Solgel2022

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POSTERS

ABSTRACTS BOOK

SOLGEL2022

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Main Menu

Chemistry and fundamentals of the sol-gel process, molecular precursors

P001

NEW INSIGHTS IN THE SOL-GEL SYNTHESIS OF GARNET STRUCTURE COMPOUNDS

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ABSTRACT:

The praseodymium substituted yttrium aluminium garnet ($Y_{3-x}Pr_xAl_5O_{12}$; YPrAG ($0 \leq x \leq 3$)) samples were synthesized by an aqueous sol-gel method and investigated. The single-phase $Y_{3-x}Pr_xAl_5O_{12}$ garnet has been obtained in the cases with $x \leq 0.30$. With further increasing of praseodymium ($x = 0.45$-2.0) the mixtures of garnet and perovskite crystalline phases have formed. The amount of perovskite in the mixture increased monotonically with increasing amount of praseodymium from around 4.89 % when $x = 0.45$ to about 91.14 % when $x = 2.0$. In the cases of $Y_{3-x}Pr_xAl_5O_{12}$ with $x > 2.0$ the formation only perovskite phases were detected. The structural transformations, the region of coexisting phases, the appearance of perovskite-like phases and the residual of garnet phase have been evidently deduced from the results of solid state NMR spectroscopy. The amorphous domains in ^{27}Al MAS NMR spectra as extremely broad unstructured spectral features were detected (Fig. 1). Since such amount of phase impurities was too small to be detected by widely used XRD or FTIR methods, this NMR result could be considered as rather unique one.

Secondly, for the first time the bulk bismuth iron garnet ($Bi_3Fe_5O_{12}$; BIG) was synthesized using a hydrothermal synthesis method. The preparation of $Bi_3Fe_5O_{12}$ in bulk is very problematic due to a non-thermodynamical character. The hydrothermal synthesis of BIG was performed on the yttrium gallium garnet ($Y_3Ga_5O_{12}$; YGG) substrate. The core-shell microstructure of hydrothermally synthesized garnets was approved by TEM measurements (Fig. 2). Individual fine spherical particles with size about 500-650 nm or 100-150 nm have formed during synthesis.

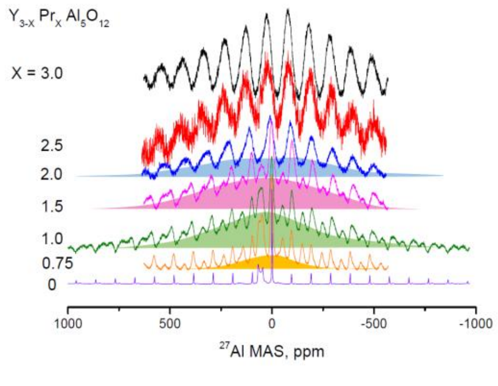

Figure 1: On the formation of broad-band features at the increasing concentration of Pr^{3+}.

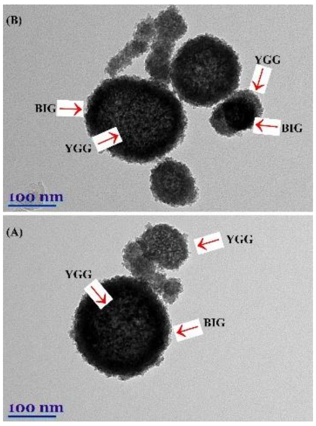

Figure 2: TEM micrographs of the core-shell $Bi_3Fe_5O_{12}/Y_3Ga_5O_{12}$ garnets showing formation of BIG/YGG and YGG (A) and BIG/YGG and YGG/BIG (B) nanoparticles.

Acknowledgements:
This work was supported by a Research grant NEGEMAT (No. S-MIP-19-59) from the Research Council of Lithuania.

P002

MANUFACTURE OF IRON OXIDE AEROGELS FOR HIGH ENERGY DENSITY PLASMA PHYSICS EXPERIMENTS

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ABSTRACT:

The AWE Target Fabrication group produces iron oxide aerogels that are used as target components in plasma physics experiments undertaken on the National Ignition Facility (NIF) high power laser system. Target Fabrication have previously produced iron oxide aerogels to a density of 50-60 mg/cc using an epoxide-assisted sol-gel synthesis[1].

A new campaign required the material at a density of 135 ± 15 mg/cc[2], with the goal to measure radiation transport through an Fe_2O_3 sample and thus determine the opacity of iron. Aerogels of this density were achieved[3] but this work has focussed on further understanding and improving the formulation to present a more reproducible and robust manufacture process.

In addition, a new capability for critical point drying was embedded in the process. Target Fabrication have previously used a Polaron critical point dryer for manufacture of certain aerogels. However, this manual and time-consuming process has been dramatically improved by the use of the automated Leica EM CPD300. Experimentation was carried out to determine optimal parameters to yield high quality, supercritically dried iron oxide aerogels from the Leica critical point dryer.

This poster will highlight the conclusions regarding optimal formulation and critical point drying variables for iron oxide aerogels at a density of ~135 mg/cc.

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P003

Insight into the formation mechanism of hollow silica nanotubes and nanospheres

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ABSTRACT:

Since the last century, a myriad of novel silica-based materials has been successfully developed via the sol-gel route and applied as catalysts or catalyst supports, vehicles for drug delivery or in many other areas. Despite significant advancements, the scientific community continues to explore the fundamental mechanisms of materials formation to achieve a precise control of the morphology, size and porosity. Beside some popular materials as SBA-15 or FDU-12, the mechanisms related to micelle-templated synthesis of promising architectures as hollow silica nanotubes and nanospheres is still at its early stage.[1] In this work, we took advantage of the parameters used in the synthesis of hollow silica nanotubes to unveil their extraordinary transition to hollow nanospheres (Figure 1). To understand in depth the tube-to-sphere transition, various parameters including the delay between the addition of the swelling agent and silica precursor as well as the stirring speed were pointed as crucial parameters. The careful study of these parameters together with an in-depth characterization of the morphology and textural properties of our micelle-templated solids, allowed collecting experimental evidences on the formation mechanism of both nanotubes and nanospheres. Moreover, structural properties show that our materials are promising candidates as catalysts or even as vehicles for drug delivery. To go further, *in-situ* liquid-phase transmission electron microscopy was used to unveil the morphologies involved in the early-stage of materials formation.[2]

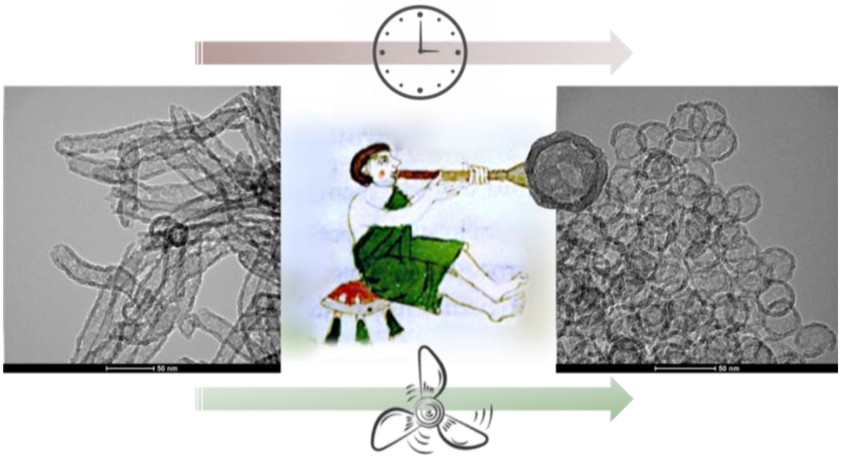

Figure 1 : tube-to-sphere transition guided by the delay between the addition of swelling agent and silica precursor or by the stirring speed. Inspired from an engraving extracted from “De Universo”.

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Low-Temperature Synthesis of Ti(OH)OF in Ionic Liquids

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ABSTRACT:

Titania can crystallize in many different modifications. Beside the well-known rutile and anatase there are other interesting modifications, like the bronze-type TiO_2(B) and fluorine-containing derivatives, such as the hexagonal tungsten bronze (HTB)-type Ti(OH)OF. Ti(OH)OF exhibits a high ion storage capacity and might be interesting for electrochemical applications.[1,2] The sol-gel-type synthesis of TiO_2(B) using a mixture of imidazolium-based ionic liquids (ILs) (C_{16}mimCl and C_4mimBF_4) was developed by Kaper *et al.*[3] Voepel *et al.*[2] showed that the fluorine content had a significant influence on the synthesis: Using only BF_4^- containing ILs Ti(OH)OF is formed, a compound with a quite peculiar crystal structure, analogue to the hexagonal tungsten bronze. As a main advantage of the synthesis, it can be carried out at relatively low temperature (95 °C) compared to other literature-known syntheses which demand quite harsh conditions. A mixture of ILs was supposed to be crucial by forming an IL-in-IL mesophase. Yet, our recent results indicate that it is possible to synthesize Ti(OH)OF by using just one BF_4^- containing IL.[4] By Rietveld refinement of XRD data of the synthesized products we found that during the reaction a slow, continuous transformation of Ti(OH)OF to TiO_2(B) and finally to anatase takes place. Also, we found that the chain lengths of the alkyl chain side group attached to the imidazolium ring influence the composition of the product. Interestingly the conversion is slower, i.e. the yield of desired Ti(OH)OF is higher, when using ILs with longer alkyl chains (Figure 1a)+b)). This finding suggests that the IL acts as surfactant attached to the nanoparticles (Figure 1c)) which slows down the conversion into the thermodynamically more stable TiO_2(B) and anatase. For a better understanding of the reaction mechanism on the atomic scale further studies are currently being carried out using NMR and Raman spectroscopy.

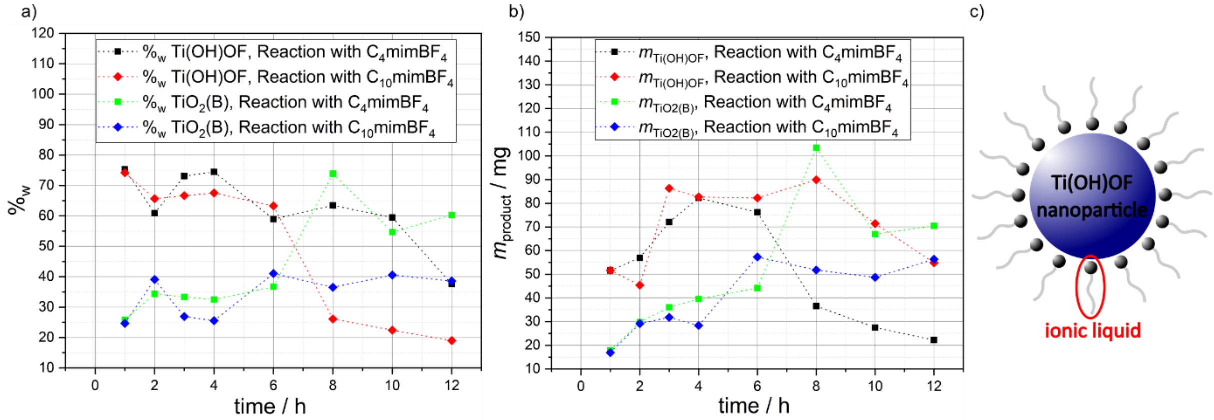

Figure 1 : a) Relative and b) absolute amount of Ti(OH)OF · 0.66 H_2O and TiO_2(B) obtained in different syntheses using different ILs. The values were calculated with Rietveld analysis. c) Schematic illustration of the shielding effect of the ILs.

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THE MODELING OF INFORMATION SINTESIS IN SILICA PRECIPITATION WITH CHIRAL MATRIX COMPOUND UNDER CONSTENT MAGNET

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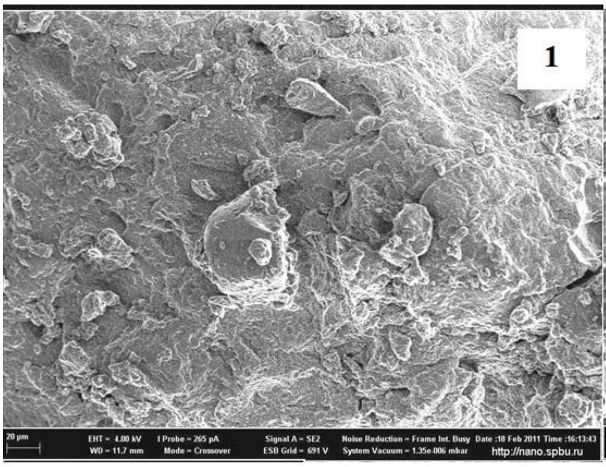
ABSTRACT:

Attempt of obtaining the sorbent selective with respect to biologically active components of essential oil Eucalyptus dives has been made. The shifting of optical activity of Eucalyptus dives liquid oil under the chiral selective SiO_2 is observed, wich was obtained under chiral matrix. It is concluded that chiral selective effect is growing for the systems adsorption synthesis under the magnetic influence. The growth of magnetic field induction for 100 times (lg 100=2) leads to growth of nano-particle size approcsimality 2 – 3 times. The growth of chiral selective adsorption activity more than 2 times was observed. Obviously, there is a decrease in chiral-selective adsorption stereochemical difficulties.

This phenomenon can be identified as informational synthesis with a decrease in entropy. The growth of magnetic field is connected with growth of nano-size chiral pores by logarithm like quantity of information with number of selecting objects. The self-organization of chiral-selective adsorption centers is comparable with formation of active centers in enzyme.



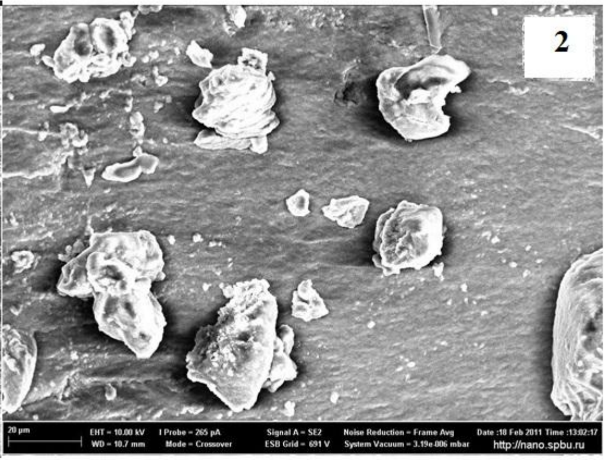


Figure 1 : Non-magnetic precipitation.

