes are liquid contact electrodes. Until recently, ISE devices were non-compatible with the principles of miniaturization and portability. However, elimination of the internal reference system and its replacement with the solid contact results in insufficient long-term stability of ISE potentials and in poor piece-to-piece reproducibility. We suppose that polyelectrolyte multilayers formed by layer-by-layer assembly have hydration activity and can serve as inner electrode solution in potentiometric sensors.

This paper describes the design and fabrication of flexible ion-sensing electrochemical adhesive tape-based analytical device for potentiometric measurements of potassium and sodium ions. This sensing platform has carbon adhesive tape that contains ion-selective electrode with conventional ion-selective membrane immobilized within a polyelectrolyte multilayer as pseudo-inner solution and ion-to-electron transducer. Within polyelectrolyte layers, potassium chloride is used as ion source. Carbon adhesive tape is a cheap flexible electronic conductor. The required selectivity for the target analyte is achieved by using a suitable ionophore. Due to unique properties such as light weight, low cost, high flexibility, excellent elasticity, flexible carbon conductive adhesive tape could serve as an ideal platform for personalized wearable devices. The sensing platform proposed demonstrates better time of response and is close to Nernstian value of sensitivity with sensor low cost. Biocompatibility of ion-selective sensing platform was demonstrated at potassium chronopotentiometric measurements in *E. coli* biofilm. For the first time, potassium level in biofilm was measured with potentiometry and showed agreement with previous results.

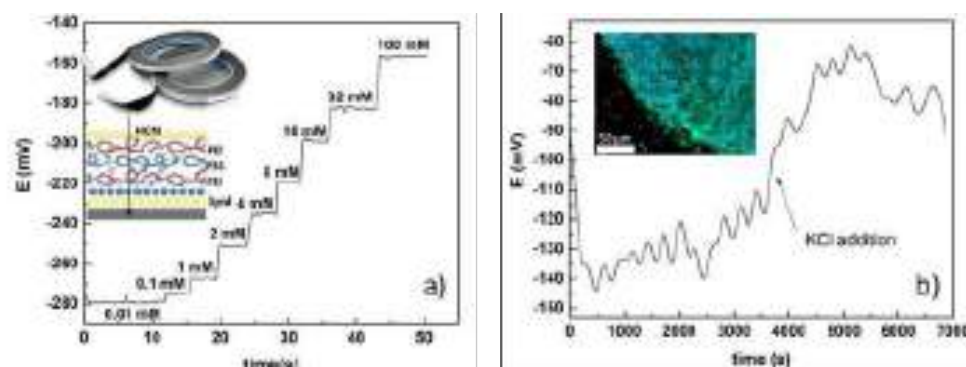


Figure 1. Example of potentiometric response for potassium ion-selective electrode. Common scheme of design of ion-selective adhesive tape (insert); b) Chronopotentiometric response for *Escherichia coli* living and with potassium chloride disruption. Bacteria representation with biomarkers thioflavin S (insert).

Holographic polyelectrolyte film formation via gel coacervate complex

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Abstract: In the present work transparent holographic PDADMAC/Heparin film has been synthesized from polyelectrolyte coacervates. Thin holographic film with 1 μm grating period and uniform surface of a polyelectrolyte complex are readily and fast-made by pressing polyelectrolyte coacervate, hydrated viscoelastic fluidlike form of polyelectrolyte complex precursor, between flat surface and holographic mask. Additionally, cobalt (II) chloride aquacomplex is added at the first stage of polyelectrolytes blending. Such advantage leads to the absence of porous polyelectrolyte complex structure. PDADMAC/Heparin holographic film has been demonstrated reversible response for humidity under diffraction detection. PDADMAC/Heparin/Co (II) chloride film proves application for the humidity sensing with colorimetric detection. Based obtained results mechanism of water incorporating including reputation model and polyelectrolyte melt behavior is proposed.

Sol-gel derived thin film composites as functional elements for optical applications

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Abstract: Thin-film transparent conductive materials are essential to optoelectronic devices technologies. Besides transparent thin films, the nanocomposites, representing transparent oxide layers with embedded noble metal nanoparticles, are of special concern [1]. Such nanocomposite is optically-transparent in the visible spectrum range and simultaneously has unique optical and electrical properties associated with the excitation of plasmon resonances in metal nanoparticles. For applied Optoelectronics, it is important to have the control over the physical properties of plasmon nanostructures, to obtain an enhancement of the electromagnetic field by selective light illumination. For example, to realize the Purcell effect in LED structures. [2] The display regularities of nanoparticles formation and controlled obtaining of resonance peaks in absorptions spectra, i.e. obtaining of ordered nanostructures, will take materials science to a new level in the creation of new smart materials for Optoelectronics. To study the possibility of nanocomposite structures with controlled physical characteristics synthesis, the sol-gel method is most suitable. This method combines the simplicity of the technological process with the possibility of varying the composition and heat treatment of the material.

In this work, the coupling of the optical and structural properties of AZO oxide films with involved layers of silver nanoparticles nanocomposites prepared by the sol-gel technology have been studied. The influence of polycrystalline grains growth in AZO film on the formation and reformation of silver nanoparticles embedded in the film has been investigated.

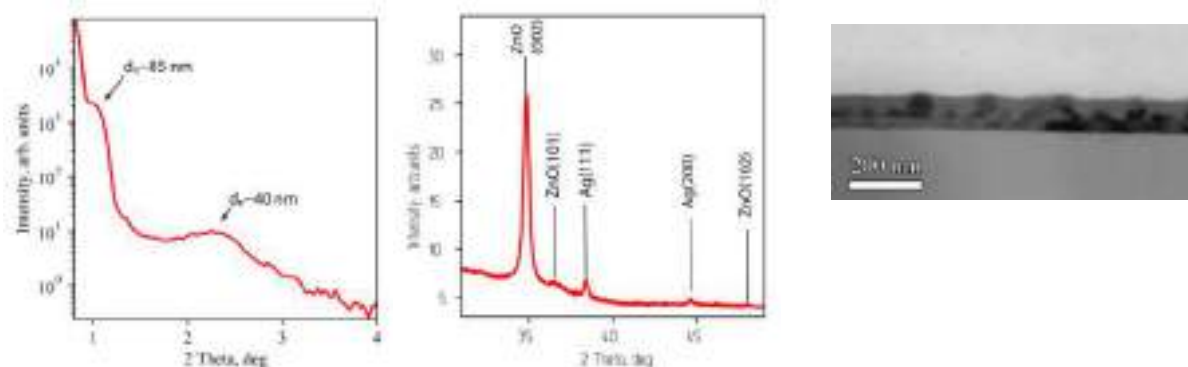


Figure 1. AZO oxide films with involved layers of silver nanoparticles nanocomposites characterization: a - SAXS data (It is displayed by logarithmic unit for better visualization. Curves indicate the periodicity in the system with the given characteristic dimensions); b- WAXS data (The WAXS spectrum demonstrates the lines corresponding to (100), (002), (101), (102) reflections of ZnO and (111), (200) reflections of Ag); c- cross-section TEM image.

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Metal oxide nanoparticles effect on siRNA hybridization

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Abstract: The history of studying the interaction between nucleic acids and nanoparticles has been around for many decades. The focus of works on this subject has continuously shifted from topic to topic, covering such fields as biosensing, nanoassembly, targeted delivery, and gene therapy. For the most part, such investigations are devoted only to the detection of nucleic acids hybridization/dehybridization, without going into details of the mechanisms of interaction of nucleic acids with nanoparticles from different materials. In our work, we set the task to find out whether there is a difference between different types of nanoparticles when studying the hybridization of the same siRNA sequences. Magnetite, gold, and silica NPs were chosen for this purpose as these systems were already used for siRNA or DNA hybridization using different linkages and were studied via addition to solutions of sense and antisense sequences and incubation for different time periods. Fabricated nanoparticles were also studied by XRD, SEM, and DLS analysis to estimate the exact composition of NPs, their size, and surface charge.

It was shown that magnetite NPs could increase the self-assembly rate of RNA molecules relatively to pure siRNA sequences while gold and silica NPs do not have a significant influence on the assembling process. We are assuming, that the primary reason to higher hybridization rates of siRNA in the presence of NPs connected with the binding of siRNA strands to the surface of NPs or with locally increased concentration of siRNA in NPs surrounding. These increasing chances of siRNA strands to meet and bond with each other. However, we observed the difference in hybridization rates between samples with MNPs and Au NPs. The possible mechanism of better siRNA assembly on the surface of MNPs connected with the optimal surface charge to nanoparticles size ratio. Having almost the same ζ -potential, MNPs and gold nanoparticles differ in diameter by 2-3 times. Considering the length of the siRNA molecule, which is about 7.5 nm, we can suggest, that upon binding to bigger Au NPs ($d=30$ nm), it changes dimensional conformation and lose spatial mobility. On the other hand, MNPs with an average diameter of 10-20 nm, probably bind siRNA strands only partially, leaving free ends for hybridization.

Work was supported by the Russian Foundation for Basic Research grant 18-33-20043.

Anticoagulant properties of magnetic polyelectrolyte-based composites

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Abstract: The Drug interventions associated with effects on the blood coagulation system play a key role in the treatment of patients with acute myocardial infarction after reperfusion therapy. The maximum therapeutic effect can be achieved with the simultaneous administration of drugs acting on different parts of hemostasis, such as thrombolytics and anticoagulants. Proper use of anticoagulants agents can reduce the risk associated with the threat of recurrence of the disease with the expansion of the affected area, and with the risk of bleeding. To prevent further thrombosis and re-embolism, direct anticoagulants, heparin and low molecular weight heparin (for example, enoxaparin), are used. However, there are some other types of chemicals, such as polystyrene sulfonate (PS) or polyacrylic acid (PA) which possess the same functional groups and potentially can also act as an anticoagulant. We have estimated the anticoagulant properties of these compounds when linked to magnetic nanoparticles (MNPs). Our design was intended to synthesize magnetic thrombolytic composites where thrombolytic – urokinase – was linked to a magnetic core via anticoagulant.

We found that adsorption onto MNPs surface led to decrease of anticoagulant activities of both heparin and enoxaparin, which resulted in a decrease of TT by 2 and 1.3 times valued 25 and 19 sec respectively. In contrast, the elevation of anticoagulant activity was observed for synthetic polymers with prolongation of thrombin time to 35 and 41 sec by PA and PS, respectively. The explanation of this strikingly different behavior can be done by taking into account the structure of the molecules: both synthetic molecules have higher charge density and shorter monomeric unit in its structure with only 2 C-C bonds, while both enoxaparin and heparin are complex glycosaminoglycans with irregular and nonlinear structures. Adsorption on the surface of MNPs is likely to reduce the selectivity of enoxaparin and heparin towards thrombin and ATIII, resulting in a drop of their activity. In contrast, both PSS and PAA are had no selectivity towards these factors and inhibit thrombin via electrostatic interactions. Adsorption of these polymers on the nanoparticles led to nonspecific adsorption of plasma proteins and a lower rate of fibrinogen polymerization.

More importantly, all of the systems except with enoxaparin showed significant thrombogenic activity via the intrinsic pathway and caused spontaneous coagulation of the samples after 10 minutes of incubation. Even for heparin-based system increase of the coagulation rate was observed by the factor 1.54 with subsequent formation of plasma clots in the whole volume of the sample. Conjugation of urokinase reduced the anticoagulant activity of all the tested materials and neglected the difference between them.

Summarizing, both heparin and enoxaparin-based systems showed moderate anticoagulant activities with prolonging thrombin time from 13 to 17 seconds that is 3.1- and 1.5-folds lower than for equal amounts of free anticoagulants. Enoxaparin-based formulation inhibited the intrinsic coagulation pathway by 30%, while all other composites were ineffective for this purpose. These

findings can be further applied for development magnetically controlled nanomedicines with dual anticoagulant and thrombolytic properties.

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Thrombolytic magnetic polyelectrolyte-based composites

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Abstract: Despite the effectiveness of thrombolytic drugs used in modern medicine, they are causing several side effects. Due to nonspecific action of thrombolytics and their fast degradation in the bloodstream these formulations are applied via bolus injections in order to destroy blood clots resulting in minor and major bleedings and related physiological conditions, blood pressure drops and in some cases can cause a fatal outcome. In order to overcome these issues, various strategies are being developed to enhance the selectivity of thrombolytics and to achieve their targeted delivery to the area of interest. One of the strategies is conjugation of thrombolytic enzymes with magnetic nanoparticles and active targeting of such nanoformulations by external magnetic fields. Various methods can be applied to bound biomolecules with nanoparticles, but preference is given for materials with fully biocompatible compositions and with multifunctional or stimuli-responsive activity.

Here we are presenting our findings on polyelectrolyte-based magnetic thrombolytic composites. The materials were produced via layer-by-layer adsorption of biocompatible polyelectrolytes onto the surface of magnetite nanoparticles and decorated with urokinase-type plasmin activator. The magnetic core of the system consisted of pure magnetite nanoparticles which were produced by US-assisted co-precipitation procedure. As a model polyelectrolytes heparin, enoxaparin, polyacrylic acid, and polystyrene sulfonate were selected. The final particles had a hydrodynamic diameter of 180 nm and highly negative charge of -30 mV and were forming stable colloidal systems in water media. The composites demonstrated superparamagnetic behavior with magnetization up to 43 e.m.u./g at 8000 Oe and low coercivity of 50 Oe. Nanoformulations were highly biocompatible and demonstrated the absence of cytotoxicity at concentrations up to 200 µg/mL. Bioactivity of the systems was measured via Thrombodynamic methodology and was comparable to free urokinase at steady state valued 7.2 µm/min. Heparin based composites demonstrated the significant acceleration of lysis rate at early lysis period with 25% faster lysis rate comparable to free urokinase and other polyelectrolyte-based composites. The observed results are discussed in terms of nanostructure of the composites and their interactions with plasma proteins. The produced materials can find their applications for cardiovascular disease treatment.

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Hybrid CNC/Fe₃O₄ Glucose Biosensors

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Abstract: As of 2014, an estimated 8.5% of adults over the age of 18 have been diagnosed with or show symptoms of diabetes mellitus, with an estimated 1.6 million deaths related to the disease occurring in 2012 [1]. A further 2.2 million fatalities that same year were attributed to high blood glucose levels [1]. Poor disease management, often as a result of inadequate blood glucose level monitoring, is the root of the problem. Therefore, finding more effective means of tracking higher than normal blood glucose levels is imperative.

Today, several methods and devices are available for measuring blood glucose levels. This present technology is, however, cumbersome and time consuming, requiring bulky main equipment and accessory paraphernalia. To overcome these limitations, state-of-the-art biosensors intended for in vivo or dermal use, are in development [2]. These sensors are designed to incorporate nanomaterials, which in turn would improve the overall sensitivity and speed of the device. Unfortunately, the possible toxicity of some of these nanomaterials is of great concern.

Taking these concerns into consideration, we present two hybrid CNC/Fe₃O₄ thin film to act as glucose biosensors. We propose that one type of film (or strip) be used on the skin and the other on the tongue. The inherent physicochemical properties of nanocrystalline cellulose makes it a very versatile biomaterial. Its low toxicity, high structural strength, biodegradability and overall biocompatibility makes it an attractive, and therefore often incorporated, component of many hybrid materials intended for use in or on the body. The other component, magnetite nanoparticles, are biomimetic, exhibiting peroxidase-like activity when in contact with glucose, resulting in a color change.

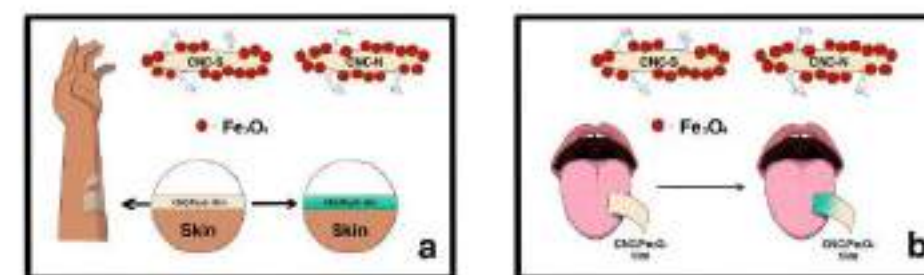


Figure 1. Hybrid CNC/Fe₃O₄ sensor for use on the skin (a) or for the saliva (b).

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The graphene heterogeneous structures as a base electronic skin sensors

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Abstract: Flexible electronic devices gain popularity in many spheres such as robotics, medicine, prosthesis, sports equipment¹. Electronic skin (e-skin) is a device with various sensors combinations. It is a stretchable, highly flexible and water transmitted circuitry matrix for measuring heart rate, skin humidity, and human body temperature². The body state measurements are synchronous due to electrochemical carbon-based substances singularities².