Figure 2 : Magnetic precipitation

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P006

A Novel Electronic Biosensor Based on Sol-gel Transition of Peptide-based Supramolecular Hydrogel

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ABSTRACT:

We developed an extended floating-gate thin-film transistor (EFG-TFT) to monitor various sol-gel phase by electronic signal. The EFG-TFT was fabricated by ZnO as channel and YOx as dielectric layer which provided an extended area to sense the analyte interacted with designed hydrogelator. Further, a peptide-based supramolecular hydrogel, i.e. 2-Naphthylaceticacid-L-Phenylalanine-L- Phenylalanine-L-O-Phosphor Tyrosine (Nap-FF-Yp), was synthesized as our sensing probe to detect alkaline phosphatase (ALP). The Nap-FF-Yp could be cleaved by ALP during hydrolysis, leading the occurring of π-π stacking, and changed to hydrogel finally. Due to the difference of potential drop between liquid phase and gel phase of hydrogel, the sol-gel transition could be monitored by electrical characteristics. In our sensing system, we successfully identified the normal to abnormal level of ALP from the concentration of 0.15 U to 1.5 U. The reaction rate of hydrogelation depends on the activity of ALP. Preliminary experiment results exhibited that the quantity of threshold voltage (V_{th}) variation could be identify ALP level. The higher extent of hydrogelation occurs, the Vth variation is smaller and shifts to left. In summary, we fabricated a low cost, fast interpretation, and specific target designed sensing system by means of the combination of sol-gel transition and electrical characteristic. The level of hydrogelation could be quantified by electric characteristics and the extraction of activity of ALP from EFG-TFT is successfully achieved. In the future, different diseases could be detected by the system via specific designed hydrogelator.

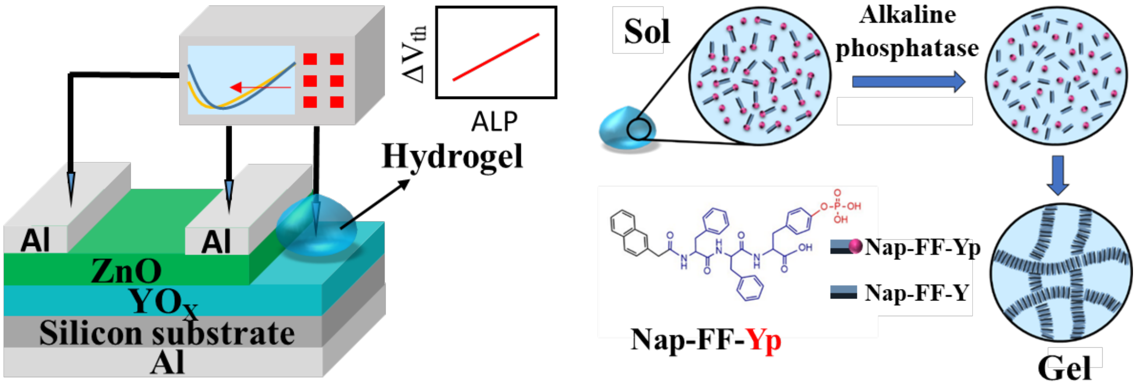

Figure 1: A Novel Electronic Assay Based on a Sol-gel Transition Reaction and a Thin-film Transistor of Supramolecular Hydrogels to Detect Alkaline Phosphatase Activity

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A new micro-structured waveguiding fluorescent architecture on glass entirely elaborated by sol-gel processing

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ABSTRACT:

Channel waveguides endowed with diffraction gratings at their input and output for light injection and extraction, respectively, are extensively exploited for optical and photonics applications. In this paper, we report on such architecture on glass entirely elaborated by sol-gel processing using a high refractive index titanium oxide based photoresist that can be imprinted through a single photolithography step. We more particularly focus on a fluorescent architecture including channel waveguides doped with a ruthenium complex flurophore. We firstly present the multi-step elaboration process leading to this architecture. Opto-geometrical properties of the channel waveguide and diffraction gratings are assessed and optimized on the basis of optical and AFM characterizations. According to these properties, best injection and extraction angles of the excitation and emission signals have been determined thanks to optical simulation. Then, we present fluorescence measurements performed in waveguiding configuration using a specifically designed optical bench. The study demonstrates that this original sol-gel micro-structured architecture is well adapted to efficient channel waveguide / diffraction grating coupling and propagation of the fluorescence excitation and emission signals in the core of the channel waveguide. This work constitutes a promising preliminary step toward the integration of our architecture in a microfluidic platform for fluorescence measurement in liquid medium and waveguiding configuration.

P008

KINETICS OF RESORCINOL-FORMALDEHYDE CONDENSATION

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ABSTRACT:

The kinetics of sol-gel polycondensation of resorcinol (R) and formaldehyde (F) under alkaline catalysis was followed by various techniques enabling the investigation of the different aspects of reaction (FTIR, NMR relaxometry, and DSC). Well-defined reaction systems with various catalyst concentrations (R/C molar ratio 25 and 50) and concentration of reactants (20 and 40 weight %) were observed isothermally at 40 °C. Kinetic analysis enabled the determination of the rate constants and parameters of the reaction model.

All methods are able to describe similar trends in rate constants, showing higher values for a higher catalyst content and a higher concentration of reactants. The differences in the obtained values of the rate constant obtained are understandable because each of the methods focuses on principally different components of the reaction system. While FTIR is dependent on bonds and groups in the reacting system, NMR follows relaxation (mobility) of water molecules affected by the presence of solid particles, and DSC measures changes in the melting point of complex mixtures of water, reactants, and various intermediates.

Analysis of the reaction model parameters allowed us to conclude that the processes followed by FTIR and DSC experiments can be described with the kinetic model of n-order with $n > 1$. On the other hand, the NMR experiments indicated Avrami-Erofeyev reaction models based on nucleation and nuclei growth.

The results indicate that all three methods can be used simply to follow the RF condensation and to study the effect of various process parameters on its kinetics. All three methods (especially DSC) can also be easily adapted for measurement at different temperatures, which opens the doors for estimation of the temperature function (temperature dependence of rate constant) and consequent kinetic modelling of the process.

P009

Kinetics and mechanism of methyltrimethoxysilane hydrolysis

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ABSTRACT:

Nuclear magnetic resonance (NMR) spectroscopy and reactive molecular dynamics (RMD) modeling were employed for methyltrimethoxysilane (MTMS) hydrolysis investigation.

NMR measurements indicate distinct decrease of the 0.12 ppm ^{1}H-NMR signal during reaction, initially associated with methyl groups. Similar observation can be found in literature [1], identified as chemical cleavage, although our studies confirm that the decrease is acid catalyst concentration dependent. Exponential approximation of kinetic curves provides initial reaction rates, indicating pre-equilibrium protonation as a step preceding hydrolysis of the organoalkoxysilane (Fig. 1). The identified mechanism is consistent with literature [2], however the presented research aims to advance the state of the art by providing reaction dynamics description.

The theory and principles of the developed RMD model are based on identification of potential energy associated with motion of atoms and ions [3, 4]. Bond breaking and making process is observed due to variable catalyst concentration, corresponding to the presented NMR studies. The outcome of numerical investigation is system dynamics description and discussion of the origin of proton addition to oxygen atoms, as well as water back-side attack to silica atom.

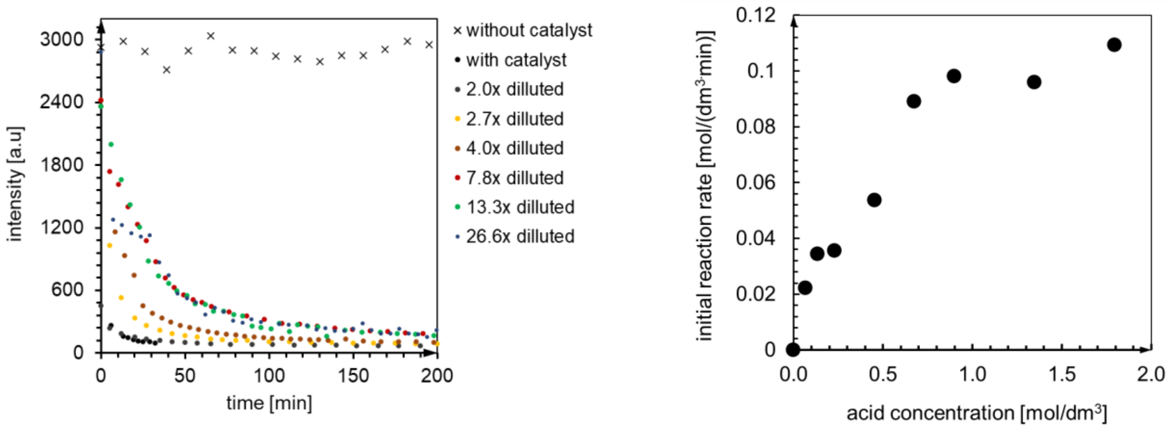

Figure 1: NMR signal intensity during reaction (left) and initial reaction rates (right) as a function of acid concentration.

Acknowledgments

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P010

REPLACEMENT OF FORMALDEHYDE AS PART OF CARBON-BASED AEROGEL PREPARATION FOR PLASMA PHYSICS EXPERIMENTS

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ABSTRACT:

The AWE Target Fabrication Group prepare carbon-based aerogels that are used as target components for plasma physics experiments at laser facilities including the National Ignition Facility in the US. The manufacture utilises the carbonisation of a resorcinol-formaldehyde aerogel,[1] to yield a material with densities between 30 mg/cc and 240 mg/cc with sufficient structural integrity to withstand machining processing for target applications.

The current process uses formaldehyde, which is classified as toxic and a suspected carcinogen. As such, to protect operators from exposure to the substance and for surety of supply of future manufacture of carbon-based aerogels, alternate reagents to formaldehyde are being explored.

This poster will provide an overview of ongoing efforts to prepare carbon-based aerogels that the density can be tailored between 30 mg/cc and 240 mg/cc and can withstand machining processes.

References

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P011

GLASS TRANSITION DURING SOL-GEL POLYCONDENSATION OF RESORCINOL WITH FORMALDEHYDE

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ABSTRACT:

The course and mechanism of resorcinol-formaldehyde (RF) sol-gel polycondensation can be investigated by different common techniques, however one of the most successful is differential scanning calorimetry (DSC). The aim of this contribution is to examine the freezing/melting behaviour of the reaction mixtures combined with appropriate isothermal steps at 40 °C by DSC. Three different RF mixtures with various catalyst concentrations (R/C molar ratio 25 and 50) and concentration of reactants (20 and 40 weight %) were investigated.

The freezing of reaction mixtures was practically unaffected with progressive polycondensation reaction. However, two variants of melting curves were observed. At the beginning and end of reaction, the simple endothermic peaks related to melting were recorded. Contrary, an additional exothermic peak was observed at low temperature in the middle stage of reaction. This peak corresponds with more complicated process and starts in the reaction phase when the samples are fully solidified, although not fully curred/cross-linked. At this stage the mixture probably contains isolated 3D macromolecules swelled with water in their structural voids of subnanometric size. During freezing, the polymer through glass transition becomes much more rigid and traps the water in the form of nanodroplets which are not able to freeze. During consequent heating, when reaching the glass transition temperature of the present polymer, the structure becomes more flexible, the water is released, and ice crystals can form. Then, the water simply melts at higher temperature. This phenomenon was not observed for the more diluted mixture.

The DSC enables to detect the phase of reaction in which polymeric structures undergo glass transition, which has not yet been observed for resorcinol-formaldehyde polymers.

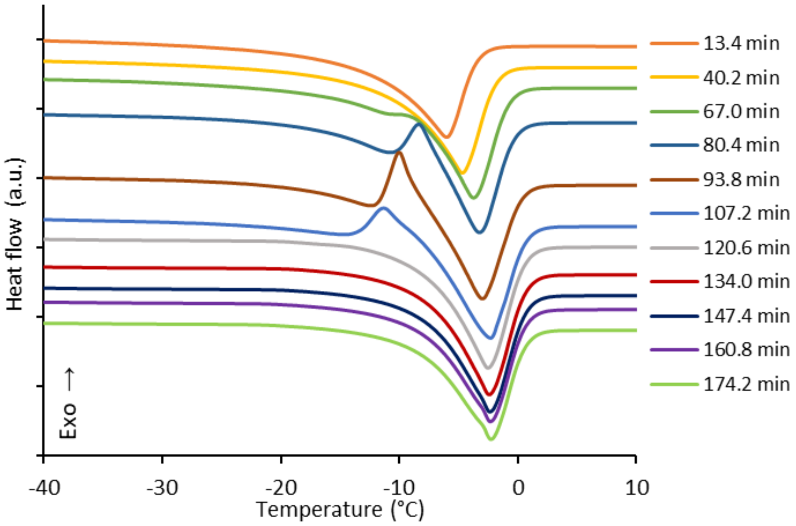

Figure 1: Melting curves for reaction mixture RC25-40 (R/C = 25, w = 40 %) over time

P012

A Temperature-Responsive Mineral Hydrogel with shape-designed and Calcium Supply in Cranial Defects, and Inflammatory Warning in Wounds

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As one of the surgical operations to realize skull deconstruction and reconstruction, cranial repair is commonly used in clinic. There are two main points for this operation. On the one hand, the chosen materials should have both excellent strength and bone induction properties, which mineralized hydrogels have been verified effectively, but the traditional mineralized hydrogel have poor plasticity to meet complex craniofacial surfaces. Therefore, we designed a temperature-sensitive mineralized hydrogel that can create shape on-demand. The second key point of cranial repair lies in the healing of the wound. Currently, the wound-dressing usually prevents inflammation from being detected in time because ordinary electronic thermometers such as infrared thermometers and colorimetric sensors record temperature based on manual measurement at intervals. Our mineralized hydrogel with temperature-responsive will give it the potential to alert the occurrence of the inflammation as the temperature sensor. The reason for mineralized hydrogel used both in cranial repair and infected wounds is that we chose inorganic particles with luxuriant calcium supply, which is one of the widely existing materials in the human body——calcium lactate. Based on the solubility of calcium lactate varied greatly with temperature, the precipitated part which provided strength, and the dissolved part which influenced the conductivity of the hydrogel transformed by temperature change.

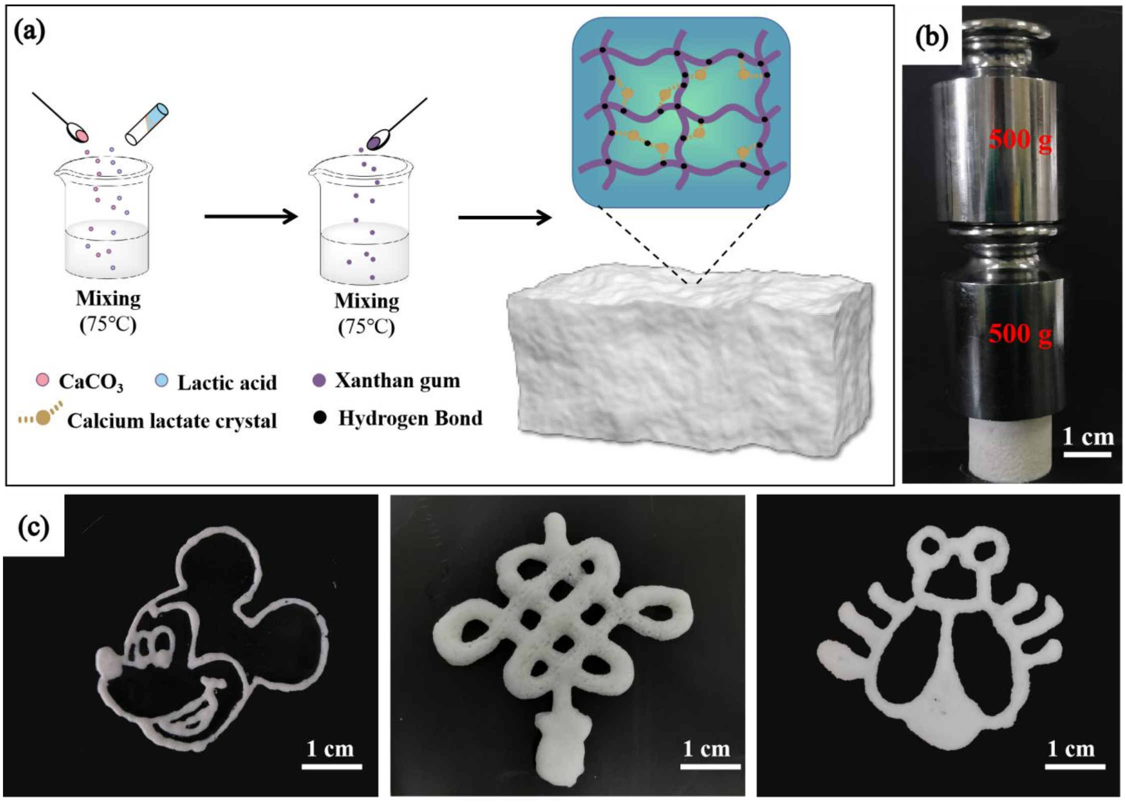

Figure 1 : (a) Schematic structure of the XG/Ca-X hydrogels; (b) Qualitative demonstration of the mechanical capability of XG/Ca-50 hydrogel;(c)The hydrogels can be manipulated into various shapes.

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P013

DEEP UNDERSTANDING ON THE FORMATION OF SILICA-ALUMINUM-PHOSPHATE HYBRID MATERIALS USING SOLID-STATE NMR

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ABSTRACT:

There is a particular interest in synthesizing hybrid sol-gel materials that can easily bond to inorganic species at room temperature to produce new optical materials. In this regard, silica-aluminum-phosphate-based compositions[1] are very interesting for laser and signal amplifiers. However, the synthesis through sol-gel route frequently results in precipitation or premature gelation. In this study, we present photopolymerizable aluminum-phosphate type-II hybrid materials compatible with alkoxysilane precursors, allowing the synthesis of silica-aluminum-phosphate hybrid materials. Stable sols were prepared with an inorganic mass content as high as 40% wt. A systematic structural study varying the P/Al and Si/P ratios using solid-state NMR, SEM and phase contrast AFM is reported. Our analysis revealed a homogeneous material despite its intricate and complex inorganic network.

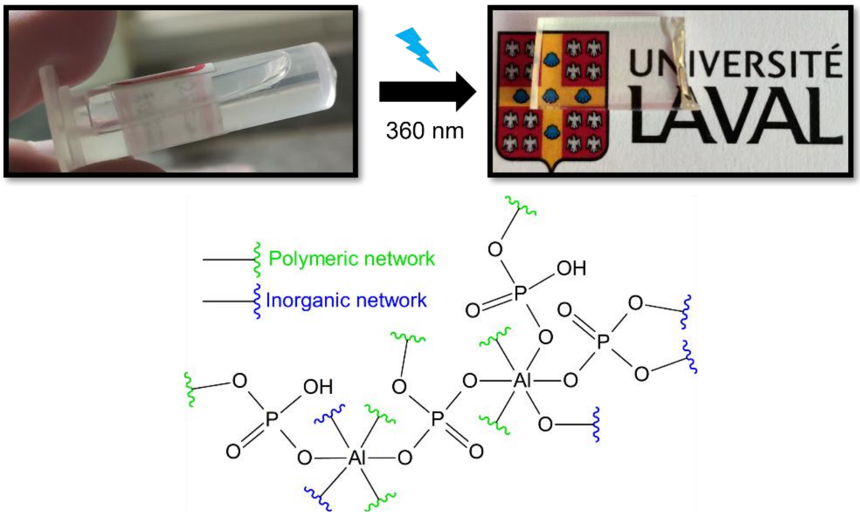

Figure 1 : 4 mm thick silicate-aluminum-phosphate hybrid material.

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P014

Effects of Acid Activation via Sol-Gel Chemistry towards Tailor-Made Nitrogen-Doped Carbon

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ABSTRACT:

Carbon activation is intensively investigated due to a widespread utilization of activated carbons as sorbents, hosting and support materials owning to its high porosity and surface area. Activated carbons are increasingly considered also for electrochemical applications *e.g.* supercapacitors and metal-ion hybrid capacitors. Those devices usually employ activated carbon electrodes, where ions are stored by means of adsorption/desorption.[1] Meanwhile, in lithium-sulfur batteries, sulfur is loaded within activated carbon pores to confine insoluble intermediates.[2] The activation is normally proceeded in top-down or bottom-up strategies. Therein pore formation (porogenesis) occurs by reaction with steam, CO_2, KOH, or the use of acidic agents. It is generally accepted, that the porogenesis mechanism is chemical leaching of carbon atoms. Recently, the sol-gel type synthesis of nitrogen-doped carbon in molten acids was presented, questioning the general validity of a leaching activation mechanism.[3] The protocol using inorganic salt melts ($MgCl_2$ or $ZnCl_2$) and organic precursors additionally generated N-functionalities. Interestingly, it can be noticed that the imprinting cations play a crucial role towards chemical structure of nitrogen-doped carbon framework. The coordinated geometry is well-known from phthalocyanine, a macrocyclic N-complexes (MN_4-sites, where M is metal cation) which are desirable surface complexes, *e.g.* in electrocatalysis. The analogous phenomenon may be observed when using H_3PO_4 and H_3BO_3 agent via sol-gel chemistry.[4] Herein, the carbonization of mixtures of organic compound with H_3PO_4 and H_3BO_3 is investigated. Therefore, associated effects regarding the presence of P and B atoms within resulting nitrogen-doped carbons as well as the porogenesis mechanism are discussed. The understanding of moieties probably offers a new perspective of non-leaching carbon activation hence, provides a feasible pathway towards improved performances in electrochemical applications.

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P015

A NEW FAMILY OF STYRYL-SUBSTITUTED CAGE SILSESQUIOXANES: T_{8}, T_{10}, T_{12} AND AN UNPRECEDENTED T_{18} CAGE

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ABSTRACT:

Among the family of well-defined silsesquioxane oligomers, the cage silsesquioxanes (also referred to as polyhedral oligomeric silsesquioxanes, POSS) have been extensively studied, with a particular focus on the T_8 cage.[1] These have been described with various organic substituents at the silicon atoms (e.g. chloropropyl, vinyl, phenyl, etc.), with the reactivity of such compound being controlled by the organic moiety. However, few articles report the synthesis and characterization of larger cages, with the largest previously isolated and fully characterized being the T_{14} cage.[2]

Here, we explore the synthesis of a new family of styryl-substituted cage silsesquioxanes. In contrast to previous report,[3] the styryl group in these compounds is linked to the silicon atom via the phenylene group, with the free vinyl group being readily functionalizable by hydrosilylation, Heck's, thiol-ene, or metathesis reactions. In addition to the more common T_8, T_{10} and T_{12} cages,[4] we also report the isolation of an unprecedented T_{18} cage silsesquioxane as a pure product.[5] The structures and properties of the compounds are established by single crystal X-ray crystallography, multinuclear NMR, mass spectrometry, etc, and the isomer of the T_{18} cage is determined among the nine possibilities previously proposed for the T_{18} system.[2]

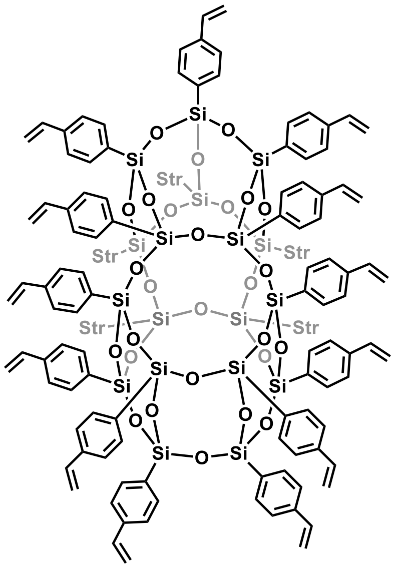

Figure 1: Unprecedented T_{18} cage

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P016

High-throughput *in vitro* analysis of engineered tumour microenvironments using 3D bioprinting

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ABSTRACT:

Traditional 2D flat cell cultures of cancer cells and *in vivo* animal experiments remain the most commonly used techniques as *in vitro and in vivo* platforms for cancer research, drug screening and toxicity tests prior to entering human clinical trials. This is due to their low cost, efficient workflows and optimised downstream analysis techniques. Evidence suggests that these traditional cell culture techniques do not accurately replicate the complexity of human tumours. For example, these models have limitations in mimicking tumour stromal heterogeneity and tumour cell-extracellular matrix (ECM) interactions, thus potentially limiting the ability to mimic *in vivo* tumours realistically. This has led to the development of three-dimensional (3D) *in vitro* models which have been shown to reflect the cellular responses *in vitro*.
Synthetic gels have been used extensively over naturally derived biomaterials, such as collagen without the complexity of cell-matrix interactions, as they offer opportunities to control and modulate cells.

Herein, we developed an electrostatically crosslinked PEG-based gels system for creating high-throughput 3D *in vitro* models using a 3D drop-on-demand bioprinter to mimic the extracellular matrix cancer environment. First, the 3-arm PEG-based polymer backbones were conjugated with various degrees of cell adhesive RGD motifs (0%, 25%, 75% and 98%) to study the influences of cell adhesive motifs on breast cancer (MCF-7) spheroid formation. Formation, stability and mechanical properties of gels were tested with and without RGD motifs in different conditions to evaluate cellular response to materials parameters in a 3D environment. Biocompatibility was tested with MCF-7 breast cancer cells by encapsulating cells within a gel for 7 days, where a high cell viability of approximately 99.0 ± 1.4% was observed. The electrostatically crosslinked gels can be degraded in the presence of salts at room temperature by breaking the interaction of oppositely charged polymer chains. As such, both MCF-7 cells and spheroids were released by simply exposing a gel in a 2 M NaCl solution for 5 min. The released MCF-7 breast cancer cells and spheroids remained highly viable with no significant differences before and after release. Finally, the released MCF-7 cells/spheroids were analysed with flow cytometry to characterise cellular responses and behaviours in more detail.

In summary, this PEG-based tuneable gel system shows great promise as a 3D ECM mimic of cancer microenvironments with controllable biophysical and biochemical properties. The ease of gelation and dissolution through salt concentration provides an innovative means of engineering tumour microenvironments, where the cells can be quickly harvested for analysis. The speed at which cells and aggregates can be reclaimed provides scope for integrated multimodal analysis, where 3D immunofluorescence imaging of the gel can be supplemented by parallel molecular analysis at the protein and transcript level after dissolution and cell collection.

P017

FUNDAMENTAL INVESTIGATION ON MOLECULAR SELF-ASSEMBLY PROCESS IN THE FORMATION OF MESOPOROUS HYBRID SILICA

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ABSTRACT:

Mesoporous hybrid silica materials carrying organic functional groups may show additional properties, which cannot be simply predicted as a sum of the contributions from single components[1]. Understanding the nature of this material would allow us to control the organic-inorganic interface, although only a little research was devoted to this matter and our knowledge remains unsatisfactory[2]. In this study, we show how the inclusion of organic functions in mesostructured materials can influence the self-assembly process, the porosity, and the local organization (domains) of organic functions in highly ordered mesoporous hybrid silica. Ordered mesoporous silica thin films were prepared by the co-condensation sol-gel process between hybrid and non-hybrid silica precursors. Self-assembly of mesopores was achieved by templating method using cetyltrimethylammonium bromide (CTAB) surfactant [3] and co-polymer Pluronic123. The evaluation of the alkyl chain length influence was based on hybrid precursors bearing bromine atoms which can be assessed using FTIR spectroscopy or High-Resolution Transmission Electron Tomography: 3-bromopropyltrimethoxysilane, 5-bromopentyltri-methoxysilane, and 11-bromoundecyltrimethoxysilane. Also, the influence of hydrogen bonds, as well as π-π stacking, are being analysed by introducing ureido, phenyl, and pyrene moieties. The microstructural and structural characterization of films was performed by infrared spectroscopy, high-resolution TEM, fluorescence spectroscopy, and ellipsometry.