A technique of manufacturing electronic equipment includes a set of methods: the Hummers' method for the graphene oxide (GO)³ and reduced graphene oxide (rGO) production⁴, graphene inks and inkjet printing⁵.

In this work graphene-based structures for human health monitoring device have been developed. Synthesized GO is a graphite monolayer with carboxylic, epoxy and hydroxyl groups⁶. As some of these groups are difficult to remove with a single reduction method, stepwise reduction was used to provide a better conductivity of the graphene. Also doping by silver nanoparticles has been done (Fig.1). These modifications enabled to obtain graphene inks for the production of electronic skin.

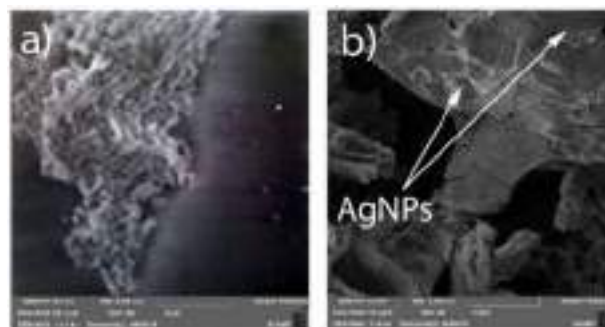


Figure 1. SEM images of (a) not doped rGO and (b) silver-doped rGO.

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Structurally colored coatings with high abrasion resistance prepared by electrophoretic deposition

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Abstract: The color of dyes is an inherent property of the material that depends on their chemical nature. Some of these dye molecules easily fade over time or upon exposure to light. On the other hand, structural color is not susceptible to fading unless the microstructure is destroyed. The most familiar structurally colored materials are arrays of monodispersed particles such as colloidal crystals. Electrophoretic deposition (EPD) is one of the most versatile procedures to prepare array of particles on conductive substrates. Recently, we have successfully prepared colorful coatings consisting of an array of SiO₂ particles via the electrophoretic deposition (EPD) method.^{1,2} Various vividly colored coatings can be produced from SiO₂ particles with diameters between 240 nm and 300 nm on the surfaces of stainless steel forks, were also successfully prepared (Figure 1). However, conventional EPD coating films prepared from only SiO₂ particles have poor abrasion resistance because both particle-particle and particle-substrate interactions are very weak. Enhancing abrasion resistance is an important issue for the practical applications of structurally colored coatings. In this study, robust structurally colored coating films were prepared by the cathodic EPD method using SiO₂ particles, black substances and Mg²⁺ ions. Monodisperse SiO₂ particles and Fe₃O₄ nanoparticles (black additives) were dispersed in 2-propanol. Then aqueous solution of Mg(NO₃)₂ was added to the dispersion. Cathodic EPD coatings were carried out using ITO-coated glass plates as coating substrates. Formation of homogeneous coating films has been confirmed for the samples prepared from dispersions containing Mg(NO₃)₂. When DC voltage was applied between anodes and cathodes in the dispersion, OH⁻ ions were generated by electrolysis of water and NO₃⁻ ions on the surface of cathode. Therefore, Mg(OH)₂ was co-deposited on the ITO substrates in addition with EPD of SiO₂ particles. Mg(OH)₂ can contribute to enhancing the mechanical stability of the coating films. Mechanical abrasion resistance of coating films was evaluated by the sandpaper test. The coating films were placed against sandpaper and weighted with 200 g of weight. The sample was moved 10 cm in a straight manner, and one cycle was finished. The coating film prepared via the conventional anodic EPD process was almost completely scratched off only after 1 cycle. In contrast, nearly 90 % (in area) of the coating films prepared via the cathodic EPD process using Mg(NO₃)₂ remained even after 5 cycles of abrasion testing (Figure 2). These results indicate that Mg²⁺ played important roles not only in endowing positive charges the SiO₂ particles with positive charge but also in serving as a binder to adhere particles to the substrate and with each other.

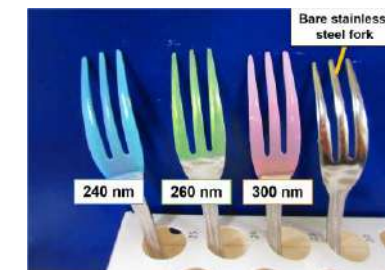


Figure 1. Photograph of the coating films prepared using SiO₂ particles with diameters of 240, 260, and 300 nm on stainless steel forks via the EPD

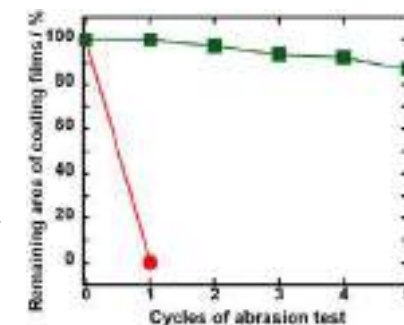


Figure 2. Remaining areas of coating films as a function of abrasion test cycles. Circle, film prepared by anodic EPD; Square, by cathodic EPD using Mg²⁺.

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Hydrophobic coatings by Low Pressure Cold Spray

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Abstract: This study shall aim at the synergy between sol-gel technique of fabrication of the powder and subsequently utilized low pressure cold spray (LPCS) method of deposition to prepare hydrophobic coating. Mentioned hydrophobicity results from the surface modification of silica cores with 1H,1H,2H,2H-perfluorooctyltriethoxysilane ($C_{18}H_{19}F_{13}O_3Si$) molecules (Figure 1). The cores are synthesized as monodispersed silica particles of ca. 500 nm diameter realized via Stöber process. It is worth of emphasizing that fabrication and modification stages proceed while a single procedure. Consequently, as prepared powder composed of fluorinated silica particles is used to deposit coating by LPCS. The LPCS method bases on the introduction of the solid feedstock powder directly into accelerated gas stream to approach the substrate with supersonic velocity. For that reason LPCS most commonly utilizes metallic powders due to their plasticity. Current literature shows [1] that the oxide powder characterized by high hardness and high brittleness can be also sprayed. Moreover, the newest research shows [2] that important conditioning factor allowing sort of plastic deformation for oxide materials is amorphicity of the feedstock powder possible to be achieved using sol-gel route. The research shows the coating is characterized by poor wetting as feedstock material itself. Not only does the resulted maximum static angle of coating reach the superhydrophobic level (CA 150,2°), but it is observed that the different preparation methods may drastically change the hydrophobic potential. Furthermore, the described superhydrophobic coating could be sprayed on different substrates, such as wood, glass, stainless steel, polytetrafluoroethylene, etc. The important finding from the study is the possibility of the large-scale production of superhydrophobic coatings on the wide variety of substrates thanks to the combination of the sol-gel and low pressure cold spray methods.

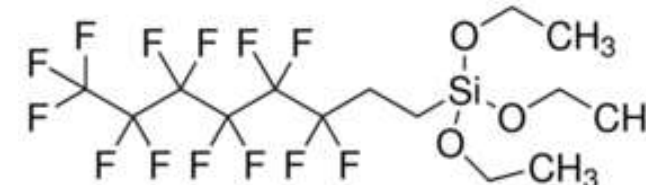


Figure 1. 1H,1H,2H,2H-perfluorooctyltriethoxysilane.

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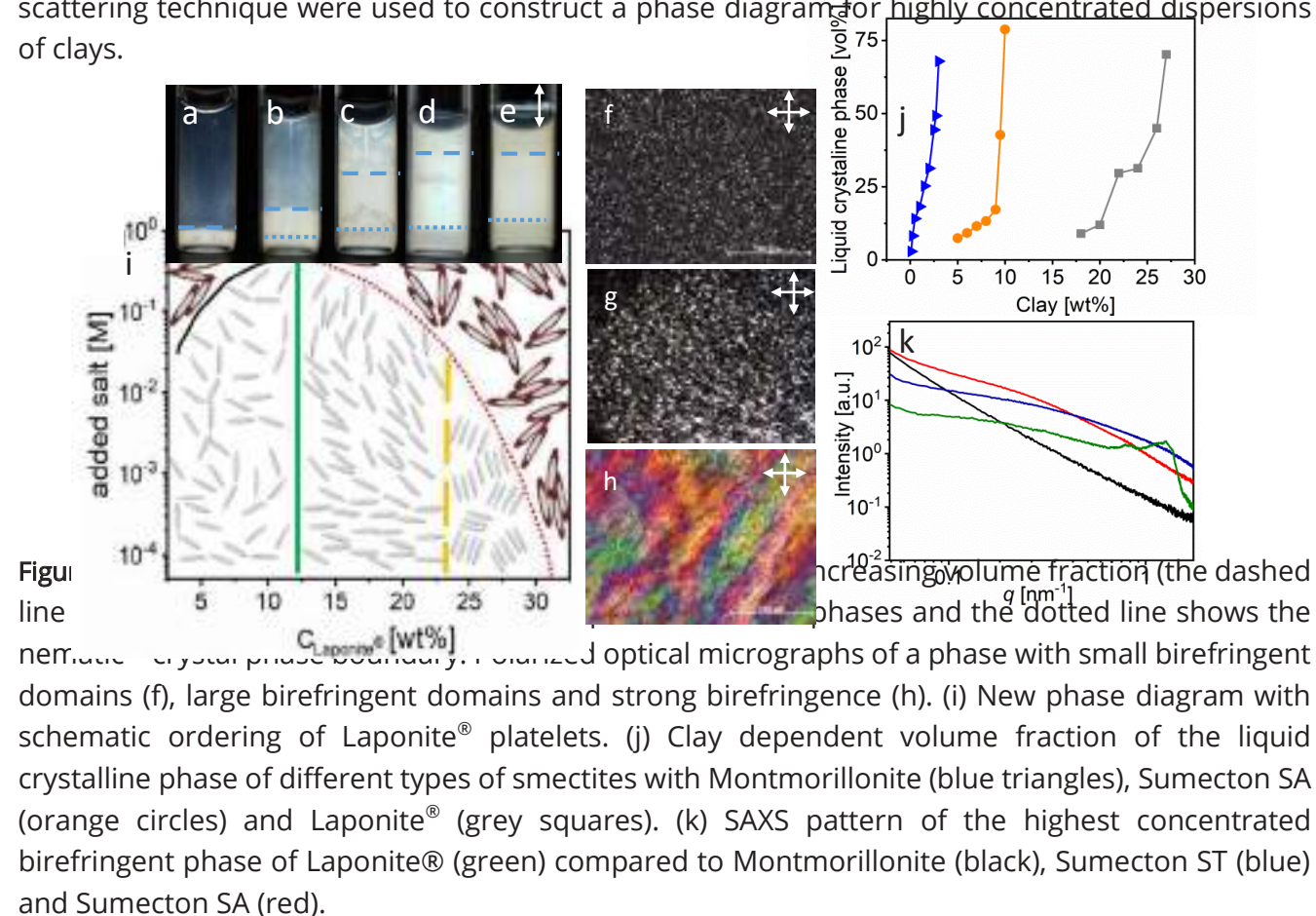
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Pushing ultrasmall nanoclays over the edge of their phase diagram

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Abstract: Synthetic hectorites find numerous applications as e.g. rheology modifiers, functional components of composite materials with gas barrier or fire retardancy properties. In all these applications, the microscopic interaction and ordering of clay platelets play a significant role. Aqueous dispersions of these materials exhibit usually isotropic, nematic and gel phases. For platelets with small aspect ratio, such as commercially available Laponite® RD or Sumecton® SA, the viscosity of the dispersion increases with the increase of concentration prior to the formation of the nematic mesophase, which was assumed to be caused by repulsive force between the negatively charged faces of the platelets. Peptizing agents such as etidronic acid (1-hydroxy ethane-1,1-diphosphonic acid) and sodium pyrophosphate were used to exfoliate clays in water,¹ resulting in phase transitions from isotropic liquid through lyotropic liquid crystal to crystal-like structure. Based on these results the mechanism for the platelet interaction and their 3D ordering has been proposed. Furthermore, rheology measurements, polarization optical microscopy and X-Ray scattering technique were used to construct a phase diagram for highly concentrated dispersions of clays.



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Peroxotellurate thin film deposition on graphene oxide and its transformation to tin(II) and antimony(III) telluride composites

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Ammonium peroxotellurates $(\text{NH}_4)_4\text{Te}_2(\mu\text{-OO})_2(\mu\text{-O})\text{O}_4(\text{OH})_2$ (**1**) and $(\text{NH}_4)_5\text{Te}_2(\mu\text{-OO})_2(\mu\text{-O})\text{O}_5(\text{OH})\cdot 1.28\text{H}_2\text{O}\cdot 0.72\text{H}_2\text{O}_2$ (**2**) were isolated from 5% hydrogen peroxide aqueous solutions of ammonium tellurate and characterized by single crystal and powder X-ray diffraction studies and by Raman spectroscopy and thermal analysis. Peroxotellurate anions in **1** and **2** contain a binuclear $\text{Te}_2(\mu\text{-OO})_2(\mu\text{-O})$ fragment with one $\mu\text{-oxo-}$ and two $\mu\text{-peroxo}$ bridging groups.¹ Ammonium peroxotellurates solutions were used as precursors to obtain high-charge-capacity sodium- and lithium-ion battery anodes based on tin(II) and antimony(III) tellurides and graphene oxide composites. Uniform nano-coating of graphene oxide is carried out from common sol of peroxotellurate and peroxyantimonate (peroxostannate) under room temperature processing. Graphene oxide/SnTe (Sb_2Te_3) electrodes exhibit exceptionally high reversible volumetric charge capacities above 3000 (2100) and 1300 (1651) mAh cm^{-3} at 100 mA g^{-1} charging rate for lithium and sodium ion batteries, respectively.^{2,3}

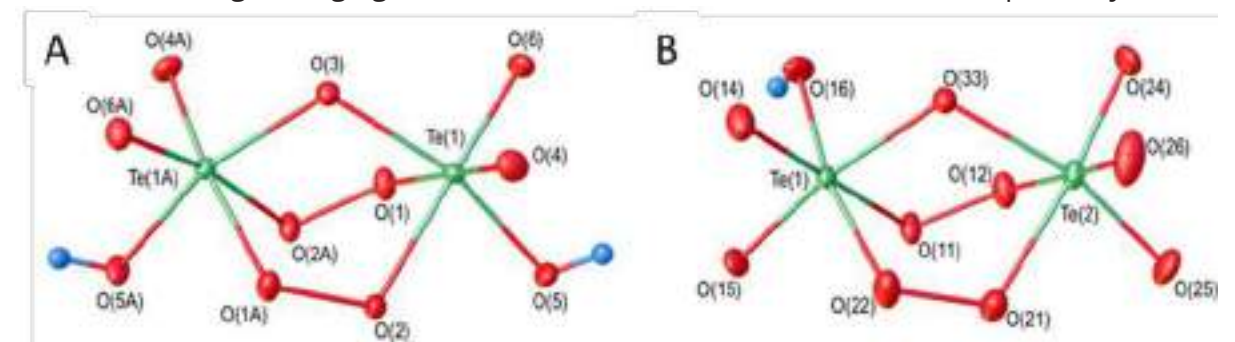


Figure 1. A) Binuclear anions $[\text{Te}_2\text{O}_{11}\text{H}_2]^{4-}$ in structure 1 and B) $[\text{Te}_2\text{O}_{11}\text{H}]^{5-}$ in structure 2.

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Bimetallic Pt/Pd nanoparticles in silica films and xerogels

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The sol-gel method is widely used to produce nano-dispersed materials. One of the promising areas of using this method is the synthesis of catalysts of metal nanoparticles of mixed composition, which include various noble metals.

We used the sol-gel method to obtain films and xerogels containing nanoscale Pt/Pd particles. Composites were formed of Pt and Pd-containing silica sols based on acid hydrolyzed TEOS in presence of dopants (Pt and Pd compounds) taken separately and together. Such methods as spectrophotometry in visible and ultraviolet regions, atomic force and scanning microscopy, X-ray reflectometry, X-ray phase analysis and voltammetry were used to study the processes of the structure formation in sols and films or xerogels based on them.

The size of crystallites formed in xerogels is 10-18 nm and of the ones formed in films is 5-6 nm. The thickness values of the films lie in the range of 20÷50 nm depending on the concentration of dopants. According to AFM and SEM data, the structure of films appears to be a silica matrix with nanoscale inclusions of Pt and Pd compounds in form of 6 nm nanoparticles and their aggregates with size ~50 nm [1].