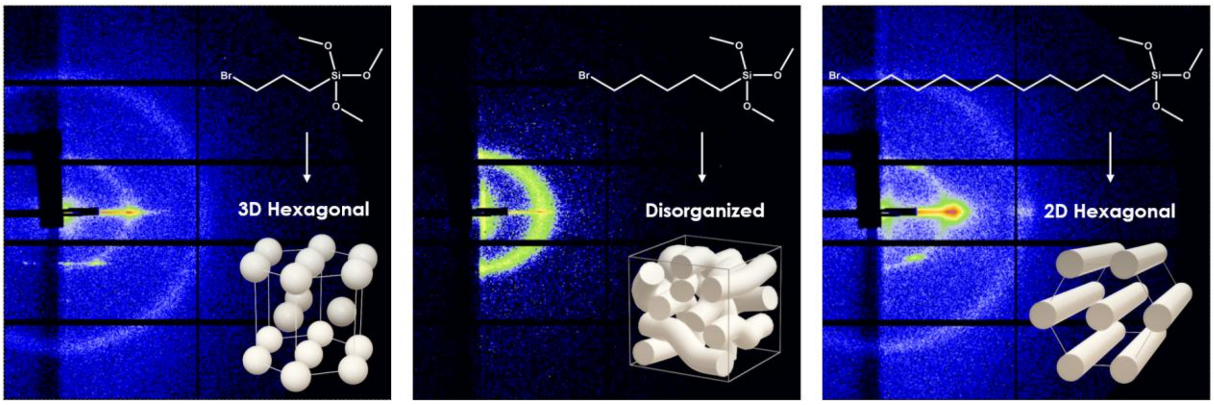

Figure 1: Evolution of the porous silica mesostructured with an introduced alkyl chain, evaluated by the Grazing-Incidence Small-Angle X-ray Scattering.

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Coatings

A NOVEL METHOD FOR COATINGS CHARACTERIZATION AT HIGH TEMPERATURE

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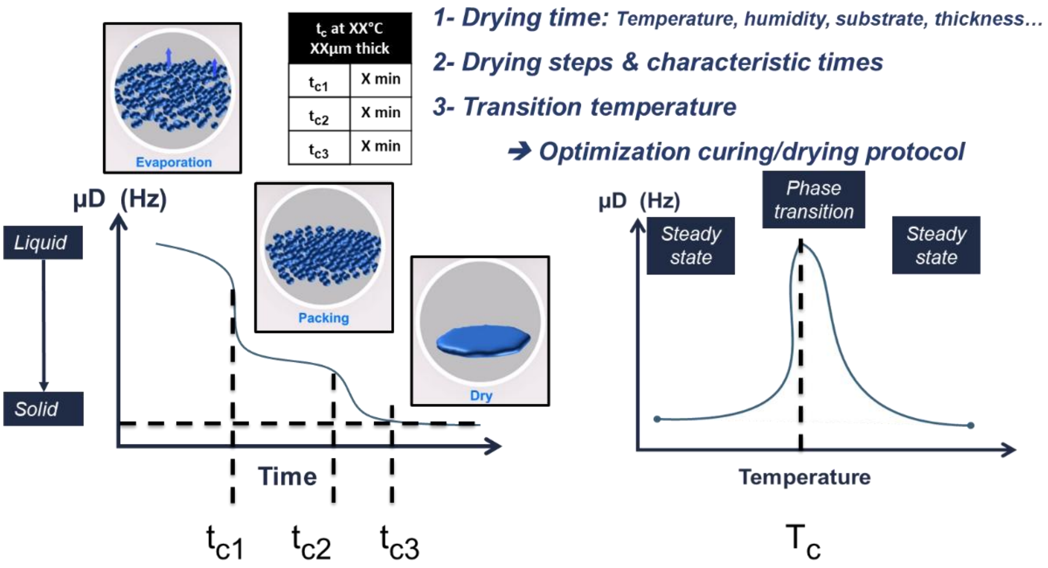
ABSTRACT:

The characterization of the microscopic dynamics of coatings materials and polymer films is a very important step in every new development or quality control.

We use a dynamic light scattering technique (Diffusing Wave Spectroscopy) to investigate the microstructure evolution (evaporation, packing, coalescence…) of a large panoply of materials at constant or increasing temperature (RT-250°C) and with humidity control.
This technology allows to detect the characteristic steps (Curing/drying time, phase transition…) with a very handy sampling protocol on any substrate and a very high sensitivity.

Figure: (left) Typical drying kinetics & identification of the characteristic steps/times, (right) Microscopic dynamics of polymer film vs temperature.



We offer a new **in-situ, non-invasive and handy** method to better understand–your different materials, allowing to:

- **Monitor** and **know** precisely the **curing** and **drying kinetics**
- **Determine the characteristic times** of the film forming process
- Analyse from room temperature **up to 250°C** with **humidity control**
- Evaluate the **impact of the formulation** and time and temperature parameters on the formation of materials
- **Optimize** the manufacturing protocol

P019

CHARACTERIZATION OF PHOTOLUMINESCENCE GARNET COATINGS DERIVED BY SOL-GEL SPIN/DIP COATING TECHNIQUES

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ABSTRACT:

Cerium doped yttrium aluminum (YAG:Ce) and lutetium aluminum garnets (LuAG:Ce) are one of the most popular materials used as scintillators. Scintillators are materials that absorb and convert high-energy radiation into light. The decay time in YAG:Ce and LuAG:Ce is about 60 ns, therefore an actual task would be to shorten this time as much as possible. For this reason, in this work, the garnets were doped with different amounts of boron ions. B^{3+} ion has a suitable neutron capture cross section and can therefore absorb gamma radiation. Due to the extremely strong absorption of thermal neutrons and the weak interaction with MeV gammas the material is an exciting new inorganic scintillator candidate for the detection of thermal and epithermal neutrons. B^{3+} stimulates and improves the absorption of such radiation [1,3].

In this study, 0.05 % cerium and different amounts of boron doped YAG and LuAG were synthesized on sapphire and quartz substrates using the dip-coating and spin-coating techniques. Boron and additional doping by magnesium are expected to improve required luminescent properties. Selected sol-gel method determines the homogeneity of compounds and low temperatures of the synthesis. Phosphor coatings were analyzed by XRD, AFM and SEM (**Fig. 1**). Emission, excitation spectra and decay times have been investigated as well. The main novelty and output of this research that boron does indeed shorten decay time, while also increasing emission intensity.

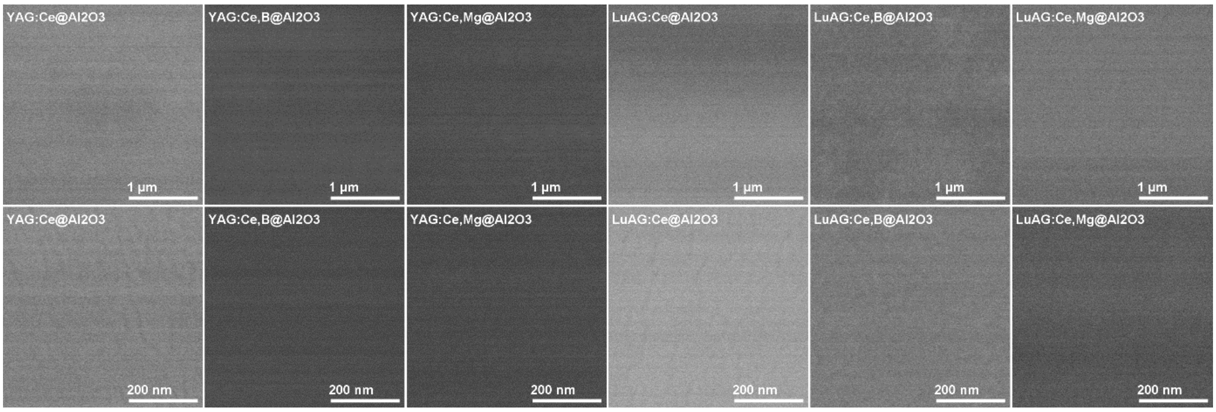

Figure 1 : SEM images of garnet coatings on sapphire (Al_2O_3) substrate using spin-coating technique.

Acknowledgements

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ADVANCED SOL-GEL IV-VI-DOPED INORGANIC THIN FILMS FOR TEMPERATURE SENSING INSTRUMENTATION

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ABSTRACT:

IV-VI quantum dots-doped SiO_2 and SiO_2-P_2O_5 thin films were prepared by sol-gel method, spin coating technique [1, 2, 3]. Different substrates were used for deposition such as glass, ITO (indium tin oxide) layered on glass and silicon, respectively [3]. Precursor composition, gelation time, substrate rotation speed, number of deposited layers and pH of the precursor sols were changed in order to regulate the hydrolysis and condensation mechanisms to accomplish uniform and homogeneous thin films [3]. H_3PO_4 and diethyl phosphate were used as precursors for P_2O_5 to explore their influence on the gelation time and deposition parameters [4]. Nanostructured materials were obtained by drying and subsequent annealing of the deposited films. The nanostructured network forming role of silicon dioxide and phosphorous pentoxide were evidenced by structural and morphological characterization of the deposited thin films [1, 4]. The optical band gap was graphically resolved in correlation with the size dependent quantum confinement effect, the latter being liable for the optical absorption cut-off and luminescence characteristics [2]. UV-VIS-NIR transmission spectroscopy, photoluminescence, luminescence decay and related measurements were also performed [2, 4]. Various excitation wavelengths were used aiming to choose the performing materials regarding the photoluminescence characteristics, showing the potential application of these nanostructured materials for temperature detection.

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P021

NANOSTRUCTURING THE SURFACE OF POROUS TITANIUM 3D STRUCTURES

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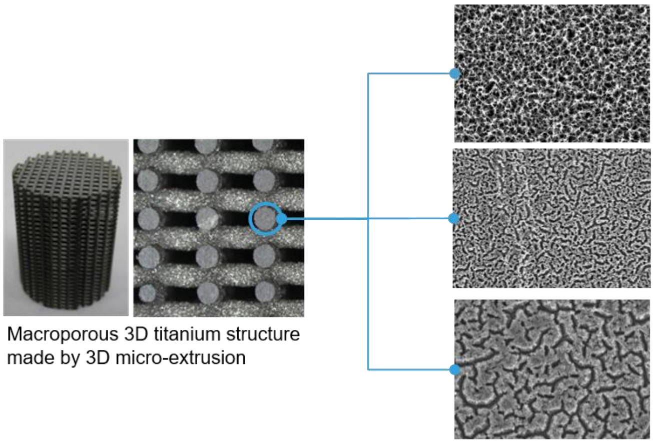
The main aim of the research is to apply nanostructuring approaches onto porous 3D micro-extruded titanium (Figure 1, left). Although often applied on flat surfaces, the knowledge to create surface controllable porous layers in/on these porous 3D materials is currently still lacking. Therefore, VITO and the university of Antwerp are exploring different strategies with different degrees of complexity and controllability.



Macroporous 3D titanium structure made by 3D micro-extrusion

Nanostructured surface obtained by different alkali conditions

Figure 1: Representation of a macroporous 3D structure (left) and the morphology of alkali treated titanium surfaces under different alkali conditions (right).

The major challenge is to provide sufficient control on layer thickness, porosity and chemistry while transferring a methodology mainly known from 2D surfaces (plates, fibers,…) to 3D porous structures. An established approach on flat surfaces is based on the reaction of an alkali solution with the titanium metal surface to form a porous layer of titanates (Figure 1, right), which can be further adapted by various post-treatments.[1,2] This state-of-the-art on nanostructuring describes either the synthesis of nanostructures [3] (as powders) or uses 2D supports [4] to modify the surface of e.g. flat sheets or beads. Transferring this knowledge to a macroporous 3D support with fine features sizes requires developments both on design of advanced experimental set-ups as well as on the nature of the applied chemistry. Also from an analytical point of view, major challenges must be overcome due to the extra complexity added by the 3D structure.

When successful, this will lead to a mechanically strong material, due to its titanium core, with a high control level on the macroporous architecture (thanks to the 3D micro-extrusion process) and very controlled and uniform nanostructured surface characteristics throughout the layer formed. These advanced functionalities will open new application domains. Depending on the results of control, uniformity and homogeneity of the nanostructured layer, different applications can be envisaged, including stationary phases for (preparatory) chromatography, photocatalytic microreactors and separation of metal ions including radionuclides.

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P022

Plasmonic oxide nanocrystals and derived sol-gel nanocomposite coatings for infrared optics and solar shielding applications.

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ABSTRACT:

Highly doped semiconductor nanocrystals are an emerging class of plasmonic materials changing the paradigm of LSPR (localized surface plasmon resonance) from a constant material property in metals to a highly modulable one through variable free carrier densities in semiconductors. Synthetic and post-synthetic control of the doping states in nanocrystals allows to tune the position and intensity of their LSPR bands across a wide optical range from visible to infrared regions [1]. We have developed synthetic routes to obtain cesium-doped tungsten oxide (Cs:WO_3) nanocrystals with controlled size and morphology thereby tuning precisely their LSPR spectra. As-prepared colloidal Cs:WO_3 nanocrystals display an LSPR strongly absorbing the near-infrared (NIR) part of the solar spectrum while maintaining high transparency in the visible range [2].

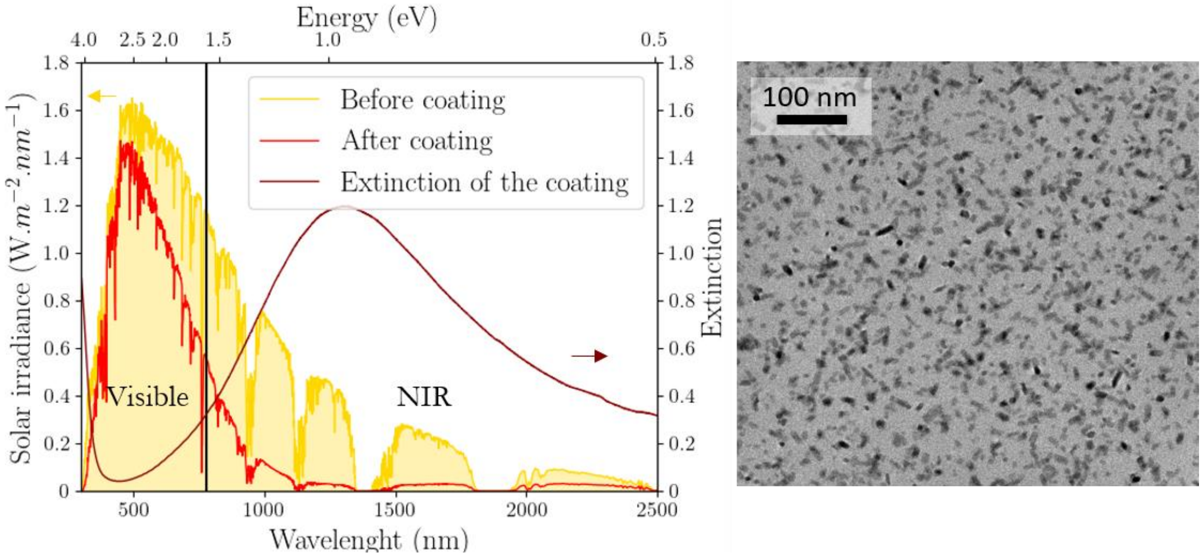

Figure 1 : Solar emission spectra beforeand afterpassing through a 7.1µm thick coating of Cs:WO3 particles in a silica matrix with its associated extinction spectrum and TEM image.