Bimetallic Pt/Pd nanoparticles in thin silica films and xerogels possess a common crystal lattice forming clusters with the structure of a mixed alloy type. The possibility of the formation of colloidal crystals and mesocrystals is discussed.

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Low temperature synthesis of nanocrystalline proton conducting BaZr_{0.8}Y_{0.2}O_{2.9-δ} halogen doped by sol-gel method

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Abstract: The development of mixed-conducting protonic–electronic ceramic materials is of considerable interest for a number of high-temperature electrochemical applications involving hydrogen. Y-doped Barium zirconate with the perovskite (ABO₃) structure have emerged as one of the best proton conducting solid electrolytes due to its high proton conductivity accompanied with high chemical stability. Also, another possibility of enhanced stability in acidic gases such as CO₂ and high water-vapour partial pressures is to dope the oxide sublattice with halogen anions in order to lower the basicity of the anion network. Although Cl and Br atoms are less electronegative (more basic) than elemental O, it may be expected that the lower charge of the monovalent halogen anions imparts less basic character in the O₂ anion network leading to improved stability of halogen-doped materials in acidic environments. Sol-gel synthesis offers the possibility of homogeneous preparation of materials, especially those with proton conductivity or able to host a proton conducting phase. Moreover, the synthesis temperature is lower and it can reduce or eliminate the grain-boundary resistance. Here, we report the synthesis of BaZr_{0.8}Y_{0.2}O_{2.9-δ} with a range of nominal concentrations of Cl doping (0≤x≤0.2), and assess the effects of Cl as additive on phase composition, including the effects of high-temperature fring. The differences in structure, stability and electrical conductivity of the parent BZY20 material and the phases prepared with Cl are studied in detail. Also, preliminary details of Br incorporation are also reported.

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Conversion of CO₂ to N-doped Porous Carbon *via* Scalable Sol-pyrolysis Reaction

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Abstract:

With regard to carbon dioxide (CO₂) usage for the sustainable production of value-added chemicals, this work provides a scalable sol-pyrolysis reaction that can be potentially scaled up in directly capturing CO₂ to produce N-doped porous carbon (NPC) as a useful carbon-based functional nanomaterial. Flammable alkaline solution of hydrazine hydrate, ethanediamine, and ethanol amine serves as CO₂ adsorbent, respectively. Magnesium (Mg) powders are involved into the reaction for the formation of sol, NPCs are collected after the subsequent self-propagating high-temperature pyrolysis reaction. On the basis of the above theories, the yield can be scaled up by increase the amount of solvent with its directly captured CO₂, and the structure and physicochemical properties of NPCs can be easily tuned by controlling the amount of Mg powders, different adsorption solvent as well as various doping additives homogeneously dissolved in sol. Benefiting from the hierarchical porous structure and nitrogen doping in situ, the as-prepared NPCs with a diversity of morphologies exhibit excellent electrocatalytic activity for oxygen reduction reaction (ORR) in alkaline medium and wider electrochemical applications in industry and research laboratories are foreseen.

Gel-like ion-conducting nanocomposites based on ionic liquids and aluminosilicates. Effect of anion type on physical and chemical properties

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Abstract: Development of new class of ion-conducting materials based on intercalation compounds of clay minerals and ionic liquids with high electrical conductivity, thermal stability, electrochemical stability, promising as the material elements of solid-state storage and energy conversion devices is an important scientific task. The report presents the results of a study of nanocomposites of ionic liquids (1-butyl-3-methylimidazolium dicyanamide, acetate, trifluoromethanesulfonate, bis (trifluoromethanesulfonyl) imide, chloride, iodide) with montmorillonite K-10, halloysite, and Na-bentonite. Methods for the synthesis of ionogels are described, including the direct mixing of an ionic liquid with an aluminosilicate, as well as the inclusion of an ionic liquid from a solution. The obtained composites were characterized using the methods of thermal analysis, X-ray diffraction, FTIR, UV spectroscopy, optical microscopy, electron microscopy, atomic force microscopy, impedance spectroscopy, cyclic voltammetry. The regularities of the influence of the structure of forming nanocomposites on their physicochemical properties and ionic conductivity are discussed.

This work was supported by the RFBR grant № 18-29-12012.

The preparation of Si-Ti hybrid phenolic resin nanostructures using sol-gel method

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Abstract: Organic/inorganic hybrid phenolic resins through sol-gel methods have become a new type of materials, which have attracted much interest in the past decade. These kinds of phenolic resins are widely applied in low density ablative materials because of their outstanding heat resistance, thermal stabilization and anti-oxidation. Therefore, in this paper, Si-Ti hybrid phenolic resin nanostructures were synthesized using sol-gel method, and the properties were systematically investigated. Fourier transform infrared spectroscopy was applied to characterize the chemical structure. The pore size and pore size distribution were characterized by Scanning electron microscopy. The anti-oxidation performance was investigated by thermogravimetric analysis under air. Thermogravimetric analysis with different heating rates (5, 10, 15, and 20 °C/min, respectively) under nitrogen was performed to study the kinetic parameters for the degradation of Si-Ti hybrid phenolic resin. Pyrolysis gas chromatography-mass spectrometry is utilized to examine the volatiles. In conclusion, Si-Ti hybrid phenolic resin nanostructures were synthesized successfully. The main conclusion can be summed as follows: (1) The pore size is average 417 nm, pore size distribution conforms normal distribution. (2) Compared with normal phenolic resin, the anti-oxidation performance of Si-Ti hybrid phenolic resin increased by 21%. (3) Si-Ti hybrid phenolic resin shows two stages of thermal degradation according to the Kissinger model analysis.

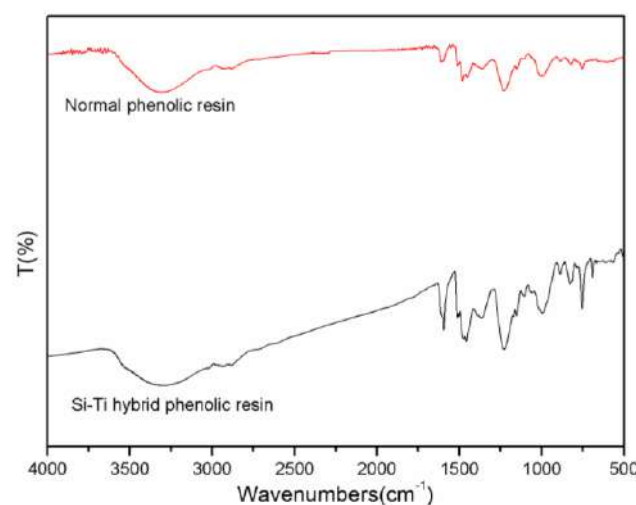


Figure 1. FTIR analysis of Si-Ti hybrid phenolic resin

Development and optimization of a hybrid solgel coating to prevent phthalates migration from medical devices

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Abstract:

Phthalates, such as Di(2-ethylhexyl) phthalate (DEHP), used to impart flexibility and softness to polyvinylchloride (PVC), are commonly present in medical devices (MD). As DEHP is not chemically bound to PVC, it can be released directly into lipid-containing solutions in contact with the MD and thus come into contact with patients. Patients may be exposed to a toxic risk since DEHP has been categorized as carcinogenic mutagenic or toxic for reproduction (CMR) 1B under the Classification Labeling and Packaging (CLP) Regulation (1) due to its toxicity on reproduction suspected in humans.

The physicochemical approach by sol-gel coating on PVC surface is one of the solutions proposed to prevent DEHP release from PVC of MD. In addition to phthalates migration prevention, the final coated PVC should be biocompatible, transparent and should preserve the mechanical properties of the original substrate, for the MD to be isofunctional.

We took advantages of the high versatility of hybrid sol-gel chemistry in order to develop an homogeneous coating, by varying and optimizing the synthesis (nature of the chemical precursors and the solvent, "organic" / "inorganic" parts ratio, temperature, aging of the sol, dilution ...) and deposition (speed of the dip-coater, number of layers, drying time) conditions. The best results were obtained through room temperature hydrolysis and condensation of tetraethoxysilane and isobutyltrimethoxysilane, the 24h-aged sol being deposited in 3 layers onto PVC strips by dip coating (216.9 mm/min). The films homogeneity and the absence of cracks were evaluated by Scanning Electron Microscopy (SEM) coupled to Energy-Dispersive X-ray Spectroscopy (EDX) (cartography of Cl and Si). In order to evaluate the barrier properties against phthalates release, migration tests were performed during 24h into an ethanolic simulant as reference to reflect lipid emulsions according to the Regulation 10/2011 (2), thus able to extract plasticizers from PVC medical devices.

Unfortunately, the coatings were degraded by ethanol. Thus, further investigations on the choice of the simulant are on-going in order to assess the barrier properties of this hybrid sol-gel coating.

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Anisotropic Nanocellulose Gel-Membranes for Drug Delivery: Tailoring Structure and Interface by Sequential Periodate-Chlorite

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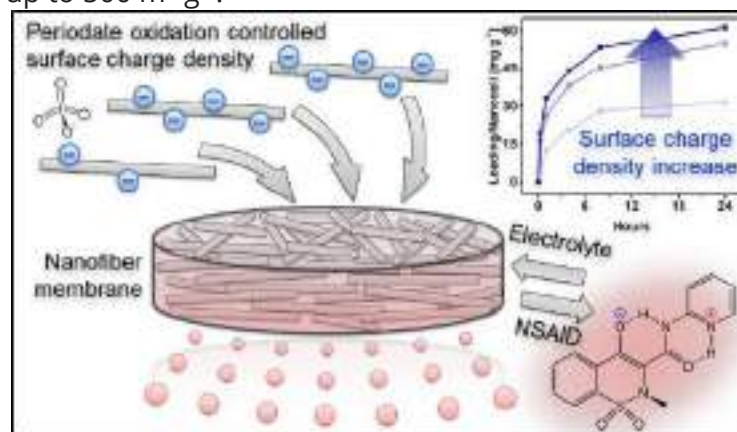
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Abstract: Assembly of cellulose nanofibers (CNF) in aqueous dispersion state can afford anisotropic layered nanoporous membranes with large internal surfaces and abounded surface charges. These properties are beneficial for adsorption of bioactive compounds which can be gradually released into wet environments, such as skin upon changes of pH or electrolyte concentration.

In this study sequential periodate-chlorite oxidation has been investigated as a chemical pre-treatment supporting mechanical delamination of cellulose into nanofibers and for tailor respective interfaces towards high surface charge densities. The obtained well-dispersed and electrostatically stabilized nanofibrils had virtually uniform diameters of about 2.5 nm but varied in length between 95-375 nm (AFM) depending on the degree of oxidation. The amount of introduced carboxyl moieties varied from 0.74 to 2.00 mmol g⁻¹ granting a range of surface charge densities. Assembling of nanofibrillated 2,3-dicarboxyl cellulose (nf-DCC) to form anisotropic gel membranes was accomplished by vacuum-supported sedimentation. The obtained materials had an open-nanoporous architecture, pore size distribution centered at around 40 nm and relatively high specific surface areas of up to 500 m² g⁻¹.



Loading of the nonsteroidal anti-inflammatory drug piroxicam from aqueous solution into CNF membranes revealed that the extent of loading is governed by surface charge density. This suggests electrostatic interaction being the principal mode of adsorption. Release of the drug into acetate buffer at pH 5 simulating human skin conditions was significantly slower compared to the loading process. Anisotropy of the membranes as caused by layered alignment of nanofibers is believed to effectuate stronger retardation of drug diffusion orthogonal to the membrane plane than in parallel direction which is beneficial for patches in transdermal drug delivery.

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Deeper insights in bioactive glass nanoparticles synthesis protocol to control their morphology, dispersibility and composition

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Abstract: The aim of this study was to investigate the effect of 3 synthesis parameters on the morphology and composition of nano-sized binary bioactive glasses particles (nBGPs) obtained through a modified Stöber process. Syntheses were conducted by varying only one parameter at the time while keeping the other entire constant. As expected, the NH₄OH volume conditioned the size of the nanoparticles. Non-agglomerated monodispersed spherical particles with a diameter between 70 and 452 nm were produced. Playing on the quantity of Ca(NO₃)₂ and on the moment it was introduced in the sol had a tremendous impact on the quantity of calcium inserted, and on the particles morphology and aggregation state. High Ca-content particles were obtained when the calcium precursor addition time was less than one hour after the beginning of the sol-gel reaction but at the cost of a strong aggregation. A better control on the morphology, polydispersity and dispersibility of the nBGPs was achieved when the Ca(NO₃)₂ addition time was increased up to 6h. However a significant decrease of the quantity of Ca²⁺ inserted was also noticed. Using an intermediate (3h) addition time, the quantity of calcium nitrate has been optimized in order to maximize the insertion of Ca²⁺ ions inside the silica particles. Finally, an optimum initial Ca/Si atomic ratio of 2, maximizing Ca insertion while limiting the salt quantity used, was found. It led to the synthesis of particles with a molar composition of 0.9SiO₂-0.1CaO without any side effects on particles stability and morphological characteristics.

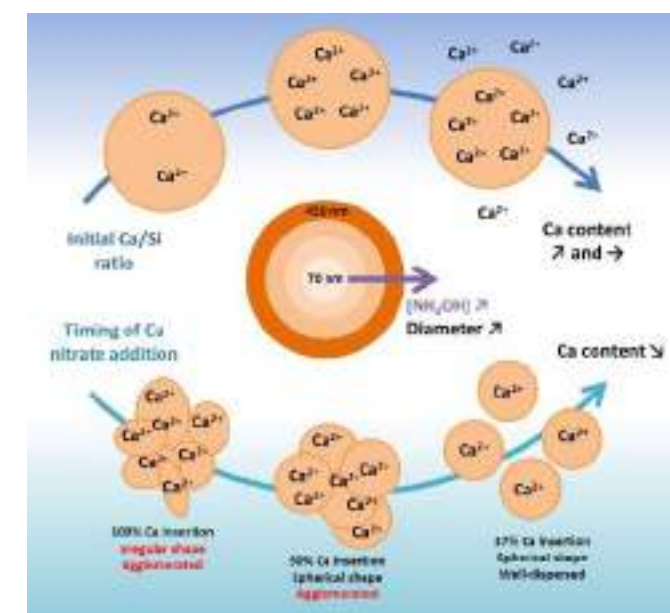


Fig. 1: Preparation scheme of BG nanoparticles of various characteristic

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Flexible Silica Aerogel for Thermal-insulation

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Abstract: Silica aerogels are attractive candidates for thermal, optical, catalytic, and chemical applications because of the low density, high surface area, high optical transmission, and low thermal conductivity. Compared to rigid materials, flexible silica aerogel composites are easy to use and more suitable for some applications, such as insulations on large surfaces.

Flexible fiber reinforced silica aerogel composites for thermal-insulation were prepared by infiltrating the silica sols into the fiber reinforcement via vacuum infiltration, followed by aging and supercritical drying. The influence of processing parameter to microstructure, chemical constitution, flexibility, thermal stability and insulating performance of the material were investigated. It was showed that the degree of cross linking of aerogel molecule was declined because of the existence of Si-OH groups, and the chain experienced flexible when suffered compression. By introducing nano aerogel, the thermal conductivity of the fibrofelt under room temperature decreased from 0.045 W/(m·K) to 0.030W/(m·K) and the flexibility of the composite reserved. And the cold surface temperature decreased significantly from 285.3°C to 186.3°C tested by quartz lamp heater at 600°C for 30 minutes with the sample's thickness of 20mm. The flexibility and insulating performance weren't reduced after testing because of the reservation of Si-OH groups, which indicated the composite experienced high thermal stability.

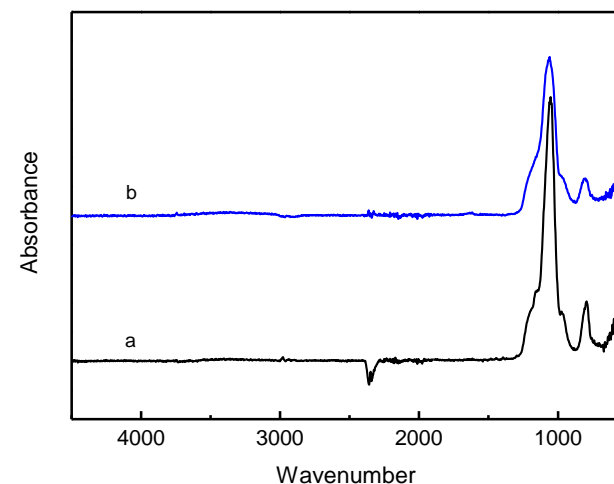


Figure 1. FTIR spectrum of flexible silica aerogel, (a) as-prepared, (b) treated at 600°C for 30 minutes.

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Magnetite-boehmite heteroaggregates as adsorbents for Cr(VI) removal

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The problem of pollution in general (and pollution of the waste water in particular) is one of the main problems of our time. The unclear drinking water is widely distributed, because the groundwater usually contains high concentrations of toxic arsenic, chromium and lead etc. Chromium mainly exists in nature in the derived form and can be in a trivalent Cr(III) or hexavalent Cr(VI) state. Compounds of Cr(VI) are common pollutants in natural waters, representing a serious threat to both the environment and human health. The maximum allowable emission standard of Cr(VI) on surface water according to World Health Organization guidelines is 0.05 mg/L. The chromium compound exhibits pronounced carcinogenic effect and ability to penetrate through the cell membrane and react with the intracellular material. The structural similarity of chromates to physiological sulfates and phosphate ions enables molecular mimicry and easy entry of Cr(VI) into cells through nonspecific anion channels. Toxic effects of chromium are respiratory problems, hemolysis, acute renal failure, weakened immune system, alteration of genetic material, lung cancer and pulmonary fibrosis.

Since polluted water is a global environmental issue, some technologies to treat waste water have been developed. Among these methods, adsorption as a green technology is considered to be one of the most promising strategies because of its relatively low-cost, simplicity of operation, and high separation efficiency.

The key to applying the adsorption method is the fabrication of adsorbents. A suitable adsorbent should be stable, low-cost, environment-friendly, efficient to remove different contaminants, have high adsorption capacity and rate of adsorption, and have high selectivity for different concentrations. The rational structure design and facile synthesis of adsorbents always play critical roles in the adsorption technology. Hydrothermal method is the most convenient and widely used for synthesis of nano- and micro-sized adsorbents with the desired properties due to the ability to control the temperature, vapor pressure and duration of the synthesis. Much attention is paid to the study of adsorbents with a hierarchical structure.

Boehmite (γ -AlOOH) and alumina, as well as iron oxide, are widely used as an adsorbent and catalyst. However, there have been several studies reporting that the mixed oxides of the metals showed better efficiency than many of the single metal oxides.

In our work, magnetite and boehmite sols were obtained, and their heteroaggregation was studied at various mass concentrations of the components. The data were processed using DLVO theory. A study of the adsorption properties of a number of systems with respect to Cr(VI) compounds was made.

Acknowledgements

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Electrical properties of Al doped zinc oxide films: influence of deposition parameters

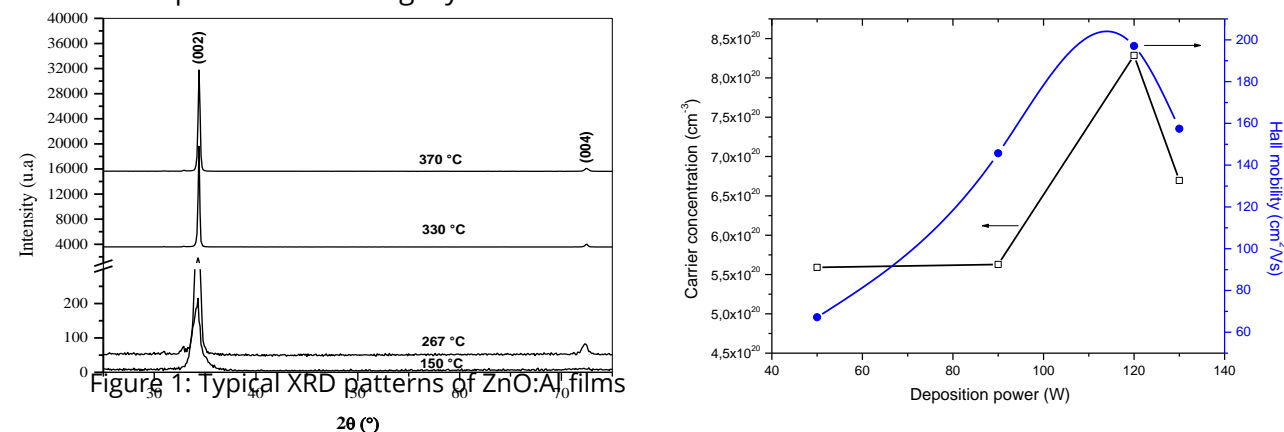
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Abstract: Transparent conducting oxide (TCO) thin films have attracted remarkable research attention in the last years owing to their wide use in optoelectronic devices such as touch screens, solar cells, liquid crystal displays and light emitting diodes. TCOs should show both high electrical conductivity and high optical transparency in the visible region.

Zinc oxide (ZnO) is an attractive alternate material for indium tin oxide owing to its good electrical and optical properties combined with the abundance in nature of Zn, low cost, non-toxicity. ZnO is an n-type semiconductor with a direct wide band gap of 3.37 eV and large exciton binding energy of 60 meV at room temperature, high electrochemical stability, high thermal stability and good stability in hydrogen plasma. ZnO:Al can be used as transparent conducting electrodes for solar cells and flat-panel displays. Good knowledge of its structural, electrical, and optical properties is necessary for these device applications.

In this work, Al doped zinc oxide thin films were deposited by DC magnetron sputtering technique from ZnO-Al₂O₃ (2%) target onto glass and silicon substrates heated at 330 °C. The film structure was investigated by XRD analysis. The XRD spectra show only the (002) peak, indicating the c-axis oriented nature of the films (Figure 1). The ZnO:Al films are transparent up to 92 % in the visible wavelength. The electrical properties were investigated by Van der Pauw and Hall Effect measurements. The film resistivity is very sensitive to the deposition parameters. At room temperature, it decreases from 5×10^{-4} to $2 \times 10^{-5} \Omega \cdot \text{cm}$ when the deposition temperature varies between 150 and 370 °C. Charge carrier concentration and mobility are also sensitive to deposition condition. They increase from $2.5 \times 10^{20} \text{ cm}^{-3}$ to $9 \times 10^{20} \text{ cm}^{-3}$ and from 25 to 250 $\text{cm}^2 \text{V}^{-1} \text{S}^{-1}$ for carrier concentration and mobility respectively. Power density has the same influence on film electrical properties. However the deposition gas ration $\text{N}_2/(\text{Ar}+\text{N}_2)$ show an inverse influence on the film electrical properties. Obtained ZnO:Al films present high transparency and good electrical conductivity, therefore, we can claim that ZnO:Al film deposited at optimised parameters can be used as transparent conducting layers.



Influence of zinc oxide nanoparticle size on the antibacterial and photocatalytic activity

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Abstract: The influence of nanoparticle size on the antibacterial and photocatalytic activity of ZnO powders was investigated using powders with different particle sizes ranging from 8 to 320 nm, obtained by sol-gel method using different concentration (ZnO 1 - 0,025M; ZnO 2 - 0,035M; ZnO 3 - 0,045M and ZnO 4 - 0,10M) of precursor, respectively zinc acetate.

We report here the synthesis, DLS measurement of nanoparticle size, morpho-structural characterization (SEM-EDX, X-Ray diffraction), photocatalytic and antibacterial properties of ZnO nanoparticles powders and coated textile fabrics (cotton 100% and cotton-polyester 50-50%) with this nanoparticles.

Photocatalytic activity was evaluated by measuring as a model organic compound, the degradation of methylene blue (MB) in water under UV irradiation for 1 hour and the antimicrobial activity of the ZnO nanoparticles and coated textile fabrics determined by using the paper disc method on Mueller-Hinton agar against the *Gram-negative* bacteria, *Escherichia coli* (*E. coli*) and the *Gram-positive* bacteria, *Staphylococcus aureus* (*S. aureus*). For the coatings applied on textile, the antimicrobial activity was investigated by UV-Vis absorption spectroscopy using TTC method, against the *E. coli* and *S. aureus*. bacteria. The investigated ZnO nanoparticles powder and coated textile fabrics showed good antimicrobial and photocatalytic activity for all samples, especially for ZnO 2 and are promising materials for use as medical applications.

Functionalization of silica particles for metal ions sequestration

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Abstract

Functionalized silica particles with thiol groups on their surface were prepared by the sol-gel process to sequester heavy metals. The group thiol has great affinity and selectivity for metal ions. TMOS precursor and "in situ" functionalization with mercaptans groups on the surface of silica sols were employed to achieve active sites on the surface to chemisorb ions by a complexation reaction with metal ions such as lead, cadmium, copper and mercury. The flocculation kinetics was monitored by dynamic light scattering, the adsorbed metallic ions on the surface were detected by EDS. The structural and morphologic changes were studied by FT-IR, Raman and electron microscopy.

Sol-gel synthesis of composites based on titania and microcrystalline cellulose

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Abstract: Microcrystalline cellulose–anatase hybrid nanomaterials were synthesized by solvothermal sol-gel method using titanium tetraisopropylate. The samples were characterized by X-ray diffraction, IR and ¹H NMR spectroscopy, transmission electron microscopy, and thermal analysis. The photocatalytic activity of the samples in decomposition of aqueous solutions of an organic pollutant, trifluoroacetic acid, was studied. The anatase nanoparticles formed in the synthesis undergo structuring on crystalline domains of cellulose owing to strong interaction of cellulose hydroxy groups with Ti⁴⁺ and TiO₂. This significantly enhances the photocatalytic activity hybrid samples compared to anatase synthesized under similar conditions method with template. Some samples surpass in the activity Aeroxide P25 TiO₂ nanopowder used as a reference. This study was aimed at developing a procedure for preparing a microcrystalline cellulose–anatase hybrid at lower temperature, so as to obtain anatase nanoparticles that would remain bound to microcrystalline cellulose particles with the preservation of the cellulose structure, and at evaluating the photocatalytic properties of the hybrid material obtained.

The formation of the mesoporous anatase–MCC hybrid was confirmed by FTIR spectroscopy and thermal analysis. In particular, the strong band of hydroxyl bending vibrations in cellulose itself and in the cellulose sample containing an anatase admixture (1630 cm⁻¹) is appreciably shifted toward lower frequencies upon hybrid formation (1620 cm⁻¹), suggesting strong MCC–anatase interfacial interaction caused by interaction of the MCC hydroxy groups with Ti⁴⁺ and TiO₂ nanoparticles. The same conclusion follows from the shift of the stretching vibration band of cellulose hydroxyls toward lower frequencies in the hybrid (3410 cm⁻¹) compared to pure cellulose (3430 cm⁻¹). Thermal analysis shows that heating of weighed portions of the samples under argon leads to their decomposition with the evolution of hydrogen, methane, carbon monoxide, and other thermolysis products. These processes are characterized by endothermic peaks in the DSC curves. In the case of the hybrid, this peak is significantly (by 42°C) shifted toward higher temperatures. The peak magnitude for the hybrid (0.57 mW/mg) is considerably lower than for the common mechanical mixture of the components (1.32 mW/mg), and the weight loss in cellulose combustion in the interval 300–400°C is 11% smaller, which also confirms binding of MCC hydroxy groups with Ti⁴⁺ and TiO₂ nanoparticles upon hybrid formation.

The photocatalytic activity of samples was studied using an aqueous solution of trifluoroacetic acid chosen as an organic pollutant. On the one hand, trifluoroacetic acid itself is insensitive to UV irradiation, which favorably distinguishes it from dyes commonly used for these purposes, such as Rhodamine or Methylene Blue. Because of steric factors, the hydroxy group at the C-6 carbon atom of cellulose is the most active; therefore, the effective amount of anatase in the hybrid cannot exceed a certain limit.

Multifunctional nanomaterials for waste water treatment-a review

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Abstract: Due to the exceptional characteristics which resulted from nanoscale size, such as improved catalysis and adsorption properties as well as high reactivity, nanomaterials have been the subject of active research and development worldwide in recent years. The utilization of multifunctional nanoparticles has opened new ways for environmental remediation. The exceptional characteristics resulted from nanoscale size, as absorption, catalysis and high reactivity of nanoparticles and nanomaterials shows the efficiency of removing various pollutants from wastewater. Cellulose nanomaterials are naturally occurring with unique structural, mechanical and optical properties. While the paper and packaging, automotive, personal care, construction, and textiles industries have recognized cellulose nanomaterials' potential, we suggest cellulose nanomaterials have great untapped potential in water treatment technologies

In this paper is presented an overview of recent advances in nanotechnologies for water and waste water treatment processes, based on the most studied materials as: nanoparticles (Ag, Fe and Zn), oxide nanoparticles as TiO_2 , ZnO , Fe_3O_4 and hybrid materials based on hybrid nanoparticles-polymers compounds.

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A Facile Way to Prepare PR/SiO₂ Hybrid Xerogel via Sol-Gel Method and Its Application in Aerospace

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Abstract: By virtue of its ultra-lightweight, low thermal conductivity, high specific area and nano-scale effects, aerogels have wide applications in many fields, such as heat & sound insulation, catalyst, electrochemistry, absorption, separation, and so on. Compared to inorganic aerogels, mechanical strength and toughness of organic aerogels, which are mainly constructed and piled up by organic skeletons and polymeric chains, are highly enhanced. Because of its chemical decomposability, organic aerogels can be used as ablative materials. Meanwhile, based on morphological reproduction effect, hyperporous structure can be preserved during carbonization of organic aerogels. Moreover, organic aerogels can be functionalized through modifying the molecular structure of precursors, which may meet some special functional demands in aerospace.

Herein, we will introduce a facile and low-cost way to prepare hybrid phenolic resin (PR)/SiO₂ xerogels via sol-gel method and ambient drying. By controlling Sol-Gel reaction and tuning gel time of hybrid solution, hybrid PR/SiO₂ xerogels with bicomponent and interpenetrating gel networks were easily produced through co-gelating reaction between phenolic resin and tetraethoxysilane (TEOS). Based on hybrid PR/SiO₂ xerogels, new lightweight ablative composites were devised and fabricated by taking full advantage of those characteristics of aerogels. Density of new ablative composite could be tuned between 0.23 g/cm³ and 0.6 g/cm³ and thermal conductivity at room temperature lowered to 0.07W·m⁻¹K⁻¹. Such a lightweight ablative composite showed an excellent thermal protective and heat insulating performance in a simulated heat flux of 6 MW/m² performed in an arc-jet wind tunnel. As the surface temperature of new composite reached 3000°C, temperature rise in depth of 50 mm was only 50°C or so. Furthermore, ablative property, heat insulating, mechanical strength and other properties of this new lightweight ablative composite can be adjusted and controlled by functionally modifying and microstructural tuning of aerogels. This new lightweight ablative composite has great potential applications in the field of advanced thermal proactive materials for deep space exploration, lunar probe and other advanced thermal protection systems of aerospace vehicles.

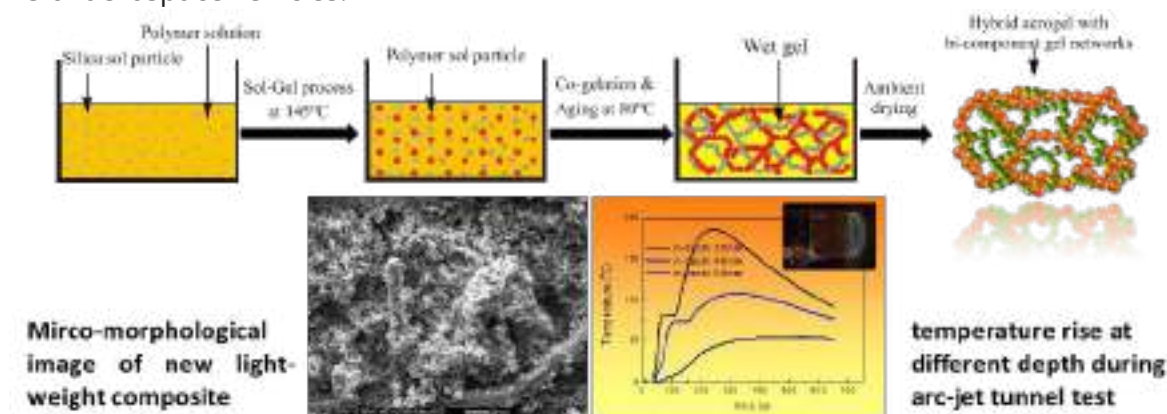


Figure 1. Schematic preparation of PR/SiO₂ hybrid phenolic aerogels with bi-component gel networks

Acknowledgements

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Fabrication of novel magnetic polyaniline nanocomposites based on diluted magnetic oxides (DMOs) of Co-doped ZnO nanostructured synthesized using sol-gel technique

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Abstract

Diluted magnetic oxides (DMOs) refer to non-magnetic metal oxide materials doped by a very small concentration of magnetic element. Such doping enables the addition of a spin moment to the properties of the host metal oxide materials that is noble for exploring new physics, ideas and concepts in the field of spintronics and their potential applications [1]. Polymer nanocomposites based on DMO nanoparticles (NPs) are promised functional nanomaterials in many potential applications due to their facile processability and capability to be used in field of magnetoelectronics or spintronics. In this respect, the fabrication a novel polyaniline (PANI) nanocomposites that loaded by NPs of Co-doped ZnO as DMO material is introduced. The Co-doped ZnO nanocrystals were synthesized using sol-gel technique. The molar ratio of Co (CH₃COO)₂·4H₂O : Zn(CH₃COO)₂·H₂O was varied from 0:100 to 9:100. Afterwards the surfaces of DMO nanoparticles were chemically treated using oleic acid (OA) in order to reduce the agglomerations of as-synthesized NPs. The microstructure characterization of the synthesized DMO-NPs confirmed the formation of wurtzite ZnO nanostructured crystals without changes in such the host structure because of adding Co atoms due to substituting the Zn sites in the lattices by Co [2]. Both of as-synthesized and OA treated are showing room temperature ferromagnetic (RTFM) behavior.