In order to efficiently use the NIR-selective LSPR of the Cs:WO_3 for solar shielding, a challenge is to incorporate them into a solid thin film structure without degradation of the LSPR. Indeed, the coupling effect of associating particles during typical coating process tends to redshift and dramatically decrease the LSPR intensity (65% loss). We present a solution to prevent this by embedding individually dispersed Cs:WO_3 nanocrystals in silicate matrices with a carefully chosen surface treatment to ensure a good compatibility and interactions with the silicate. The precise microstructure of the as-obtained composite films is shown by a 3D tomographic TEM analysis and guarantees its optical quality identical to that of the colloidal solution. A coated film with a thickness of 7.1µm and a particle density of 3.5 vol% absorbs 80% of the NIR part of solar irradiance while transmitting 74% of the visible. This high performance is promising for making windows reducing energy consumption in eco-buildings and greenhouses for agriculture.

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P023

Hydrophobic coatings based on sol-gel derived hybrid materials for self-cleaning applications

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In the past few years, self-cleaning and transparent surfaces based on hydrophobic behavior have been widely investigated for a variety of applications, such as glazing facades, solar panels, automotive glass, and safety goggles. Herein, to better understand the parameters governing hydrophobic coatings in order to control the surface wettability, a transparent hydrophobic surface with self-cleaning properties was prepared by Sol-Gel process.

In this work, high transparent and hydrophobic hybrid coatings deposited on glass substrate was achieved by hydrolysis/polycondensation reactions of Tetraethyl orthosilicate (TEOS) and polymethylhydrosiloxane (PMHS) precursors. The PMHS catalysed by NaOH was used as a hydrophobic agent and the polymeric silica obtained by formulation of TEOS in an acidic medium was used as a binder to improve the mechanical resistance of the coating. Several parameters influencing the properties of the deposited coatings were investigated, including the SiO_2 / PMHS molar ratio (ranging from 1 to 20), the concentration of PMHS (0.025, 0.01 and 0.05 M), heat treatment temperature (150 and 250 °C) and the effect of aging solutions over a 6-day period. FTIR, TGA, SEM, UV-Vis, Ellipsometry and contact angle (CA) are the principal characterization used in this work. The obtained results have revealed that the surface hydrophobicity is strongly influenced by the molar ratio and the aging solution. A CA greater than 140 ° were obtained with the molar ratio of 11.5. The transmittance values for all the nanocomposite films are between 87.39% and 93.93% compared to ordinary glass located at 90.88% which prove in excellent optical quality that does not deteriorate with solutions storage time. To demonstrate the self-cleaning effect, sand and carbon black were used as contaminants sources, the glass treated with hydrophobic coating exhibits a self-cleaning effect due to its hydrophobic behavior, which reduces the friction force between the water and the surface, allowing the droplets to roll along the surface more easily than on the hydrophilic surface, i.e. ordinary glass, which allows the water to wash away the dirt towards the edge of the substrate.

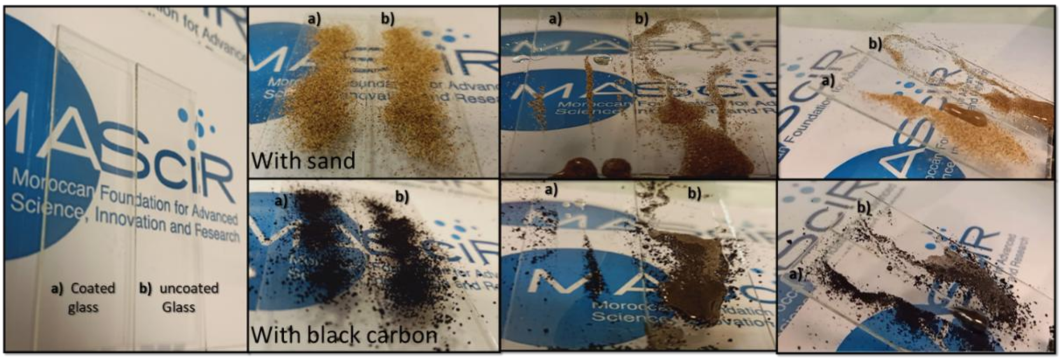

Figure 1. self-cleaning effect illustrated by sand and carbon black on (a) coated glass with SiO_2-PMHS nanocomposite and (b) ordinary glass.

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NANOSTRUCTURED TRANSPARENT HYDROPHOBIC COATINGS WITH FAST ROOM TEMPERATURE CURABILITY

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Photo Voltaic (PV) plants are exposed to the soiling phenomenon (the deposition on the panels of dust, sand, animal manure) which over time leads to a decrease in electrical efficiency and to an increase in maintenance costs.[1-3] To overcome these problems, several patents have been proposing nanostructured coatings with hydrophobicity, because this property is strictly linked to anti-soiling, but they have either durability problems or cannot be applied on site on PV field.

The present invention (patent pending) relates to a new family of innovative nanostructured coatings with the major advantage of (1) being curable at 25 °C within 120 seconds (thus allowing their direct deposition on PV field) and (2) being durable (tested on lab scale for more than 1,000 h in UVCON test and on PV panels). They are hydrophobic, transparent, resistant to UV-Vis and IR radiations (no yellowing or dulling), resilient to sharp variations in temperature and humidity, resistant to common cleaning products and operations. Their silicon-based hybrid organic inorganic sol-gel formulations are stable for months and are easy to handle (so that no specialised training is required); several techniques can be used to deposit them (they can be applied by spray, wipe, bar, dip, and slot-die coating). These nanostructured coatings are advanced materials with enhanced durable and hydrophobic properties which can boost the transition to the greener PV technologies both increasing the effective efficiency and reducing water costs (thus reducing environmental impact). The main foreseen application is indeed for photovoltaic panels, but they can also be applied to building glasses, automotive, marine. In fact, they have a wide compatibility not only with glass but also with metallic and ceramic surfaces.

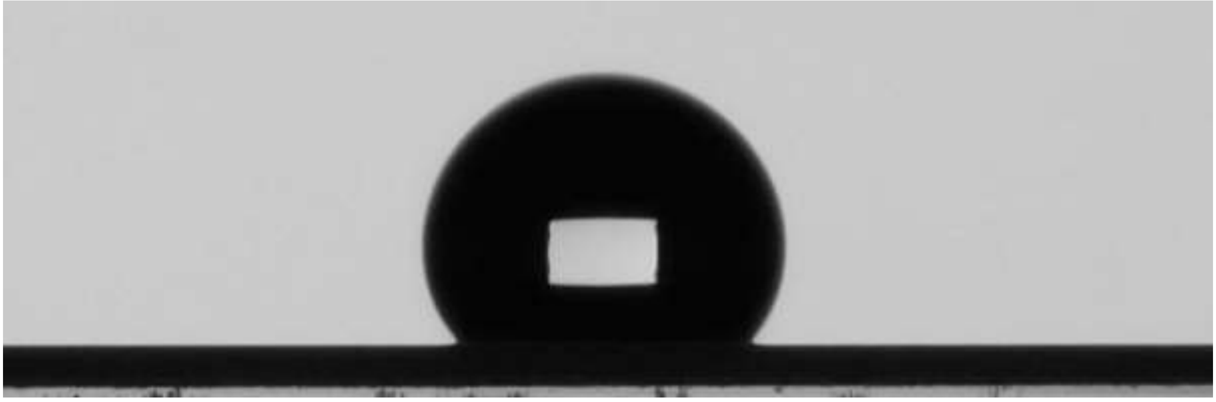

Figure 1 : Water Contact Angle of a coated glass sample.

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Smart hybrid sol-gel coating to induce active protective functioning for the plasma electrolytic oxidation (PEO) layer on AA2024

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Al2024 alloy has been attracted huge interest due to its favorable weight to strength ratio as a structural material for aerospace industries and its good mechanical properties due to the copper addition. The most common drawback of Al2024 is its vulnerability to the local corrosion phenomenon which is why a surface treatment is required to lengthen the lifetime and to enhance the corrosion protective properties of Al2024 alloy. Regarding, PEO as an eco-friendly and versatile procedure plays a significant role among the various methods of surface treatment for lightweight alloys. It can be compared to an anodizing process obtained at high voltage and associated with thermal diffusion of species, plasma reactions, and electrochemical reactions taking place at the electrodes. Due to the intrinsic porosity of the layers formed by the PEO process, the application of silane-based coatings as an eco-friendly layer is a promising way to diminish penetration of the corrosive species into the PEO coating by pores sealing. In this study, inhibitor modified sodium montmorillonite (Na-MMT) was added in a hybrid sol-gel solution based on tetraethoxysilane (TEOS) and 3-glycidoxypropyltrimethoxysilane (GPTMS) with 30% V/V concentration to achieve dual-functional sol-gel coating with self-healing/barrier anti-corrosion performance. Electrochemical impedance spectroscopy (EIS) results reported the huge impact of the sealing ability of the sol-gel system for the PEO layer in 0.1M NaCl solution especially for the solgel coatings modified with clay/inhibitors nanoparticles. The morphology and the duplex coating structure were highlighted by using a scanning electron microscope (SEM). To this end, scanning vibrating electrode technique (SVET) outcomes reflected the self-healing ability of the coatings modified with clay/inhibitor nanoparticles. The lamellar structure of clay nanoparticles not only increased the barrier performance but also being as reservoirs provided the controllable leaching of the active specimens to attain a long-lasting protective system.

Keywords: *Plasma electrolytic oxidation (PEO); Sol-gel coating; AA2024; EIS; Clay.*

“This project was performed in the framework of SEALCERA ARC project.”

P026

INSULATING COATINGS OF WINDING WIRES FOR HIGH TEMPERATURE APPLICATIONS

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Electrical machines (electric motors, generators, and electromagnets) for aerospace applications and nuclear reactors are closer to energy sources and need to function at high temperatures. The temperature of the electrical machines can be increased up to the Curie point of the core materials, the temperature of 630 ℃. However, the operating temperature of the winding wires is limited by the decomposition of polymers used for the insulating wires. Most heat-resistant polymer insulation is capable of withstanding temperatures up to 300 ℃.

The objective of the work is to develop an isolating material and a coating process that the winding wire will be suitable to resist the temperature decomposition up to the Curie point temperature or melting point used for winding wires.

This problem can be solved by using inorganic materials like silicon dioxide (SiO2) with a melting point of 1600 °C. However, silicon dioxide is a very hard and brittle material. In connection with this, primary insulation must be flexible. However, after some heat-treating, it should become hard, dense, and strong. After that, it must withstand high temperatures and be resistant to electrical breakdown.

This scheme may be implemented within the sol-gel process. Earlier, we used similar processes to create composite materials for aerospace and rocket technology [1]. However, several technological approaches may be used.

The coating consists of soluble organic silicates. These compounds are similar to alkali metal silicates in their properties. In addition, they do not contain in their composition alkali metals, which reduce the melting point of silicates. Above a certain temperature, organic silicates are decomposed to form silica SiO_2 and volatile compounds.

Soluble organic silicates can have the viscosity necessary for coating the metal wire. After drying, the coating is obtained, which can withstand a certain bending force. It is sufficient for winding induction coils' predetermined shape and size. Finished coils are thermally treated as finished products. Then, it is possible to carry out additional impregnation of finished coils with organic silicate. This impregnation allows increasing the thickness of the coating further, reducing the voids between the turns of the wire, and healing defects on the surface of the wire. After that, secondary heat treatment is necessary to carry out for the final fixation of silica coating.

To create a coating on the surface of the wire, you can use the equipment used to apply a protective coating to the surface of the fibres in the manufacture of composites.

Also, for these purposes, a variant of acid or alkaline hydrolysis of silicon alkoxides can be used. This variant sol-gel process allows forming a three-dimensional polymer network. Carrying out controlled hydrolysis of silicon alkoxides, we get products that are precursors to silica coatings.

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ENHANCING THE REGULATION OF INDOOR HUMIDITY OF CLAY PLASTER THROUGH TITANIUM OXIDE-BASED SOL-GEL COATINGS

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This is a pioneering study in which sol-gel technology has been used to enhance the hygrothermal properties of clay-based plasters at the nano level. Clay-based construction materials, due to their porous nature, inherently behave as passive relative humidity regulators. However, clay's uncontrolled high affinity to water can be detrimental to its own durability. The latter is usually dealt with by applying a finishing material (paint), however, it reduces the vapor permeability of the clay-based plastered walls. In this study, commercially available topcoat clay plasters were coated with sol-gel-based titanium oxides (TiO_2). The TiO_2 coatings altered the clay plaster's breathability by tailoring the pore structure of plaster-TiO_2 coating without compromising on durability. The pore structure of the TiO_2 coating was manipulated by varying two synthesis parameters, i) Triton X-100 surfactant dosage and ii) synthesis temperature. The surfactant/TiO_2 was varied from 1 to 3 and two synthesis temperatures were used 260°C and 360°C. The TiO_2 was spin-coated on the clay plaster samples. The moisture transport was investigated of the various formulations of the TiO_2 coating using Dynamic Vapor Sorption (DVS). It was noticed that TiO_2 coatings were able to alter the clay plaster's breathability by tailoring the clay plaster pore structure. The TiO_2 coatings did not show signs of cracking or peeling, demonstrating good adherence and compatibility between coating and substrate. The sol-gel TiO_2 coating developed in this study delivered controlled hygrothermal behavior in clay plaster systems, this will thus reduce the overall energy consumption of buildings and help to maintain a healthy indoor environment.

Preventing The Toxicity Of ZnS:Mn Quantum Dots In Aquatic Media, Using The Sol-gel Technology

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[†] In memory of Roberta Brayner (2021), who initiated this research work.