PANI/Co-doped ZnO and PANI/OA-Co-doped ZnO nanocomposites were fabricated via the direct oxidation of aniline in acidic solution using ammonium persulfate as a chemical oxidant in the presence of NPs. The acidic level kept constant for all composites. However, the weight ratio of NPs to aniline was 50:100 for all as- synthesized DMO-NPs and OA- DMO-NPs samples. Indeed, the interaction between NPs and polymer matrix play a crucial role in determining the quality and properties of polymer nanocomposites. The high-resolution transmission electron microscope (HRTEM) examination of PANI nanocomposites confirmed the role of the surface treatment of DMO using of OA on enhancing the dispersibility of NPs in the polymer matrix. Such effect plays significant role in increasing the interfacial regions between NPs and polymer, which reflected on RTFM characteristic parameters. The obtained results enabled to get a facile fabrication of novel PANI nanocomposites based on DMOs.

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Preparation of an ultra-low density aerogel and a modified supercritical drying treatment process

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Abstract: An ultra-low density silicon dioxide aerogel is prepared by a two step sol-gel process. Due to its weak mechanical strength, the problem of insulating property decreasing and size shrinkage of the ultra-low density aerogel after an normal supercritical drying process is often unavoidable. Therefore, a modified supercritical drying treatment process is presented. By applying a cold extraction fluid circulation, controlling the temperature increasing rate in the drying step and the pressure decreasing rate after the drying, the nanoporous structure of the aerogel can be well retained and the bulk material with a low heat conductivity coefficient can be achieved. Due to its high insulation efficiency, the composite aerogel enhanced by the organic foam has great potential to be applied in the aerospace field.

Sol-gel synthesis of nickel and chromium co-doped TiO₂ nanocrystals

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Titanium dioxide nanocrystals (TiO₂ NCs) have been doped and codoped with the combination of nickel and chromium metal ions. Doping is an effective method to extend the light absorption to the visible light region. The doped and co-doped TiO₂ were synthesized by sol-gel method with doping levels of 0.25 to 10.0 wt.%. The resulting materials have been characterized by X-ray diffraction, Raman, UV-vis diffuse reflectance and Fluorescence spectroscopies.

XRD patterns of as-synthesized Ni and Cr single doped and co-doped TiO₂ nanocrystals exhibit diffraction peaks at around 2θ = 11.5, 17.0, 22.0, 24.0, 24.8, and 28.0° assigned to anatase crystal phase of TiO₂. The only single Ni-doped TiO₂ powders (with 10 wt% Ni) annealed at 500 °C showed crystalline structure for mixture of anatase-TiO₂ and nickel titanate (NiTiO₃) phases. In the range of 5-40°, the nature of diffraction peaks of the pure TiO₂ crystal planes is reasonably related to that of Ni and Cr single doped and codoped TiO₂. The XRD patterns did not show any Ni and Cr phases (except very small peaks of NiTiO₃ and NiO), so it is established that nickel and chromium ions are equally dispersed between the anatase crystals.

The Raman active modes of the anatase structure (space group I4₁/amd) were observed at approximately 158 cm⁻¹ (E_g), 197 cm⁻¹ (E_g), 399 cm⁻¹ (B_{1g}), 519 cm⁻¹ (A_{1g}, B_{1g}) and 639 cm⁻¹ (E_g). Raman spectra show that the relative intensity of the active modes decrease, i.e., the peaks broaden increase, as the amount of Cr and Ni in the NCs increase. Moreover, it can be observed that E_g and A_{1g}+B_{1g} modes are red-shifted in Cr and Ni (co)doped spectra. Since the co-doped TiO₂ samples were prepared with identical procedure as the undoped TiO₂ NCs we rule out that the preparation method influence the observed results. Effect of transition metals and amount of dopant on the band structure/band gap energy has been shown in terms of Kubelka Munk function (Figure 1a). As comparison to undoped, TiO₂, red shifts in the absorption edge were observed with the single doped and co-doped TiO₂. The observed red shift in the reflectance spectra of the co-doped TiO₂ samples are related to the incorporation of Ni and Cr within the network of the TiO₂ NCs. The increase of the amplitude of this red shift is much greater in the samples doped with Cr than in the samples doped with Ni. Besides, the absorption of light increases much more high with increasing the wt.% of Cr in the TiO₂ lattice than when increasing the wt.% of Ni.

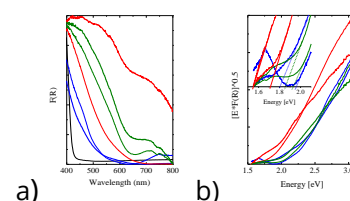


Figure 1. (a) Kubelka Munk absorption, (b) Tauc plots of TiO₂ NCs

The PL spectrum of co-doped TiO₂ is dominated by the broad band emission in the range of 400-550 nm. This transition corresponds to the relaxation of the excited electrons from the 3d level of titanium to the 2p level of oxygen. The PL intensity of that transition was drastically decreased with the incorporation of Ni in the TiO₂ nanoparticles.

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Titanium phosphonate oxo-alkoxide “clusters”: solution stability and facile hydrolytic transformation into nano titania

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Abstract: Titanium dioxide (TiO₂, titania) nanoparticles are of great technological importance. The applications include photocatalysis, medical implants, white pigment in toothpaste, food (E171) and paints and as drug carrier for controlled drug delivery. The formation of metal oxide nanoparticles from metal alkoxides proceeds via formation of oxo-clusters as intermediates [1, 2]. The ligands from the alkoxides precursors will follow the transformation into nanoparticles and remain on their surfaces. Exchange of ligands in the alkoxide precursors allows for tailoring of the ligand coating of nanoparticle surface, being of interest for production of organic-inorganic hybrid materials. Phosphates and phosphonates occur also in many biologically important molecules, including drugs and phosphorylated proteins. Their high affinity for titania surface [3] has been employed in delayed drug release [4] and for anchoring of functional groups in hybrid materials [5].

A series of new titanium phosphonate complexes were synthesized and structurally characterized by single crystal X-ray diffraction, NMR spectrometry and infrared spectrometry as models for interaction between titania and phosphonates. Titanium phosphonate complexes with both bi- and tridentatly binding phosphonates were obtained at different ratios of *tert*-butylphosphonic acid (0.85 0.5, 2 and 4 eq.) to Ti(OR)₄, R = Et, *i*-Pr. ³¹P NMR spectrometry revealed varying solution stability of the complexes, highlighting the need to characterize solution stability of complexes intended for use in for example organic-inorganic hybrid materials [6]. Electron microscopy and atomic force microscopy showed the facile hydrolysis of the titanium (oxo)-complexes into titania structures in aqueous environment, demonstrating their high sensitivity towards water [6].

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Inverting swelling trends in hybrid self-oscillating gels cross-linked by redox-active metal complexes

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Abstract: The developing field of active, stimuli-responsive hybrid materials is in need of new dynamic architectures that may offer unprecedented chemomechanical switching mechanisms. Belousov-Zhabotinsky (BZ) reaction, being one of very few examples of oscillatory chemical processes, was used in developing self-oscillating gels capable of chemomechanical responses governed by their swelling and deswelling dependent on the oxidation state of a metal complex incorporated into gel network. We report on the syntheses of polymerizable and crosslinkable bipyridine and biquinoline ligands, and Ru and Fe complexes with them. These redox-active complexes can serve as active crosslinkers in a series of poly(N-isopropylacrylamide) (polyNIPAAm)-based self-oscillating gels exhibiting under the conditions of BZ oscillating chemical reaction a unique feature: their swelling/contraction mode switches its dependence on the oxidation state of the metal center, upon changing the fraction of a hydrophilic comonomer, such as 2-acrylamido-2-methyl-propane sulfonic acid (AMPS), in the gel network. These results¹ expand the toolbox of the

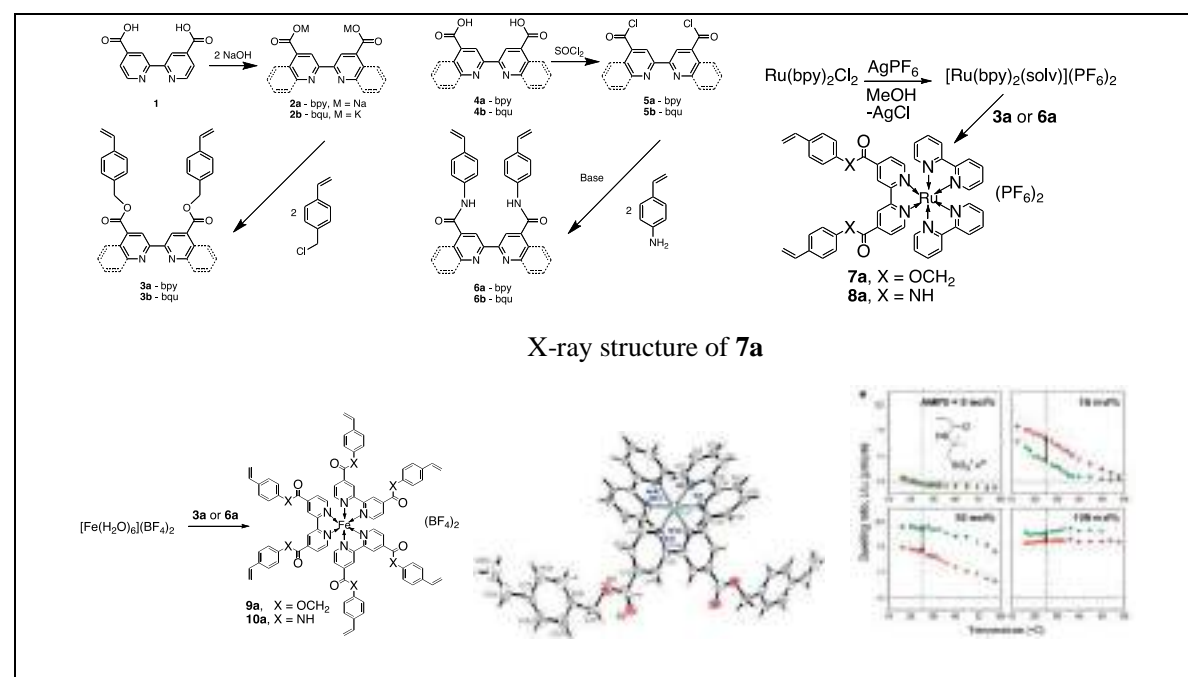


Figure 1. Syntheses of polymerizable bipyridine and biquinoline ligands, Ru and Fe complexes with these ligands, and inversion of the gels' swelling as a function of the network hydrophilicity.

BZ-active gels and may also offer new and straightforward entries into active and responsive hybrid materials comprising bipyridine- and biquinoline-containing polymer ligands, as well as metal complexes with them.

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<https://doi.org/10.1002/adfm.201704205>

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Recent Progress on the Adsorption Performance of Silica Aerogel on Volatile Organic Compounds

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Abstract: The regular silica aerogel was synthesized by using TEOS as precursor, ethanol as solvent and hydrofluoric acid as catalyst, one-step process. After alcohol supercritical method the silica aerogel sample was characterized by SEM, FTIR, and nitrogen adsorption-desorption isotherms to better understand the relationship of the adsorption mechanism-property. The results indicated that the sample has a high specific surface area of 519 m²/g, pore volume of 1.9 cm³/g and a large pore size of 13.2 nm, which could be an excellent adsorbent material. The prepared sample was tested for using as an adsorbent for volatile organic compounds (VOCs) disposal. Methylbenzene, paraxylene and benzene were selected as typical adsorbates with different structure due to their extensive utilization in industrial processes. Silica aerogel has achieved high adsorption amounts for all of them. The high adsorption ability of silica aerogel is attributed to the nanonetwork structure, the little pore diameter. The maximum adsorption capabilities are up to 1422.8mg/g, 707.4mg/g, 1299.4 mg/g for methylbenzene, paraxylene and benzene, respectively. But among them, silica aerogel has the perfect adsorption performance for methylbenzene because of the molecular polarity. Therefore, the silica aerogel is a promising potential adsorbent for VOCs disposal with the superior adsorption ability and the high diffusion rate.

Keyword: Silica aerogel, VOCs adsorption, adsorbent

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Acknowledgements

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Sol-Gel synthesizing of strontium ferrite–cobalt nickel ferrite exchange spring magnets with maximum energy product

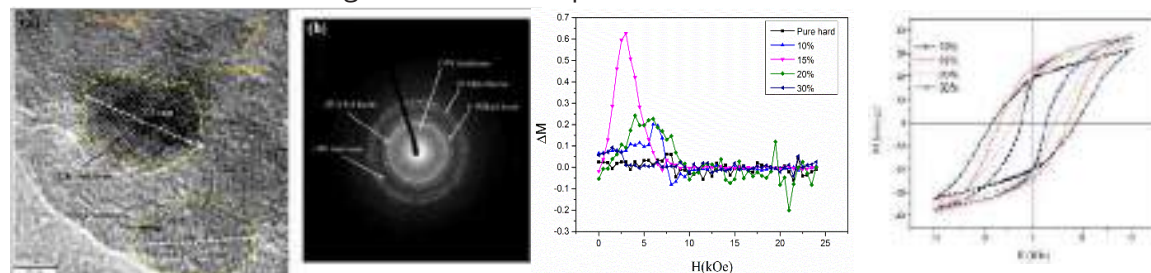
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Abstract

Magnetic composites contain two phases, one a hard magnetic material with high coercivity (H_c), and the other a soft magnetic material with high saturation of magnetization were fabricated by sol gel process. Effective processing parameters of sol-gel were deeply controlled for finding the spring behavior in exchanged coupled nanocomposites. Strontium ferrite, and cobalt-nickel ferrite were chosen as initial phases for this research. Hard/soft magnetic nanocomposites of two mentioned composition were produced by one-pot sol-gel combustion and physical mixing method. The soft phase content in the nanocomposites was taken at 5, 10, 15, 20, 30, 40, 50, 60, 70, 80 and 90 in weight percent. Various characterization methods including X-ray diffraction for phase identification, scanning and transmission electron microscopy with energy disperse spectroscopy for microstructure evaluation, particle size measurements, particle size distribution and elemental analysis, Fourier transformed infrared spectroscopy for evaluation of functional groups in ferrites and Mössbauer spectroscopy for determination of cation occupancies were employed to characterize the samples. Magnetic properties of samples including plotting hysteresis loops, saturation magnetization, remanence, coercivity and switching field distribution were measured by means of vibrating sample magnetometers. Magnetostatic and exchange interaction between particles were determined by switching field distribution and Henkel plots. It was found that composites fabricated by physical mixing method didn't show exchange spring interaction and indicate "bee-waist" like shape in their hysteresis loops. On the other hand, existence of exchange interaction in sol-gel auto-combustion fabricated nanocomposites was demonstrated for nanocomposites with soft phase lower than 30 wt%. The maximum exchange coupling was obtained for nanocomposites contain 15 wt% soft phase made by sol-gel combustion method. The highest value of $(BH)_{max}$ was obtained for this sample and increased from 26.7 kJ/m³ for pure hard ferrite to 29.5 kJ/m³. More accurate analysis such as transmission electron microscopy, magnetic force microscopy and Kerr magneto-optical microscopy illustrated formation of two distinct phase in the vicinity of each other and the length between them was on the order of nano-scale ranges (smaller than 30 nm) for (85 wt%) SrFe₁₀Al₂O₁₉/(15 wt%)Co_{0.8}Ni_{0.2}Fe₂O₄ nanocomposites. The maximum energy product obtained in this work has larger value as compared to similar researches in the field of hard/soft magnetic ferrite composites.



TEM micrograph, EDP analysis, Δm curve and hysteresis loops of SrFe₁₀Al₂O₁₉/Co_{0.8}Ni_{0.2}Fe₂O₄ nanocomposites prepared by one-pot sol gel auto-combustion route.

Description of atomic properties of TiO₂ nanoparticles/electrolyte interface using Molecular Dynamics

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Abstract: Specific and often enhanced properties of TiO₂ nanomaterials make them suitable for various applications such as adsorbents for different organic molecules and heavy metal ions. Furthermore, TiO₂ nanomaterials can be used for degradation of environmental pollutants by exploiting their photocatalytic properties. Almost all applications are governed by processes in aqueous electrolyte solutions. Therefore, it is understandable that the TiO₂ nanomaterial charge properties have an important impact on the efficiency of those applications. We have used Molecular Dynamics simulations to predict and describe the atomic properties of TiO₂ anatase surface in various electrolyte solutions with different pH. Such simulation allows determining how many ions bind and how they bind to surface. Namely, some ions are in the Stern Layer, strongly bonded and electrokinetically inactive, whereas others are more distant from the surface and form part of the diffuse layer. Thereby, we have applied specific methods^[1] to describe such parameters as zeta-potentials, ion distribution profiles and velocities for both bulk and electric double layer. Moreover, the selectivity of potassium and sodium ions on the anatase surface was investigated. The simulations were carried out in the box that was represented by the electrolyte solution confined between two titania surfaces. The change of pH was given by the change in functional surface groups of titania^[2].

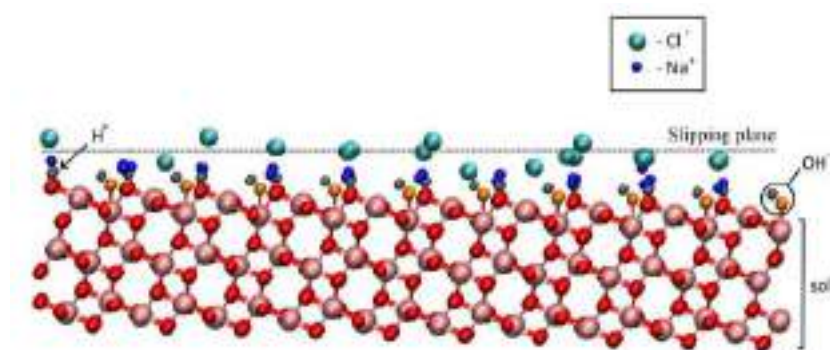


Figure 1. Snapshot of Electric Double Layer near the anatase surface

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rGO/MoS₂ hybrid system for enhancing fluorescence of carbon dots self-assembled multilayers

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Abstract: The conventional plasmonic nanostructured noble metal materials including Ag and Au, were the most widely used surface-enhanced fluorescence (SEF) substrate materials [1-2]. However, these materials have several shortcomings, such as poor light stability, low biocompatibility and relatively large optical loss. These shortcomings limit the application scope of SEF sensors. Graphene and molybdenum disulfide are reported to have a certain plasma effect [3-4]. In this work, we prepared a graphene/molybdenum disulfide (rGO/MoS₂) composite substrate by photochemical reduction method. The number of polyelectrolyte layers can be tuned to control the distance between carbon dots (CDs) and rGO/MoS₂ in self-assembled multilayers (SAMs). The experimental results showed that the fluorescence intensity of the CDs SAMs with rGO/MoS₂ composite substrate could be enhanced by ca. 6 times higher than the CDs SAMs with rGO or MoS₂ alone (Fig. 1A). Meanwhile, we found that the lifetime of the fluorescence enhancement film was correspondingly reduced and the quantum yield was correspondingly increased (Fig. 1B). Therefore, we speculated that the fluorescence enhancement effects of rGO and MoS₂ should be similar to those of metal-enhanced fluorescence.

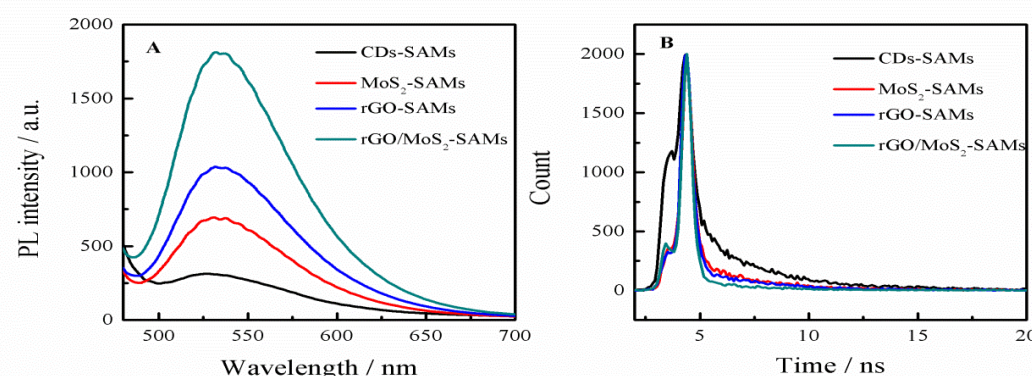


Figure 1. Fluorescence spectra (A) and fluorescence decay curves (B) of different SAMs.

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Novel Fibrous Materials for the Treatment of Chronic Wounds

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Introduction: Chronic wounds are a drain on global health services and remain a major area of unmet clinical need. In 2015 the annual cost of managing these wounds in the NHS was estimated at £5.3 billion¹ and while the burden is rapidly growing, treatments remain limited and ineffective. Chronic wounds are characterised by a stubborn multi-species biofilm which hinders immune responses and delays healing. Novel materials are required to deliver antibacterial and tissue regenerative factors in a controlled, stepwise manner. Electrospinning has been applied to the formation of bioactive glass (BG) scaffolds, which degrade rapidly due to their high surface area. BG can be designed to release inorganic ions (E.g. Cu, Zn, Co, Ca, Si) which have been shown to play significant roles in wound healing.²

Materials & Methods: Hydrolysis and condensation of TEOS to form Si-O-Si network was carried out in ethanol under acid catalysis. Calcium nitrate tetrahydrate was added to obtain a 70S30C (70 mol% SiO₂, 30 mol% CaO) precursor solution, which was aged at 40°C for 24 hrs. A binder solution of 10 wt% Butvar B-98 in ethanol was mixed with the precursor in equal volume and loaded into a plastic syringe attached to a metallic needle. High tension field was applied to the needle and glass fibers were collected on aluminium foil positioned below the capillary. The fibers were subsequently sintered at 650°C for 300 minutes. To produce formulations doped with silver or copper oxides, n mol% Ca(NO₃)₂·4H₂O was substituted for n mol% AgNO₃ or Cu(NO₃)₂·3H₂O. Images of the fibers were produced using scanning electron microscopy (SEM). Glass was incubated in broth at 37°C for 4 hours. Solutions were filtered and used to treat planktonic *Staphylococcus aureus* and *Pseudomonas aeruginosa*. The optical density at 600nm was measured every hour for 24 hrs using a Tecan plate reader.

Results and Discussion: Un-doped glass (70S30C) has been synthesised and imaged using SEM, showing bead-free, ribbon-shaped fibres with diameters of 0.65-1 µm (fig 1). Antimicrobial studies showed no inhibitory effect of 70S30C on the growth of *S. aureus* or *P. aeruginosa*. Furthermore, silvercontaining formulations have been synthesized and growth curves showed no significant difference between 1 mol% Ag and the negative control. Conversely, filtrates containing 3 and 5 mol% Ag inhibited bacterial growth over 24hrs as the curves show no significant difference from the positive control (fig 2).

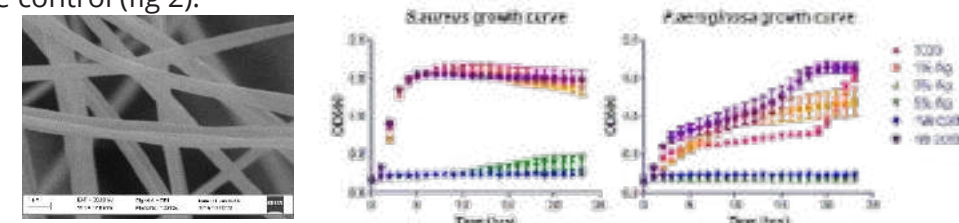


Figure 1. SEM image of Figure 2. Growth curves of *S.aureus* and *P.aeruginosa* treated with solutions of 70S30C glass fibers. 70S30C, 1,3 and 5 mol% Ag glass incubated in BHI broth for 4hr at 37 °C.

Conclusions & Future: 70S30C and 1 mol% Ag show no inhibitory effect on the growth of planktonic cultures of two clinically relevant strains of bacteria, whereas 3- and 5 mol% inhibited growth over 24hrs. Future work will involve synthesis, characterisation and testing of formulations intended to have antimicrobial, anti-inflammatory and angiogenic effects. Agar diffusion assays will

be carried out using compressed glass fibers and inductively coupled plasma atomic emission spectroscopy (ICP-AES) will be carried out to obtain ion-release profiles. Finally, to achieve the correct order and duration of ion release, methods of altering ion dissolution rates will be explored.

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Unexpected dual mesoporosity formation in a Periodic Mesoporous Organosilica

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Abstract: Periodic mesoporous organosilicas (PMOs) are nano-structured hybrid materials obtained by the hydrolysis-condensation of organobridged-triethoxysilane precursors in the presence of surfactants.¹ After template removal, the resulting material exhibits periodically arranged mesopores with uniform size. As it combines the robustness of inorganic/organic materials and the inherent properties of the organic group, PMOs have been used in a large range of application including catalysis, drug encapsulation/delivery, adsorption, gas storage, etc.² To our knowledge, few PMOs exhibiting two distinct types of mesoporosity have been described. Furthermore, the secondary porosity is generally due to the degradation of a precursor³, the clogging of part of the pores⁴ or the use of a secondary template⁵.

By using a single structure-directing agent, we report the preparation of a new PMO exhibiting two distinct types of mesoporosity without degradation of the precursor. This result is confirmed by TEM images, N₂-sorption analysis and SAXS-WAXS measurement which demonstrate the presence of 2D hexagonal porosity in the PMO material, together with a second pore network that is tentatively identified as having a cubic structure.

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Nanopatterning of metallic nanostructures on flexible substrates by “sol-gel” of noble metals

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Abstract: The fabrication of electronic, chemical and photonic components on flexible, stretchable, nonplanar, and biocompatible substrates as opposed to conventional rigid substrates can open doors for the next generation of advanced devices with new functionalities.¹ In this context, one great challenge consists in the development of new technologies to generate, localize and stabilize metallic nano-objects on flexible surfaces by industrially viable processes.

Currently, the metal patterning strategies are mainly based of physical deposition methods coupled to lithography.² These approaches are not practically viable on flexible substrate because they present several issues such as: (i) they allow fabrication of features but with limited resolution (> 100 nm); (ii) they require multi steps processes; (iii) the fabrication procedures are difficult to be implemented on large surfaces.

In this contribution, we propose a direct patterning approach from chemically derived materials that relies on the sol-gel process of noble metals (Ir, Ru, Rh) and respective oxides. This strategy is a single step, scalable and compatible with flexible substrate. From a chemical point of view, the metal formation is obtained by two ways: reduction in reducing atmosphere or carbo-reduction at low temperature. The films are deposited by dip-coating or spin-coating. We use different patterning strategies such as block copolymer templating, Nano imprinting lithography, Deep x-ray lithography to fabricate nanostructures at different scales from 20 nm to 100 µm.

Various techniques are used to characterize the films (AFM, SEM FEG, ellipsometry). The evolution of the mesostructure and crystallinity during formation of the materials is investigated by in situ GIWAXS/GISAXS coupled with a thermal chamber.

By using our original approach, we can envision these materials to be applied as lithographic masks, electrodes, electronic contacts or for optical applications.

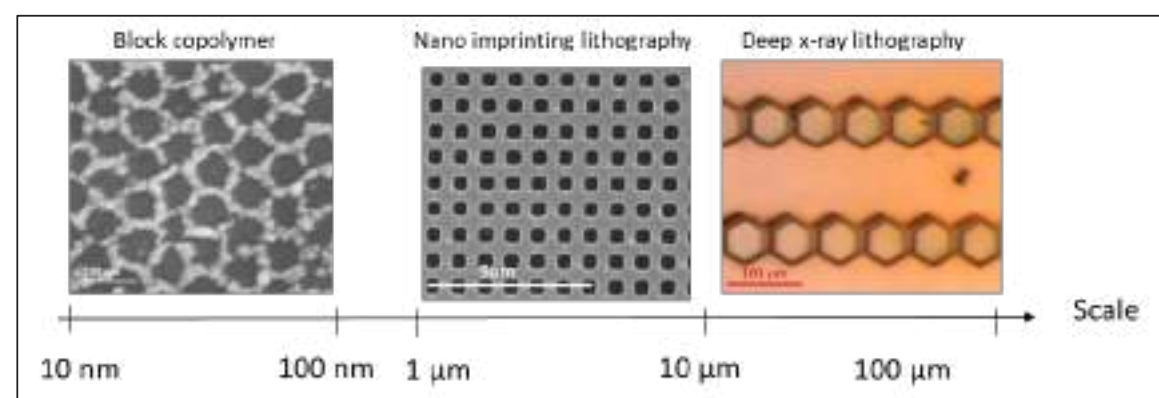


Figure 1. Multiscale of patterning

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Preparation of soluble polyamides by condensation of POSSs containing carboxyl and ammonium groups

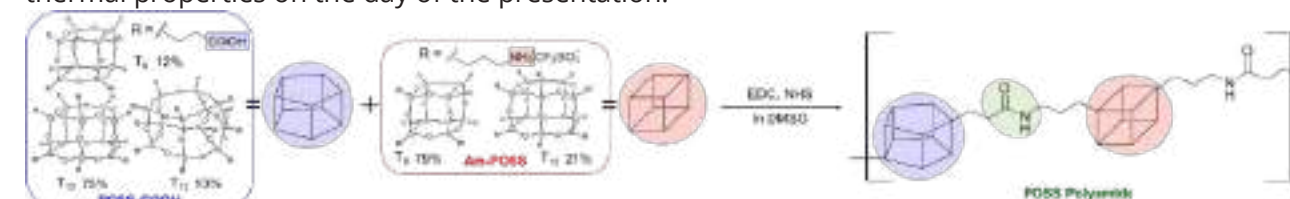
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Polyhedral oligomeric silsesquioxane (POSS) has attracted much attention as an inorganic framework compound with thermal and chemical stabilities and solubility. However, since POSS is an oligomer, it is difficult to apply it alone as film or bulk materials. Therefore, the preparation of POSSlinking polymers has been actively performed in recent years. However, as POSS generally has multiple functional groups, a polymer obtained by its polymerization usually forms a network structure and becomes insoluble. In order to prepare soluble POSS-linking polymers, it is necessary to prepare POSSs in which the number and arrangement of different substituents are controlled.^{1,2} However, to prepare such POSSs, complicated reactions and purification processes are required.

Meanwhile, we have reported that POSS-linking polymer can be easily prepared by hydrolytic condensation of a mixture of 3-(2-aminoethylamino)propyltrimethoxysilane and bis[3(trimethoxysilyl)propyl]amine in a superacid trifluoromethanesulfonic acid aqueous solution.³ However, this POSS-linking polymer could not form a self-standing film, probably because the alkylammonium group linking POSSs has a flexible structure.

In this study, when an ammonium-group-containing POSS (**Am-POSS**) and a carboxyl-group-containing POSS (**POSS-COOH**), which were previously reported by us,^{4,5} were polycondensed using condensing agents, we found that soluble POSS-linking polymer (**POSS Polyamide**) were successfully prepared. Formation of amide bonds was confirmed by FT-IR and ¹H NMR measurements. The ²⁹Si NMR spectrum of **POSS Polyamide** indicated that the POSS structure was maintained even after polymerization. **POSS Polyamide** was soluble in polar solvents, such as water, DMSO, and methanol. In addition, a self-standing film can be formed by heating and evaporating aqueous solution of **POSS Polyamide**. We will explain the detailed average molecular weight and thermal properties on the day of the presentation.



Scheme 1. Preparation of **POSS Polyamide**.