ZnS quantum dots (QDs) find applications in many fields: e.g. biolabels[1], multicolors displays[2], due to their additional physico-chemical properties, especially when they are doped with paramagnetic metal cations, like Mn^{2+}. However, the toxicity of such NPs remains little explored, they may have some uncontrolled toxicological effects on the living microorganisms after they are disposed in the environment, such as water, soil and sediments. So, the idea is to coat these nanocrystals with a silica shell using sol-gel chemistry, made by hydrolysis and condensation of selected silane precursors, as a protective barrier to prevent the toxicity of the NPs, while maintaining their physical properties (optical and magnetic).

In our work, the ZnS:Mn QDs were produced by *chimie douce*, using the polyol method; the NPs are blende cubic single crystals of 6-7 nm in size. Hydrolysis and condensation reaction of tetraethoxysilane (TEOS) precursor were then performed in presence of the particles operating in reverse microemulsion. The resulting composite particles were found to be of the embedded morphology for a total diameter of about 40 nm. Photosynthetic assays performed on selected microalgae, ie. Chlorella Vulgaris, showed that the particles are non-toxic even for high doses and long contact times, confirming our hypothesis and highlighting the interest of the sol-gel process to produce protective barriers to inhibit the toxicity of QDs.

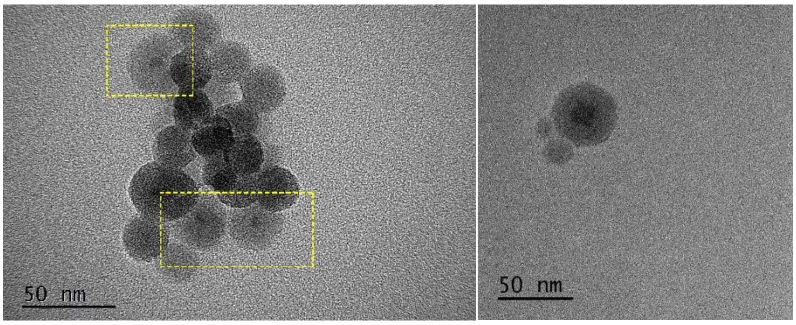

Figure 1 : TEM image of 10%Mn-ZnS@SiO_2

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P029

Low ICR coating for fuel cell electrodes

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In an effort to limit the temperature rise of about 1.5°C by 2050, governments and private companies are looking for less carbon dioxide emitting technologies. Replacing fossil energy means developing renewable power generation technologies like wind turbines or solar collectors. Preferably, this energy should be stored either in batteries or as dihydrogen thanks to electrolysers. In the transportation sector, electric cars are already on the market but battery weight limits efficiency. Hydrogen storage and distribution is an issue but once solved, with fuel cell technology, the power generation is compact and light. Our present development aims to simplify the electrode production by applying on a roll-to-roll process with roll-coating or spraying techniques a conductive coating with low interfacial resistance and corrosion protection for the metallic substrate. This coated metal strip will further be cut and formed to the desired size and patterned with the optimised gas channel profile. Different lab test methods were created or adapted and important know-how was generated in that field of fuel cell characterisation.

Figure 1 : Title 1

References

INFLUENCE OF NON-HYDROLYZING ORGANIC GROUPS ON MECHANICAL PROPERTIES OF SILICA SOL-GEL COATINGS.

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The surface properties of materials can be modified by applying coatings with specific properties. One of the methods allowing to obtain easily modifiable thin films is the sol-gel method. The sol-gel coatings can be modified by introducing non-hydrolyzing groups into the matrix. These groups affect the functionality and integrity of the layers. They also condition the fulfillment of other functions by these thin films, i.e. anti-corrosive, hydrophobic, antibacterial, etc. The layers should be without cracks and delamination. It is important because cracks and delamination result in the propagation of element degradation. Therefore, it is necessary to know the influence of modifying groups on the mechanical properties of the thin films. Non-hydrolyzing groups significantly change such mechanical properties of coatings as hardness, adhesion to the substrate or wear resistance [1,2]. Used the organics moieties changes the wear mechanism of the layers [3]. It was decided to check the influence of small and large in size non-hydrolyzing groups on the mechanical properties of silica sol-gel coatings, as they are one of the most commonly used sol-gel films. In order to synthesis the layers the following precursors were used: TEOS, dMdES, GPTMS and APTES. Such precursors are good representatives to show the influence of the oxide structure on the mechanical properties – the key factor is the different sizes of the organic substituent. The coatings were applied with the dip-coating method. The influence of substituents on the hardness, Young's modulus, friction coefficient, adhesions and the wear mechanism of the coatings was investigated. The scope of the influence of organic substituents on the mechanical properties was demonstrated.

The research was supported by the National Science Centre, Poland under the OPUS + LAP project ‘Research on the influence of self-healing, organic-inorganic sol-gel layers on the corrosion resistance and fatigue of steel in the VHCF range’ UMO-2020/39/I/ST5/03493

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Influence of mechanical factors on the continuity of sol-gel coatings

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The sol-gel method is commonly used to obtain thin protective coatings due to its ability to control physical parameters and the high purity of the materials obtained. Due to their chemical composition, sol-gel coatings can be divided into organic, inorganic, and hybrid. Depending on the chemical composition, the coatings have different mechanical properties and have different types of defects. Coatings containing organic moieties are usually more flexible. The greater flexibility of the thin coating reduces the risk of cracking, but may favor the appearance of delamination. In contrast, inorganic coatings are hard and brittle and therefore prone to cracking. Defects of coating mean that it no longer protects the surface of the substrate, does not fulfill additional functions, and may look unsightly.

Re-coating is an additional cost, and discontinuity situations lead to premature wear or deterioration of the substrate. For this reason, the industry has been struggling with the problem of the formation of defects in thin coatings for several decades. The difficulty in determining the cause of defects is related to the complex nature of stress formation mechanisms in the coating and poorly understood material properties.

The work compares hybrid coatings with an increasing share of the organic part and subjected them to mechanical tests to determine the influence of the organic part on the formation of defects under the influence of various external factors.

HIGHLY FLEXIBLE SiO_2-TiO_2 COATINGS FOR PHOTONIC APPLICATIONS – THE SYNTHESIS PARAMETERS AND PROPERTIES DEPENDENCIES

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Sol-gel oxide materials can find plenty of applications in different fields thanks to the versatility of controllable properties, dependent on a variety of synthesis and processing parameters. In photonics, such materials are successfully applied, both in form of pure and mixed oxides. However, the classical oxide materials are rigid and fragile. Thus, to follow the most current trends in photonics, there is a need to receive functional structures, which are flexible and can be bent without deterioration of their properties. One of the approaches to make oxide materials more flexible is using them in form of very thin films. However, for high flexibility, it can be insufficient. A possible way to make such coatings even more flexible is a modification of their structure with organic groups, which strongly increases the flexibility of the oxide network and hence of the final material. Notwithstanding, another obstacle to overcome is the rigidity of the most common substrates for optical coatings. To provide the coating-substrate system, which is flexible, the substrate also has to be elastic. Currently available transparent flexible substrates are polymers and flexible glasses, but both are characterized by reduced thermal stability. Due to that fact, coatings applied on these materials require appropriate thermal treatment strategies, which highly influence the received materials' structure. In this work, we focus on optical properties and mechanical resistance of the organically modified hybrid silica-titania coatings, with particular emphasis on their relationship with synthesis and processing parameters. The obtained results show the potential for the application of SiO_2-TiO_2 organically modified coatings on flexible substrates. Coatings were obtained by sol-gel method, with low-temperature treatment imposed by the flexible substrates' stability.

This research is performed in the framework of the projects Polish National Agency for Academic Exchange (NAWA) grant no. PPN/IWA/2018/1/00104 and CNR-PAS "Flexible Photonics" (2020-2021).

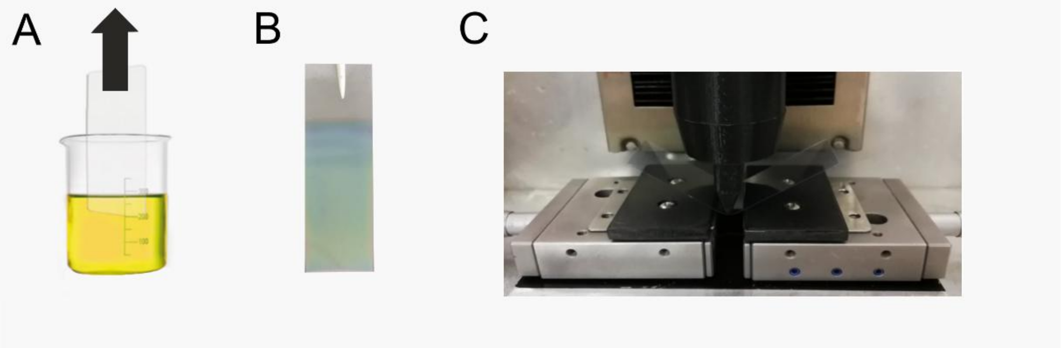

Figure 1. Illustrative representation of (A) deposition method (B) received multilayered SiO_2-TiO_2 organically modified coating (C) sample bending

P033

SOL-GEL SILICA COATING OF PHOSPHORESCENT NANOPARTICLES

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The applications of functional nanoparticles often depend on them having properties different to the bulk or being deliverable in environments where larger particles are disadvantageous. Hence the functionality of nanoparticles can be protected by coating their surfaces. A silica coating has advantages of being biologically benign, water-resistant, durable, amorphous, and not inhibiting functionalities, e.g. it is transparent. In the field of luminescent materials, $SrAl_2O_4:Eu^{2+},Dy^{3+}$ is recognised for its persistent phosphorescence [1]. This makes possible the use of nanoparticles to deliver phosphorescence into microscopic (e.g. biological) environments. However, the phosphorescence is susceptible to degradation by hydrolysis and oxidation, and this is more detrimental for nanoparticles. Hence, there is the goal to overcome this limitation via silica coating [2]. The sol-gel technique is indeed adaptable to the coating of nanoparticles [3]. There have been limited previous reports of sol-gel coating of $SrAl_2O_4:Eu^{2+},Dy^{3+}$ particles, with sizes ranging from 100s nm to microns. This presentation reports new work on sol-gel silica coating of sub-100 nm $SrAl_2O_4:Eu^{2+},Dy^{3+}$ nanoparticles. The work has involved preparing nanoparticles by combustion synthesis and applying silica coatings by sol-gel methods. The coated nanoparticles have been characterised using x-ray diffraction, electron microscopy and fluorimetry to establish the effect of coating on the structure and phosphorescence.

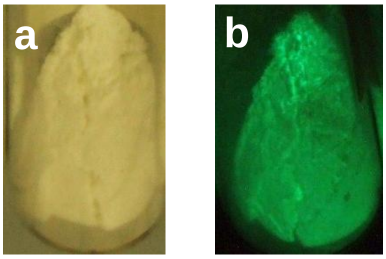

Figure 1 : (a) $SrAl_2O_4:Eu^{2+},Dy^{3+}$ nanoparticles, and (b) phosphorescence in the dark.

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Resuspensible titanium xerogel for optical application

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Titanium dioxide possesses the high photocatalytic and optical activity (high refractive index) which could change the properties in regard of the particles size and crystal face.

Hereby we obtain the new synthesis of titanium nanoparticles based on aqueous and aqua-alcohol solutions which approved sol-gel transition in the presents of peptizing agent. This technology provides the low-temperature sol-gel synthesis of titanium nanoparticles near room temperature (60°C). In contrast with other methods described in the literature[1,2]. We synthesized the titanium xerogel by drying under vacuum in low temperature with control drying rate. The final compound was approved the following characteristics: Z-potential (30 mV), average particle size (64 nm), X-ray phase analysis and others.

The functionality of the xerogel was estimated by holographic application the resuspension properties of titanium xerogel was achieved in the aqua-alcohol solution (80 g/l) and then coated their surface of rainbow (microembossed) holograms with the high reflective index properties. At the end we achieved the high holographical effect in the masked and patterned zones and high adhesion properties of titanium nanoparticles.

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P035

COMPARING DIFFERENT SOL-GEL ROUTES TO YTTRIA-STABILISED ZIRCONIA THERMAL BARRIER COATINGS

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In the present work a comparison is reported among three different sol-gel routes to produce thermal barrier coatings (TBCs). As of today, TBCs are industrially produced via Electron Beam Physical Vapour Deposition (EB-PVD) or Air Plasma Spray (APS) but new techniques, such as sol-gel, are being investigated at lab-scale. These techniques could potentially have some advantages for coating complex geometries, i.e. hot gas path components in gas turbines, compared to the traditional line of-sight techniques, and be more cost effective.

Sol-gel technique can produce TBCs by coating the substrate in the desired colloidal solution (sol) comprising the desired TBC or its precursors. The sol can be prepared via three routes:

a) by dispersing nanopowders (e.g. Yttria Stabilised Zirconia, YSZ) in a solvent[1];
b) by reacting metal alkoxides (e.g. $[Zr(OPr)_4]$) in alcoholic medium[2];
c) by combining route (a) and route (b)[3].

In order to compare them, YSZ sols were prepared (1) via aqueous slurry, (2) alcoholic slurry, (3) metal-organic route, and (4) a combination of the latter two (alcoholic slurry plus metal-organic route). YSZ sols were then deposited via dip-coating on steel substrates and nickel-based superalloy substrates. The samples were thermally treated and characterised via SEM-EDS (Figure 1) to analyse the microstructure.

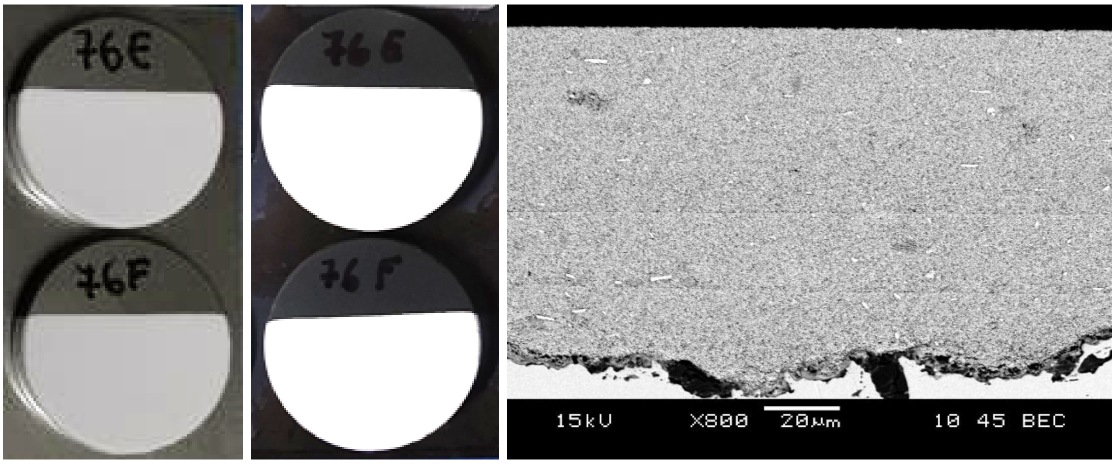

Figure 1 : Nickel-based superalloy disks coated with YSZ aqueous sol: (left) before and (middle) after thermal treatment; (right) SEM characterisation of the coating.

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P036

Transparent inorganic-organic hard films from 3-glycidoxypropyltrimethoxysilane and zirconium propoxide

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The surface of tiles and sanitary ware is covered with glassy and transparent glaze films. The sol-gel method can be used to fabricate the films at lower temperatures than conventional methods, and thus it can reduce the energy to make glassy films. However, the preparation of films with large thicknesses is challenging because of cracks formed by shrinkage during heat treatment.

In the present study, 3-glycidoxypropyltrimethoxysilane (GPTMS) and zirconium propoxide were used to prepare transparent thick GPTMS-ZrO_2 films with high hardness, durability, and gloss at low temperatures. Precursor sol was prepared by hydrolyzing GPTMS under acidic conditions, and then zirconium(IV) n-propoxide stabilized with acetylacetone was added to the sol. Thick films were prepared by dip-coating or casting the precursor sol onto a substrate and heating.

Thick films with a thickness of more than 100 μm without cracks were obtained by casting the precursor sol onto a glass substrate. Figure 1 shows the relationship between the thickness, heating temperature, and the pencil hardness of the GPTMS-ZrO_2 films. The pencil hardness of the films increased with an increase in the heating temperature. This increase must be because of the development of the inorganic network by heating. The thick films with up to 60 μm thickness showed the highest pencil hardness of 9H with heat treatment at 100 °C.

The present study was supported by JST A-STEP.

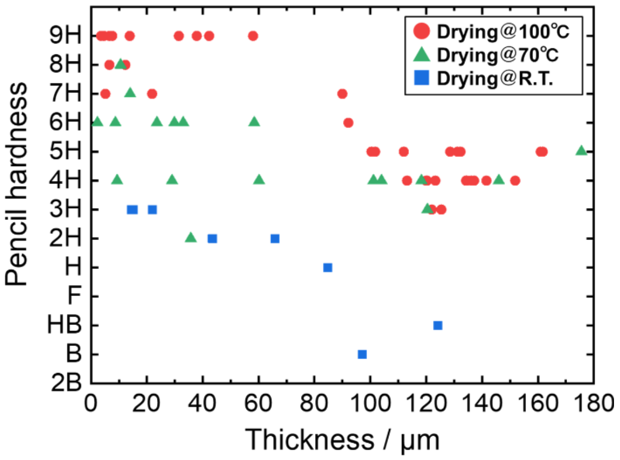

Figure1. Pencil hardness of GPTMS-ZrO_2 thick films on glass substrates.

P037

HIGH TEMPERATURE OXYGEN BARRIER TO PRESERVE TITANIUM ALLOYS USED IN AERONAUTICS

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Since 30 years, the aeronautic industry has been intensifying its efforts to continuously reduce the polluting emissions of aircraft engines. One approach is the increasing of operating temperatures of the turboreactor to enhance its performances and reduce fuel consumption as well as CO_2 emissions.

In that context, our study aims to increase the operating limit temperatures of specific titanium-based alloys parts of the reactor to a temperature over 500°C and to increase their lifetime. To do this, it is necessary to reduce the oxidation of the alloy at high temperatures. Actually, the oxygen diffusion in the titanium structure drastically decreases its macroscopic mechanical properties and especially the material ductility due to the formation of an oxide coating on its surface, named α-case, which is extremely brittle [1]. The technological issue of our research is to design multifunctional coatings to reduce those phenomena and increase the lifetime of the metal pieces in operating.

Our strategy to get protective coatings is based on the sol-gel chemistry and more specifically on the design of a mixed oxide-based coating. Actually, this process is highly versatile and allows, under certain conditions, to produce dense coatings (to stop the oxygen diffusion) displaying tenacity (to reduce its fragility during oxidation cycles). The influence of the composition and synthesis parameters on the substrate oxidation are studied. Then, the validation of each system is done by realizing various characterizations (mechanical properties, topography, etc..) and in particular by monitoring the mass gain of the sample in relation to the penetration of oxygen into the substrate (figure 1).

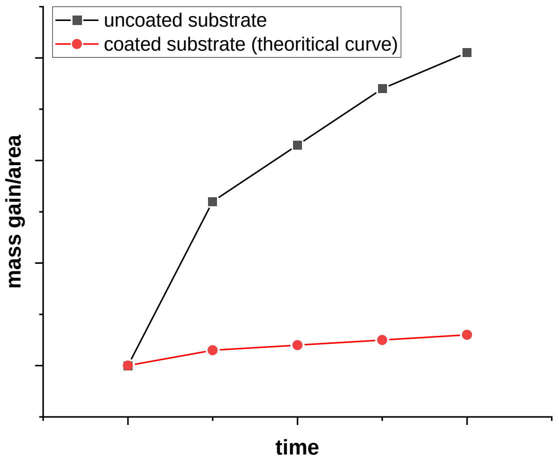

Figure 1 – Mass gain normed by the surface in function of the oxidation time of a coated substrate and an uncoated substrate

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Main Menu

Functional organic-inorganic hybrid materials

REMOVAL OF ARSENIC (III, V) FROM AQUEOUS SOLUTION BY IRON OXIDE COATED CTAB

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In the present work, synthetic nanoscale iron oxide stabilized with cetyltrimethylammonium bromide (CTAB) was examined for ability in removing of arsenic from aqueous solutions. Iron oxide such as magnetite and maghemite are the most promising iron nanoparticles for arsenic removal.

The crystal structure and phase purity of the synthesized CTAB coated iron oxide (IO-CTAB) composite were examined by XRD analysis. The calculated value of lattice parameter of IO-CTAB is in agreement with the previously reported value [1]. The average crystal size of IO-CTAB was 17.26 ± 3 nm. No obvious XRD peaks corresponding to other phases were found in the XRD model of the analysed sample, which shows a good purity of the IO-CTAB prepared sample. The shape and morphology of IO-CTAB was examined by TEM and SEM analysis. The TEM analysis demonstrated that the sample was composed of a number of nanoparticles with spherical shapes. The observed IO-CTAB nanoparticles had the sizes between 10 and 25 nm. The mean particle size was 19.86 ±1.7 nm which is in accordance with the result achieved from the XRD analysis.

The efficiency of the IO-CTAB nanoparticles in the removal of arsenic ions from aqueous solutions was investigated using flame atomic absorption spectroscopy. The best removal efficiency of As (III) from aqueous solutions using IO-CTAB nanoparticles was obtained for pH 5. These results are in good agreement with studies regarding the „applications of CTAB modified magnetic nanoparticles for removal of chromium (VI) from contaminated water" conducted by Elfeky et al [2]. The XPS analysis showed that during the adsorption process As (III) can be oxidized simultaneously to As(V) which has contributed to the decrease of arsenic toxicity. The data determined using the Langmuir and Freundlich models emphasized that IO-CTAB nanoparticles were favourable for the adsorption of As (III) ions from aqueous solutions.

Acknowledgments: This work was supported by the Romanian Ministry of Research and Innovation through the project PN-III-P2-2.1-PED-2019-0868 contract no. 467PED ⁄ 2020 and project PN-III-P2-2.1-PED-2019-1375 contract no. 331/PED/2020.

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P039

HYBRYD FIELD EFFECT TRANSISTOR (HFET) : A FULLY COVALENT TRANSISTOR WITH A PI-CONJUGATED ORGANOSILICA

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Here we demonstrate the use of novel organosilica materials embedding π-conjugated moieties as semiconductor into field effect transistors. The π-conjugated core chosen is [1]benzothieno[3,2-b][1]benzothiophene (BTBT),[1] first functionalized with hydroxyl groups[2] and then modified with hydrolysable and cross-linkable triethoxysilyl moieties. After polycondensation, this compound forms a hybrid material composed of charge transport pathways as well as insulating layers (SiOx). However, overall, the material is found to be a semiconductor and can be incorporated into field effect transistors. Taking advantage of the solgel chemistry[3] involved here, we built Hybrid Field Effect Transistors that are fully cross-linked with covalent bonds.[4] Molecules are cross-linked to each other, covalently bonded to the silicon oxide dielectric and also covalently bonded to the gold electrode thanks to the use of an appropriate additional interfacial monolayer in between. This is the first report of fully covalent transistors. Those devices show impressive resilience against polar, aliphatic and aromatics solvents (even under sonication). This study opens the route towards a new class of hybrid materials to create highly robust electronic applications.

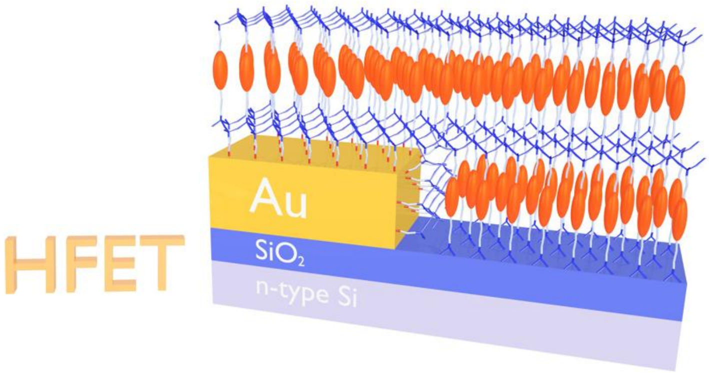

Figure 1: Hybrid Field Effect Transistors (HFET), First example of a field effect transistor based on an entirely reticulated organosilica active layer.

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P040

FUNCTIONAL BLOCK COPOLYMERS FOR *IN-SITU* FUNCTIONALIZATION OF MESOPOROUS SILICA FILMS

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Nature provides the ultimate inspiration – able to direct, gate and selectively transport through pores and channels with technologically unreached performance. To approach this performance, the precision in nanoporous material design has to be significantly improved. For example, material architecture and structural as well as functional hierarchy have to be precisely designed. To do so nanoscale layer-wise material build up, e.g. using printing techniques for nanoporous structure formation in combination with *in-situ* functionalization approaches, is envisioned to allow precise structural and functional hierarchy design at the nanoscale.

Specifically, stimuli-responsive mesoporous silica films were prepared by evaporation-induced self-assembly through physical entrapment of functional block copolymers as structure directing agent, which simultaneously serve as functionalization of the mesopores. By this way highly filled pores with e.g. PS-*b*-PAA that exhibit remarkable gating ionic permselectivity with changes in pH[1], enabling the switching between cation- and anion-selectivity under basic and acid conditions, were achieved. Stimuli-responsive transport characteristic can also be observed in partly filled pores. Different examples of functional templates for *in-situ* functionalization and the resulting ionic permselectivity will be presented. Mesoporous films are characterized regarding their porosity and film thickness using ellipsometry, TEM and SEM. Ionic permselectivity is determined using cyclic voltammetry and correlated to porous structure and *in-situ* functionalization. Using functional templates for *in-situ* functionalization of mesoporous layers bears the potential for localized stimuli-responsive polymer functionalization within a precisely designed architecture[2] and fabrication of *in-situ* functionalized porous silica films by high throughput printing methods[3]. This direct and simple approach of *in-situ* functionalization of mesoporous silica using functional block copolymers is expected to be highly relevant for a variety of technologies based on molecular transport in nanoscale pores, such as sensing, separation, catalysis and energy conversion.

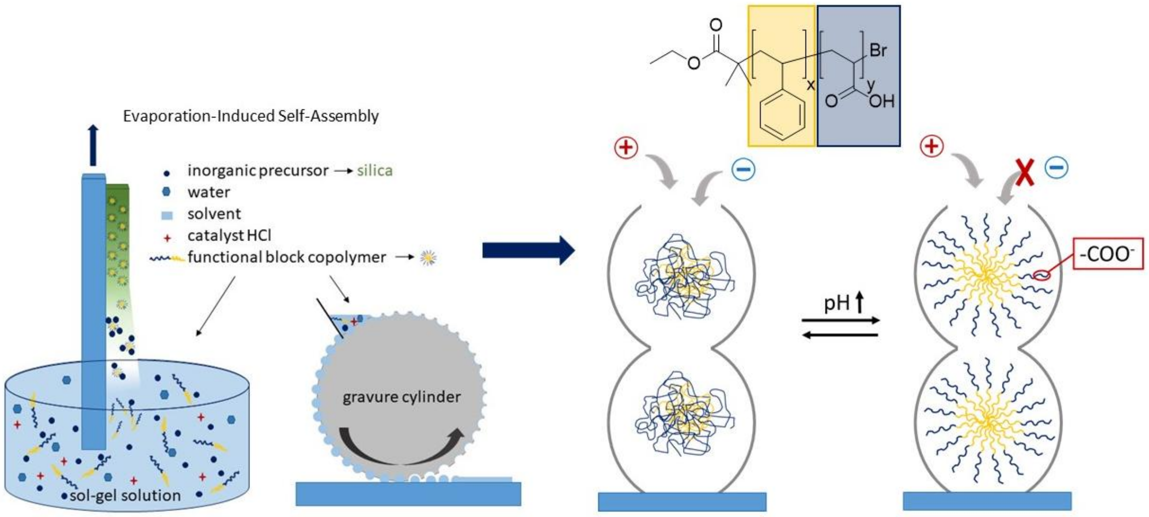

Figure 1 : Stimuli-responsive mesoporous silica thin films prepared in an one step procedure by Evaporation-Induced Self-Assembly (EISA) have achieved tunable ionic permselectivity, thereby demonstrating their high potential for developing multifunctional, complex architectures with to date unreached transport performances.

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P041

CREATING A NANOCOMPOSITE BASED ON ENCAPSULATED HEMIN IN ZIF-8 AND TITANIUM DIOXIDE NANOTUBES

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Tissue regeneration *in situ* is one of the main tasks of functional materials science, aimed at restoring functional and anatomical properties after traumatic, infectious, or degenerative diseases. New therapeutic approaches include the use of advanced medical devices for the controlled delivery of bioactive molecules or growth factors to the affected area. [1] In this study, an alternative method of biocomponents localization is proposed to recover the structural integrity of the integuments.