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Flexible and mechanophoric porous polysilsesquioxanes

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Abstract: Stimuli responsive materials are receiving increasing attention and have been the subject of many investigations over the past decade. Because of the ability of performing functions without any human input, they are often also called “smart materials”. The response activation ranges from irradiation, temperature, pH to also mechanical force. Especially, covalent chemistry provides a lot of strategies to design compounds which can be used as mechanophores in bulk materials. A wellknown example is the embedding of spiropyran into elastomeric polymers⁽¹⁾. The special feature of these organic molecules is their ability to undergo isomerization reactions at external stimuli. Spiropyran can exist in two states. The ring-closed form contains a spiro C-O bond and appears to be colorless because of its absorption maximum in the UV region. In comparison, the highly colored open merocyanine (MC) form has a fully conjugated π -system throughout the molecule (Figure 1). So far, not much is reported about the introduction of such mechanophores in porous silsesquioxane based “aerogels”, probably due to their poor mechanical properties. Limited flexibility and brittleness are a big challenge here. Recently, new mechanical reinforcement strategies showed huge improvements, like polyvinylsiloxane or polymethacryloxysilsesquioxane (PolyMAS) networks⁽²⁾.

In this work, current results of incorporation bis-functionalized spiropyran derivatives into the framework of different silsesquioxane based aerogel systems are presented. A synthesis strategy for spiropyran precursors that can be used for the sol-gel process is shown. The conditions for the successful incorporation of these organic compounds open opportunities to the design of ultra-light stress and strain sensors. Also, the change of the optical and mechanical properties of spiropyranembedded aerogels is discussed. The state of the art might give ideas for the development and design of more mechanophoric porous materials.

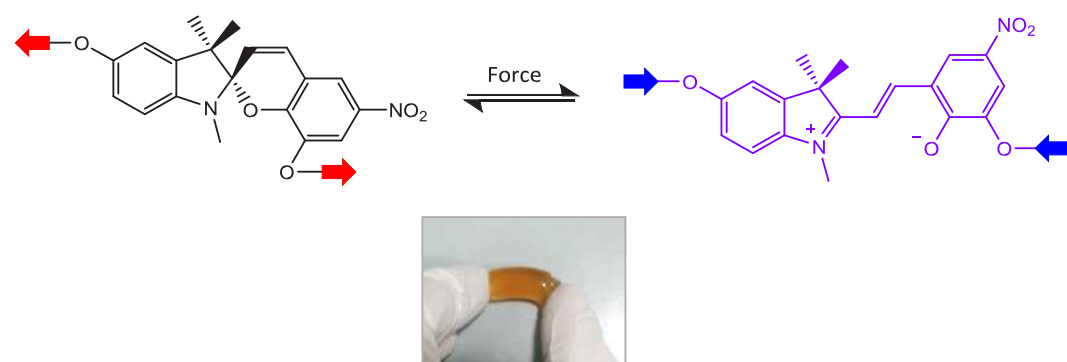


Figure 1. Mechanical force-induced ring-opening of spiropyran (SP) isomer leads to the activated colored merocyanine (MC) form. Bis-silyl functionalized derivative incorporated into PolyMAS silsesquioxane alcogel (below).

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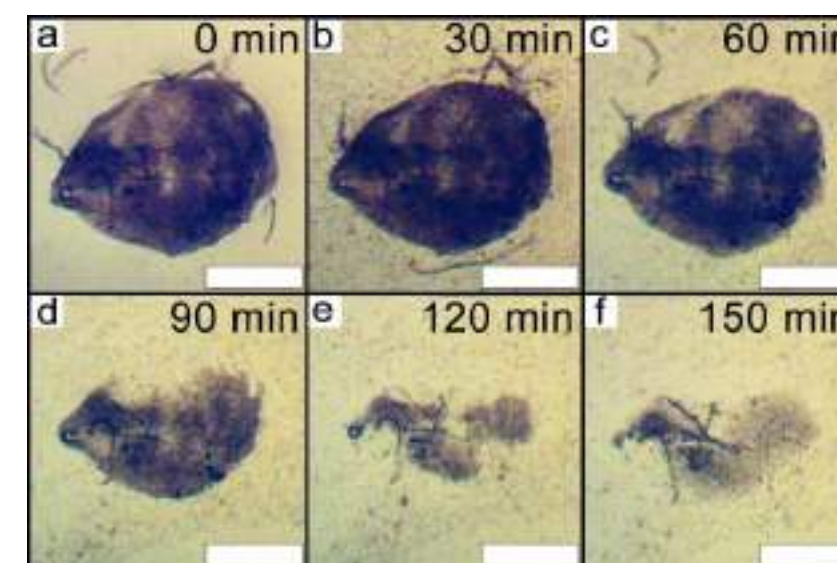
Synthesis of plasmin-loaded $\text{Fe}_3\text{O}_4@ \text{CaCO}_3$ nanoparticles: towards next generation of thrombolytic drugs

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Abstract: A major obstacle in the development of next generation of thrombolytic drugs has been the fact that plasmin - a serine protease that acts to dissolve fibrin blood clots - despite being the only enzyme suitable for the clot cleavage, still is not used in therapy due to very fast inactivation. Here we point to a potential solution of this problem by developing magnetically-controlled system for targeted delivery and recrystallization-driven release of plasmin showing tremendous therapeutic potential.



Thrombolytic activity of the plasmin-loaded $\text{Fe}_3\text{O}_4@ \text{CaCO}_3$ nanoparticles (white scale stands for 250 μm).

Acknowledgments: This work of Prilepskii A.Y. was supported by Russian Science Foundation Grants №18-7300119 and №16-13-00041. We are also grateful to Saint Petersburg State University Scientific Park for providing confocal microscopy investigations ("Chromas" Core Facility). TEM images were obtained at Center for the Collective Use of Research Equipment «Simbioz», IBPPM RAS.

Styryl cage silsesquioxanes: novel building blocks towards functional hybrid materials

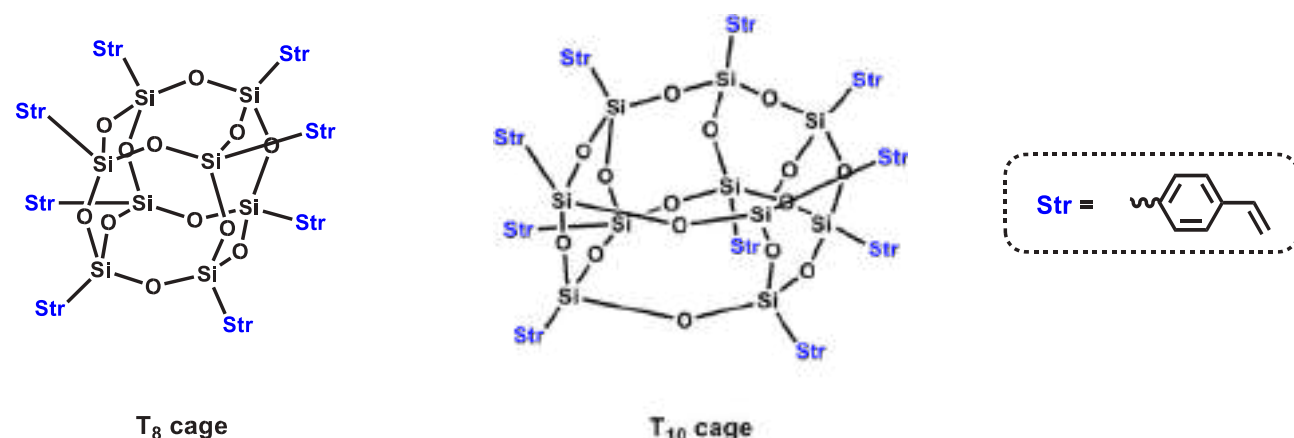
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Abstract: Among the oligomeric silsesquioxanes which are well-defined organosilica molecular structures, the T₈cage silsesquioxane, also called T₈-PolyhedralOligomericSilSesquioxane (T₈-POSS), is the most commonly described and studied. Indeed, the structure has been reported with various organic groups attached to the silicon atoms including methyl, phenyl, chloropropyl or vinyl groups^[1]. They are generally obtained by the direct hydrolysis of the corresponding trialkoxyorganosilane. Larger cage silsesquioxanes have also been described such as T₁₀, T₁₂ or T₁₄ but limited information is available concerning their synthesis and isolation as pure products^[2]. For all POSS, the organic substituents can facilitate post-synthesis functionalisation of the cage and thus open the way to applications in such diverse fields as in optics, catalysis, materials chemistry, etc. Our aim is to create new functional POSS with styryl groups which can be post-functionalized via readily accessible routes (e.g. hydrosilylation, Heck's, thiol-ene, hydrophosphination, hydroboration and metathesis reactions), the styryl entity being connected to the silicon cage through the phenylene moiety. Indeed, due to the terminal C=C double bond of the styryl group, these aforementioned reactions can facilitate further functionalization of the silsesquioxane cage with tailored structures for targeted applications, depending on the properties of the organic groups. Here, we report a new POSS family based on octastyryl T₈ and decastyryl T₁₀, including preliminary structural characterization based on NMR and IR data.



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Fabrication of PS spheres assisted nanoarrays by inkjet printing and spin coating

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Abstract: Polystyrene (PS) spheres can self-assemble into colloidal crystal monolayers that are widely used in photonics and as a base component in template synthesis. The most promising methods for PS spheres deposition in form of self-assembled layers are deep coating, inkjet printing, and spincoating. This work is devoted to fabrication of PS spheres assisted nanoarrays by inkjet printing and spin coating and investigation of optimal process parameters. Monodispersed PS spheres with average diameter of 315, 450 nm were synthesized by emulsifier-free emulsion polymerization of styrene. The round bottom flask acting as the reactor was placed into a beaker filled with water. Agitation was controlled using a magnetic stirrer. In a typical synthesis, deionized water (150 ml) was charged into the flask, then St (7.7 g), KPS (0.06 g) were added as initiators, and subsequently NaCl. The synthesis was conducted at constant stirring (800 rpm), the temperature of water bath was maintained at 80 °C. Colloidal crystallization matrixes obtained by spin-coating are shown in Fig. 1a. Here, the thickness of deposited PS spheres layer is adjusted by the rotation speed and solution viscosity. However, inkjet printing technique allows precise and selective material deposition and the desired design can be changed easily. In this study, different patterns of PS spheres were inkjet printed on silicon and glass substrates, the optimal printing parameters were investigated.

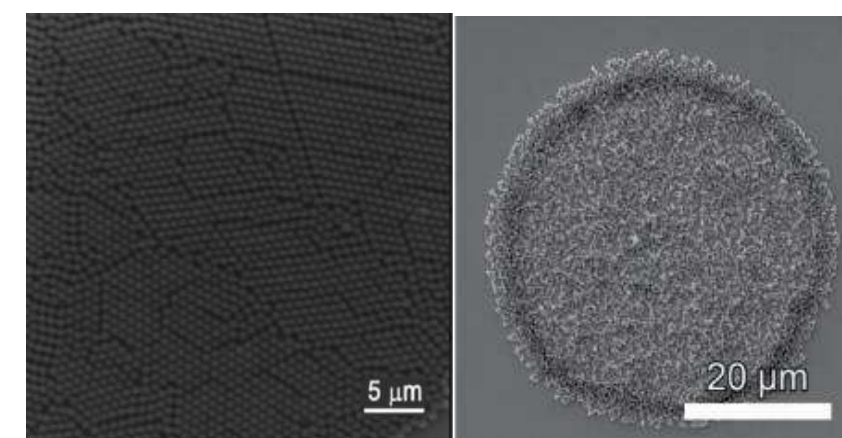


Fig.1 a) PS spheres assisted nanoarrays applied by spin coating on a silicon substrate; b) PS spheres assisted nanoarrays applied by inkjet printing on a silicon substrate

Such PS spheres opal matrixes combined with chitosan find their application in humidity sensors and as anti-counterfeiting marks. This work was supported by the Russian Science Foundation Grant No. 16-19-10346.

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Large area luminescent solar concentrators

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Luminescent solar concentrators (LSCs) are luminescent waveguides layers that convert sunlight into specific wavelengths. The converted radiation is guided by total internal reflection to a photovoltaic (PV) device located at the edges of the LSC. Their ability to concentrate sunlight onto small areas makes LSCs a useful complement to PVs in a series of applications, such as urban integration and flexible fabrics towards mobile solar-energy.

A critical parameter for these devices considers the ratio between the exposed surface area to the sun light and the emitting surface area coupled to the PV device. In this way we have been working with cylindric concentrators. Different geometries are being considered for the LSC. Plastic optical fibers (POFs), hollow-core POFs, triangular hollow-core POFs and fibers bundles are being applied.

Materials are then filled or coated with sol-gel materials. Downshifting organic-inorganic hybrids are prepared with organic dyes and lanthanide luminescent complexes [1-4]. Special focus relies on (i) optically active layer design, (ii) energy conversion mechanisms, (iii) performance and geometry and (iv) figures of merit in PV cell enhancement.

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Ion gradients in solutions for logic operation and iontronic devices

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Abstract: Adjustment of the environmental acidity is a powerful method for fine-tuning the outcome of many chemical processes. Numerous strategies have been developed for the modification of pH in bulk as well as locally. Electrochemical and photochemical processes provide a powerful approach for on-demand generation of ion concentration gradients locally at solid-liquid interfaces. Spatially organized in individual way electrodes provide a particular pattern of proton distribution in solution. It opens perspectives to iontronics which is a bioinspired approach to signaling, information processing, and storing by spatial and temporal distribution of ions. We prove here that soft layers allow to control of ion mobility over the surface as well as processes of self-organization are closely related to change in entropy. In this work, we summarize the achievements and discuss perspectives of ion gradients in solution for information processing. Here, we demonstrate a proof of concept of basic logic operations that use ions as input and/or output signals which allows unequivocal output reading. The system under investigation is presented by an array of gold or platinum electrodes particularly embedded in an epoxy resin and immersed in the electrolyte solution. The simplest model systems containing two electrodes are shown in Figure 1. The electrodes may be designated as inputs and the acidity of the space between the electrodes as output in terms of logic gates. Simple AND logic operations may be performed. The main processor of any computing device is basically a bunch of interconnected logic gates, thus performing these simple logic operations is an important step toward biomimetic iontronic calculations.

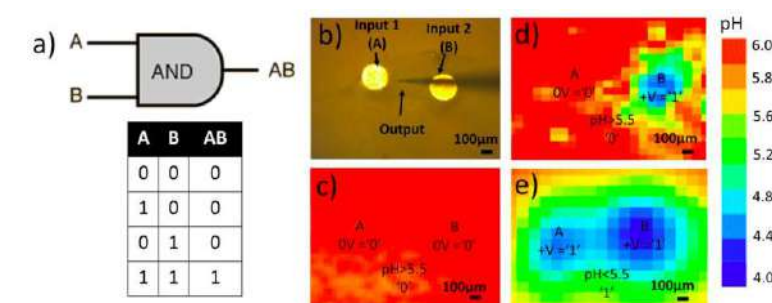


Figure 1. (a) Basic AND logic gate and corresponding truth table, (b) system of two WEs embedded in epoxy holder, (c-e) 2D pH-maps via SIET of two input electrodes in hydroquinone solution during polarization of electrodes in different regimes and interpretation in terms of logic gates, positive polarization +V is determined as input "1," no polarization 0V as input "0," pH >5.0 is determined as output "0" and pH<5.0 as output "1," (c) no potential applied, both inputs are "0," as a result, no pH drop – output "0," (d) positive potential is applied to the right electrode "1," left one is not polarized "0," resulting pH drop localized on right electrode and doesn't propagate to output area "0" (e) positive potential applied to both electrodes "1," resulting proton wave reaches output area giving output "1". Adapted from [1].

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The combination of copper oxide nanoparticles and N-acetylcysteine as a possible agent for chronic myeloid leukemia treatment

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Abstract: Chimeric BCR-Abl tyrosine kinase is known target for chronic myeloid leukemia (CML) treatment [1]. Inhibitors of this kinase dramatically prolong the patient's lifetime and lead to a complete remission in the first - chronic phase, however, their effectiveness at subsequent stages of the disease becomes significantly less, as CML cells develop resistance to them through cooperation, when paracrine interactions intensify. This study proposes a new agent to solve this challenge. Combination of copper oxide nanoparticles and N-acetylcysteine (NAC) showed significant toxic effect on CML cancer cell line K-562 through reactive oxygen species (ROS) production. It can be used either as therapeutic agent or as a foundation for supramolecular system that realizes target delivery of BCR-Abl inhibitor and provides additional damage in the presence of NAC.

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Photoactive metal sulfide and metal oxide modified bacterial cellulose aerogels for environmental applications

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Photocatalytic and adsorption processes employing nanostructured materials are capable of promoting both organic pollutant and heavy metal ions removal and thus regarded as promising approaches for water purification and wastewater treatment. Due their high surface area, monolithic nature and unique structural/textural properties, aerogels are excellent choices for the development of high-performance photocatalysts and adsorbents. While inorganic aerogels such as metal oxides and metal sulfide show suitable surface and electronic properties to act as photocatalyst and/or adsorbents, polymer based aerogels offer higher processability, mechanical stability and manuseability. Preparation of organic-inorganic hybrid aerogels offers the possibility of combining the desirable properties of both organic and inorganic components in order to obtain high performance functional materials. In this presentation, we will present an overview of our ongoing studies on the development of photocatalytic membranes and nanostructured adsorbents based on metal oxide and metal sulfide supported on bacterial cellulose hydrogels for the preparation of hybrid organic inorganic aerogels. Research results will be shown regarding the following topics:

- i) Entrapment of MoS₂ and WS₂ exfoliated nanosheets in sol-gel derived titania wet gels
- ii) MoS₂/Bacterial cellulose and WS₂/Bacterial cellulose aerogels for photocatalytic-assisted removal of Cr(VI) and adsorption of other heavy metals
- iii) Metal oxide/Metal sulfide based nanostructures supported on Bacterial cellulose aerogel membranes for continuous flow photocatalytic water purification

We aim to discuss the correlation between structural and physical-chemical properties of the developed hybrid aerogel materials with their performance as environmental photocatalysts and adsorbents, as well as their potential for application in wastewater treatment and environmental clean-up, with particular emphasize on their use in membrane photocatalytic reactors.

Acknowledgements

The authors would like to thank São Paulo Research Foundation (FAPESP) for financial support (grants #2015/22828-6 and 2018/01934-0,)

Detection of TNT and other Nitroaromatic Explosives using Porphyrin-Doped Silica Sol-Gels

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Abstract:

Development of a reproducible and reusable method for the detection of 2,4,6-trinitrotoluene (TNT) and other nitroaromatic explosive precursors in aqueous and vapor phase systems is of great significance in forensic science. Porphyrins and metal-porphyrin complexes immobilized within silica sol-gels were fabricated and used to study the binding of TNT to the porphyrin. Silica sol-gels were doped with free-base *meso*-tetrakis(4-carboxyphenyl)porphyrin, H₂TCP, *meso*-tetrakis(4-hydroxyphenyl)-porphyrin, H₂THPP, and its zinc (II) derivative, ZnTHPP, during the polycondensation process. Absorption spectroscopy of the silica gel materials showed that the immobilized porphyrins maintained their intrinsic properties and no aggregation was observed. Sol-gel monoliths with and without entrapped porphyrins were crushed into powders and analyzed by ¹H MAS NMR, ¹³C and ²⁹Si CP MAS NMR as well as ¹³C and ²⁹Si DP MAS NMR. Solid state NMR of the powders revealed that introduction of porphyrin moieties decreases the Q¹ intensities of the silica groups. The interaction of the porphyrin with nitroaromatics, the porphyrin functionality and the structural integrity of the doped sol-gel were examined using thermogravimetric analysis and fluorescence and UV-vis spectroscopy. The results of the study including the binding of the TNT in aqueous phase with the pyrrole nitrogens in the porphyrin will be presented.

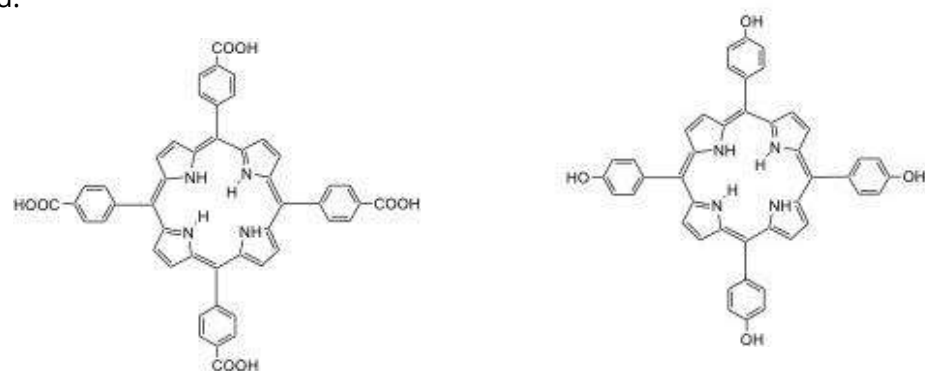


Figure 1. Chemical structures of (a) H₂TCP and (b) H₂THPP

Acknowledgements

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Redox behavior of two-component systems based on MgO obtained via sol-gel route

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Abstract: Sol-gel technology as known gives a lot of opportunities to prepare various metal oxide-based nanostructured materials with desired properties [1-3]. In the present work, a series of M_xO_y-MgO systems, where M is Cu, Ni, Co, Fe, Mo or W, was prepared using sol-gel approach. Aqueous solution of inorganic salt precursor was applied as a hydrolyzing agent instead of distilled water, which allowed us to exclude the usage of metalorganic precursors. Prepared xerogel and final oxide samples were characterized with a set of physicochemical methods including low temperature nitrogen adsorption, scanning electron microscopy, X-ray diffraction (XRD) analysis and diffuse reflectance UV-vis spectroscopy. Decomposition of xerogel systems was investigated by means of differential thermal analysis (DTA). According to XRD analysis, all xerogel samples exhibit a turbostratic structure regardless the nature of secondary metal added. At the same time, a presence of inorganic salt in the Mg(OH)₂ lattice increases the interlayer distance in the latter and thus facilitates the decomposition of Mg(OH)₂. It was also found that textural and structural properties of MgO-based oxide systems strongly depend on concentration of the additive. Formation of a joint phase was observed in the case of cobalt oxide only. Additives are believed to be distributed uniformly within the MgO bulk in most the cases. The only exception was WO₃, which has formed large agglomerates due to low solubility of its precursor.

Behavior of the prepared samples at reductive and oxidative conditions was investigated by TPR and *in situ* XRD techniques. It was found that MgO affects to the properties of the second component significantly. Generally, there are two species of transition metal oxide: weakly bonded nanoparticles uniformly distributed within the MgO matrix and strongly bonded M_xO_y species. Starting from the second redox cycle, each system was reduced reproducibly. It can be assigned to the phase transformations taking place. Therefore, reducibility of transition metal oxides can be noticeably changed by a strong interaction with the MgO lattice. This feature can be used in a number of applications such as chemical looping processes, dehydrogenation of light hydrocarbons and so on.

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Acknowledgements

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Mechanical properties of porous sol-gel films

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The sol-gel method is widely used to obtain porous materials with different porous structures: aerogels, membranes, films prepared by evaporation-induced self-assembly (EISA), etc. As a rule an increase of porosity leads to mechanical properties degradation, so control of Young's modulus (YM) is important for applications of porous materials. Normally nanoindentation (NI) is used for YM determination, but it has many limitations, including substrate effect (for thin films), low space resolution, etc. Atomic-Force Microscopy (AFM) in the PeakForce Quantitative Nanomechanical Mapping (PFQNM) mode is a promising technique based on the surface interaction effects and can be used to evaluate of the YM values of any layered structures, micro-sized objects and so on [1]. However this method has not yet been applied to porous sol-gel materials characterization.

Our first attempts to study various sol-gel derived films showed poor reproducibility. Sol-gel porous materials typically have free hydroxyls on the surface as a result of incomplete condensation. Terminal methyl (CH₃) groups are introduced into the matrix material to provide hydrophobicity. Thin films with different CH₃ content were prepared to clarify an effect of sorbed water on the PFQNM measurements. The CH₃/Si ratio was varied from 0 to 1 with the step of 0.2. The concentration of surfactant Brij® L4 was 45 wt.%. The films were spin-coated on Si wafers and cured at ~150°C for 5 min and at 400°C for 30 min. The pristine samples were formed a month before the experiment and stored at room temperature and atmospheric humidity.

Comparison of the PFQNM data with the NI data showed that the YM values are significantly differ for the films with low methyl content CH₃/Si < 0.6. FTIR shows water and organic residuals sorption (carbonyls and hydrocarbons), this effect is the most pronounced in the films with low CH₃ content, see fig. 1. The difference in the YM values obtained by NI and PFQNM becomes significantly lower after drying at 200°C for 30 min and it correlates with FTIR data. All traces of the uncharacteristic for the pristine films groups are completely disappear (see fig. 1) after drying at 350°C for 30 min and the difference in the YM values disappear as well. Thus, PFQNM can be used for YM estimation of the sol-gel thin films, nevertheless their hydrophilic properties and the refreshing annealing before the measurements should take into account to obtain robust and proper YM data.

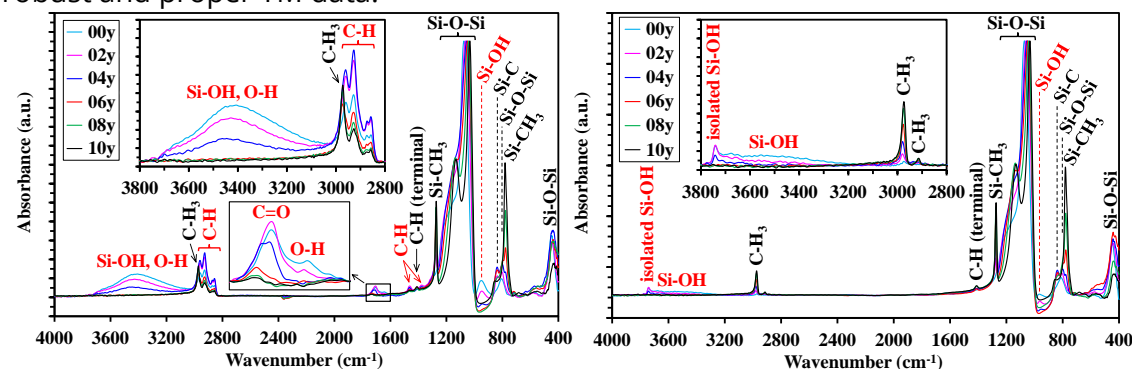


Figure 1. FTIR spectra of samples before drying (on the left) and after drying at 350°C for 30 min (on the right).

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Influence of curing temperature and deposition rate on the structure and properties of a sol-gel polyurethane-silica based coating

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Abstract: The sol-gel process makes possible organic-inorganic hybrid (OIH) materials that can be used as a corrosion barrier for protection of metal surfaces. Low-cost and “environmentally friendly” hybrid coatings can already be found¹, but their anti-corrosion performance is still limited by the short life time. In order to improve this property, a polyurethane-silica hybrid having as monomers the most produced diisocyanate worldwide, and the glycerol, a by-product of biodiesel production, was developed. The inorganic phase produced from TEOS by sol-gel process was chosen due to the prior knowledge of its functional properties. This work focused on the effects of the curing temperature on the materials structure and how it reflects on the coatings properties. Different deposition rates were applied using the dip-coating method and the influence on the coatings properties measured. The curing temperature was varied from 150 to 200°C and the deposition rate from 7 to 21 cm.min⁻¹ using carbon steel as substrate. The material structure was analyzed by FTIR and NMR (fig 1a) techniques, and its properties evaluated by TG, EIS (Fig 1b) and wettability measurements. From the obtained results it was possible to determine that the curing temperature of 166°C resulted in higher thermal stability and corrosion resistance, with an impedance value greater than 1GΩ.cm². The properties of this hybrid material undergo a great influence of curing and deposition rate, and control of these processing parameters allows to produce coatings thinner than 10 μm and with an impedance higher than 1GΩ.cm².

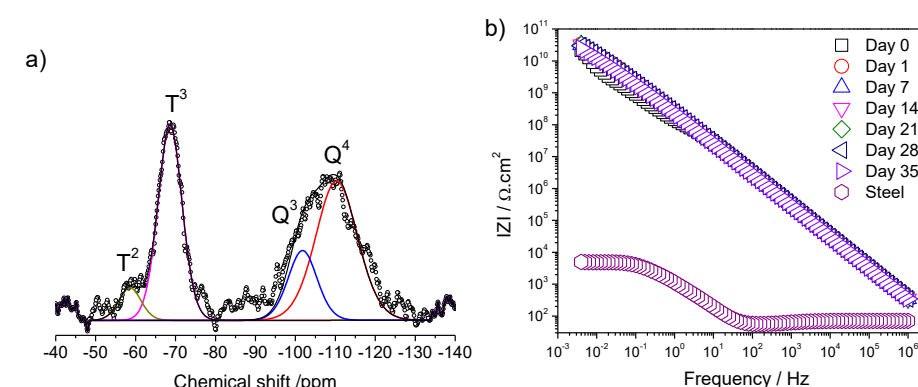


Figure 1. a) ²⁹Si NMR spectra and b) Impedance spectroscopy throughout 35 days in salt solution.

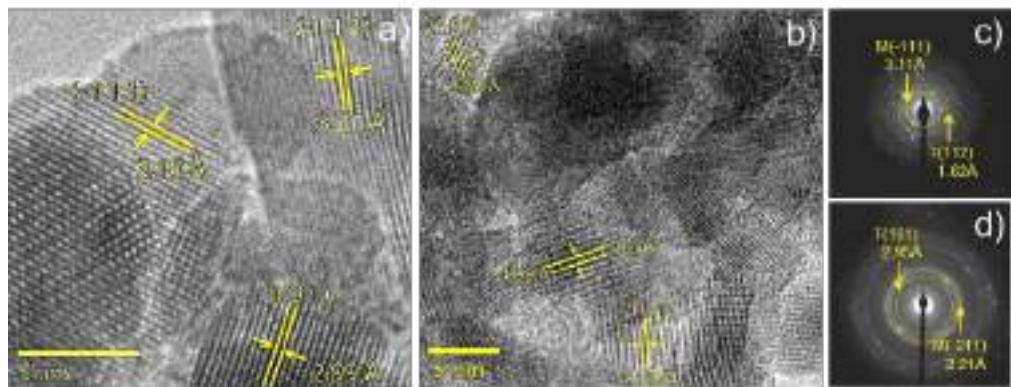
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Liquid crystals as pores template for sulfated zirconia ceramics

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Abstract: Porous sulfated zirconia was prepared by using the sol-gel process associated to liquid crystal templates (LCT). The Zr⁴⁺:SO₄²⁻ molar ratio and the ageing time were evaluated since the LCT gel formation to the final ceramic powders. Polarized light microscopy (PLM) and small angle X-ray diffraction (SAXD) analysis of the 8 days aged LCT wet gel samples revealed the hexagonal as the prevalent mesophase. The thermal treatment of the samples resulted in sulfated ZrO₂ ceramic powders, in which infrared (FTIR) spectra exhibited bands characteristics of mono- and bi-dentate SO₄²⁻ groups bonded to ZrO₂ (1056-1220 cm⁻¹). X-ray diffraction (XRD) patterns showed a mixture of monoclinic and tetragonal phases of zirconia in which the tetragonal phase rises in function of sulfate amount. The lattice fringe distances observed by selected-area electron diffraction patterns (SAED) and high resolution TEM confirmed the mixture of tetragonal and monoclinic crystalline phases. Analysis of the region of power-low scattering from SAXD pointed that the particles of non sulfated samples initially with rod-like morphology becomes something less dense as a network of branches with fractal surface when sulfate is inserted in the zirconia structure, favoring better porous characteristics. The scattered objects have radius of gyration around 17 and 4 nm associated to the crystallite and mean pore sizes, respectively. The LCT generated higher pores size diameter (5.7 nm) in the non sulfated Zr sample. This parameter decreases (≈ 3 nm) as the sulfate content increases, while the surface area rises 146 m²g⁻¹. The gel ageing process promoted the reinforcement of the pores walls structure, prevented shrinkage effects during calcination, and allowed reaching higher surface areas. Images from scanning and transmission electronic microscopies (SEM and TEM) elucidated the pores walls as platelets of irregular format and the presence of mesopores, respectively. The porous structure combined to the presence of acid catalytic sites, improved by sulfate groups at the zirconia surface, makes the materials promising for application as acid catalysts in dehydration reactions.



TEM images (a-b) and SAED patterns (c-d) of the tetragonal (101) and monoclinic (100) and (-111) zirconia atomic planes of sulfated (a, c) and pristine (b, d) samples.

Acknowledgements: FAPESP, CNPq and CAPES

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