This approach involves the production of nanotubes consisting of titanium dioxide and capable of self-ordering on titanium substrates by electrochemical anodizing. They can be easily integrated into current titanium implant technology having improved bioactivity, mechanics, and surface modification compared to conventional analogs. [2] Doping the nanotubes with Er^{3+} ions makes it possible to obtain up-conversion properties ($^2H_{11/2}\rightarrow{}^4I_{15/2}$ with a maximum of 520 nm, $^4S_{3/2}\rightarrow{}^4I_{15/2}$ with a maximum of 550 nm, and $^4F_{9/2}\rightarrow{}^4I_{15/2}$ with a maximum of 670 nm) when they are illuminated by IR-light. The penetrating power of IR-rays is higher than that of UV-rays [3], which makes it possible to use the nanocomposite in different focal points of the organism. The application of the process of converting electromagnetic radiation with an increase in the energy level of the system optimizes the photocatalytic characteristics of traditional UV-active photocatalysts. [4] UV-radiation promotes proton generation due to the fact that the photoinduced "holes" firstly reach the water molecules and interact with them. The zeolite imidazolate framework (ZIF-8) used for growth factor encapsulation is capable of decomposing in an acidic environment, which makes it attractive for targeted delivery of bioactive components, for encapsulation, transport, and selective pH-mediated release. [5] The exarticulation of gemin into the biological environment during the metal-organic framework destruction leads to the division and reproduction of living cells, as well as to their further proliferation.

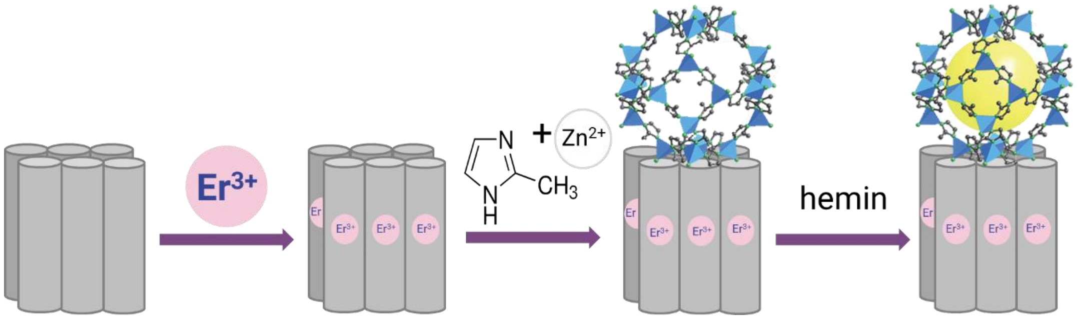

Figure 1 : The scheme of the project

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SIZE-TUNING OF HOLLOW PERIODIC MESOPOROUS ORGANOSILICA NANOPARTICLES (HPMO-NPs) FOR THERANOSTIC APPLICATIONS

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During the past two decades, much work has been devoted to the development of mesoporous organosilica nanoparticles (MO-Nps) for application in bioimaging and drug loading/delivery. The mesopores, obtained with a surfactant (soft template route, STR), is a key parameter as they allow high drug loading. MO-Nps are formed by grafting method and by co-condensation of organosilanes with TEOS. The sol-gel hydrolysis of organo-bridged silanes gives TEOS-free hybrids called Bridged silsesquioxanes (BS) (Fig. 1, Top). Using the STR, hybrid called PMO (Periodic Mesoporous Organosilica) with interesting high organic content can be formed and PMO-Nps with hierarchical structures can be designed.[1]

Recently mesoporous hybrid silica Nps with variable structures have been reported (Core/shell and Yolk/shell, etc)[2] and PMO-Nps turned out to be a promising platform for several applications. We are interested in designing such multifunctional nanoplatforms for theranostic applications. Our work is focused on the synthesis of Hollow PMO Nps (HPMO-NPs) with a controlled core cavity and a PMO shell. To engineer these porosities, we used subsequently two templating routes: (1) spherical silica as hard template to form the core cavity and (2) CTAB as soft template and BTEB (1,4-Bis-triethoxysilylbenzene) to achieve the mesoporous shell (Fig. 1, Bottom). Na_2CO_3 and HCl are used to successively deliver the two kinds of porosity. Core silica with fixed diameters allow to control HPMO-NPs sizes and also the core cavity. An extension to multi-shell HPMO-NPs will also be presented

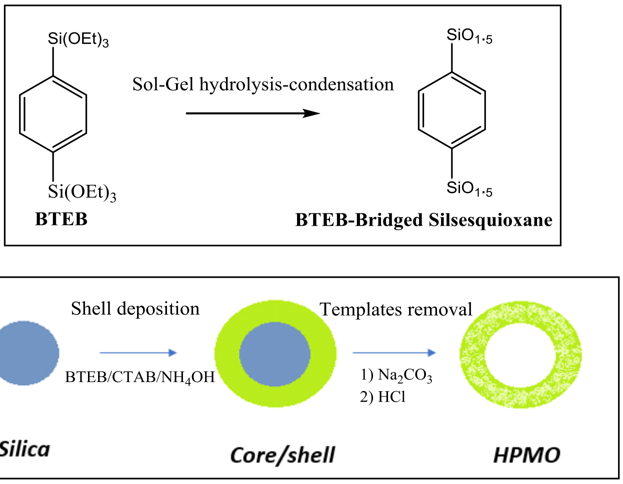

Figure 1: Synthesis of BS and HPMO-Nps

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FABRICATION OF LEDS USING SOLUTION-PROCESSED ORGANIC-INORGANIC HYBRID MATERIALS BASED ON THIOL-EN REACTION

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Recently, organic-inorganic hybrid thin films by radical polymerization of an organic emissive material having a vinyl group and a vinyl silane coupling agent were fabricated, in which organic emissive materials are surrounded by SiO_2.[1] Due to the sealing effect, photoluminescence (PL) lifetime was improved. However, it was difficult to prepare uniform thin films because the peroxide used was highly active but forms carboxylic acid as a by-product. In this study, chemical bond based on the thiol-ene reaction was introduced for preparing organic-inorganic hybrid materials to improve compatibility between organic and inorganic materials. Finally, the prepared organic-inorganic hybrid materials were applied to active layers in light-emitting diodes (LEDs).

For fabricating organic-inorganic emissive hybrid solution, the following three materials were mixed in ethanol; 4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran (DCM) was used as an emissive polymer, (3-mercaptopropyl) trimethoxysilane (MPS) was used as a silane coupling agent with thiol group, and 2-Benzoyl-2-propanol was used as a photo radical initiator. The solution was irradiated by UV light to generate thiol-ene reaction. Due to Fourier-transform infrared spectroscopy (FT-IR), we found that the thiol-ene reaction was completed in 10 minutes.

For fabricating LEDs, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) was used as the hole injection layer (HIL) on an indium-tin-oxide (ITO)-coated glass substrate. In addition, poly(9-vinylcarbazole) (PVK) was used as the hole transport layer (HTL). The hybrid thin film was fabricated on HTL, in which Alq3 was added as a host material. Consequently, electroluminescence (EL) emissions were successfully observed. In particular, the lifetime of the LEDs containing the hybrid active layer was drastically improved. This result clearly demonstrated that the organic-inorganic hybrid active layer is effective for improving the organic LED's (OLEDs) operating lifetime.

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ORGANIC, INORGANIC AND HYBRID MATERIALS OBTAINED BY THE SOL-GEL PROCESS AND MICROWAVE HEATING

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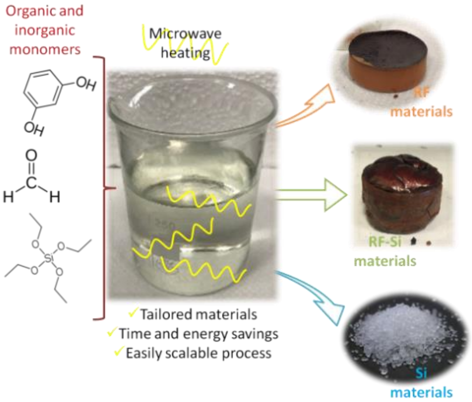
ABSTRACT:

The sol-gel process is one of the most popular routes for material synthesis due to its high adaptability and versatility. Its use has been extended to a large number of species of different nature, making it possible to synthesize hybrid materials through a simple methodology that includes all the advantages of this process, i.e. high purity, designed properties and diverse structures [1]. On the other hand, the use of microwaves as a powerful and efficient heating technology is also well known, and its use in material synthesis has become relevant. Thus, improvements on energy consumption and processing time are already reported when microwave heating is involved in some stage of the synthesis [2].

The advantages of the two mentioned approaches are combined in this work. Materials from organic and inorganic precursors, as well as their resultant mixtures, are obtained through sol-gel routes involving microwave heating. In each case, the combined effect of microwave heating with the different chemical variables involved in the sol-gel process was studied in order to elucidate the feasible porous properties that can be obtained with this procedure [3,4]. In addition, working with monomers of different nature, which have different interaction with microwaves, leads to detect an active role of this radiation in the development of the gel structure. As a result, this sol-gel microwave-assisted process is able not only to save synthesis time and energy [5], but also to produce materials with specific desgined properties, making them optimum for many different applications such as thermal isolation, energy storage, adsorption and catalysis, among others.

Figure 1. Organic/inorganic materials obtained by sol-gel route assisted by microwave heating.



✓Tailored materials
✓Time and energy savings
✓Easily scalable process

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Organic-inorganic epitaxial interfaces for orientated Cupper benzene-1,3,5-tricarboxylate thin films with in-plane anisotropic conduction

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Metal-organic framework (MOF) has been attracted huge interests due to a variety of framework structures and unique chemical interactions between guest molecules and host frameworks. These properties make them promising materials for MOF-based electronic devices because the rational charge transfer path can be designed by optimizing the host-guest interactions at molecular level.[1] For example, $Cu_3(BTC)_2$ MOF (BTC; 1,3,5-benzenticalboxylate) thin films incorporating conjugated molecules, 7,7,8,8-tetracyanoquinodimethane (TCNQ) (hereafter TCNQ@$Cu_3(BTC)_2$), has been reported to show tunable electrical conductivity.[2] Theoretical study predicted that the conductive pass along {111} crystalline planes of $Cu_3(BTC)_2$ seems to be the most plausible.[3] The high efficiency of carrier transfer and anisotropic conductivity of TCNQ@$Cu_3(BTC)_2$ thin films could be maximized by optimizing the orientation of framework structure, which allows for sophisticated MOF-based electronic devices such as field effect transistor. However, the fabrication of $Cu_3(BTC)_2$ thin films oriented along in-plane direction remained a significant challenge due to the complex and 3-dimenasional crystal/framework structures. We have recently reported the fabrication of Cu-based MOF thin films with orientations along three crystallographic axes on an oriented $Cu(OH)_2$ nanobelts thin film.[4] The carboxylic acid-based organic linkers of MOFs are aligned on $Cu(OH)_2$ reflecting the lattice of the $Cu(OH)_2$, which enables the epitaxial growth of MOFs. The heteroepitaxial growth system using lattice-matched organic-inorganic interfaces on $Cu(OH)_2$ was adapted for the fabrication of $Cu_3(BTC)_2$ thin films with both out-of-plane and in-plane orientation. The $Cu_3(BTC)_2$ film was synthesized by reacting $Cu(OH)_2$ nanobelts thin film in the water-ethanol solution of BTC. Importantly, the optimized reaction conditions (water-ethanol ratio) allowed for the fabrication of the oriented $Cu_3(BTC)_2$ film over the substrate. The $Cu_3(BTC)_2$ film with {111} crystalline planes along the in-plane direction was fabricated under the water-rich condition(Fig. 1(a)). The different conductivities depending on the in-plane direction was confirmed by *I*-*V* curve measurement using two probe method (Figure 1(b)). The conduction along parallel to {111} planes ({111}-parallel) was found to be tenfold higher than that of along {111}-vertical. The oriented TCNQ@$Cu_3(BTC)_2$ MOF thin films with anisotropic conductivity would be applied to future organic electronic devices designed by combining patterning technologies.

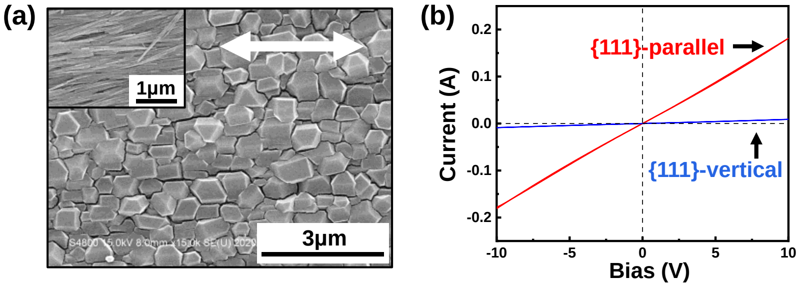

Figure 1 : (a) SEM image of oriented $Cu_3(BTC)_2$ film (Insert: original $Cu(OH)_2$ nanobelts thin film). {111} crystalline planes were aligned along the white arrow. (b) *I*-*V* curves of TCNQ@$Cu_3(BTC)_2$ thin film applied voltage along parallel and vertical to {111} planes.

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RED-NIR LIGHT-EMITTING MEMBRANES BASED ON POLYUREA GEL CONTAINING MOLYBDENUM CLUSTER SALT

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Polyurethanes-polyurea derived materials acting as versatile and moldable matrices used for flexible/rigid foams, cast elastomers, paint-coating and adhesives.[1,2] Here, we demonstrated a facile preparation of polyurea gel by the reaction of a polyetheramine (Jeffamine ED-2001) and a polyisocyanate (hexamethylene diisocyanate trimer). A molybdenum cluster salt ($Cs_2Mo_6Br_{14}$) was homogenously dispersed into the polyurea gel at room temperature thanks to the sol-gel chemistry. The influence of cluster salt content (1 – 10wt%) into the polyurea matrix was in-deep studied by Fourier transform infrared spectroscopy (FTIR), Differential scanning calorimetry (DSC) and X-ray fluorescence microanalysis (µ-XRF). Moreover, the emission properties of the loaded polyurea gels were evaluated. Regardless of the amount of cluster loaded into the polyurea, the integrity of these species was preserved and homegeneosly dispersed as showed by mapping µ-XRF. Spectroscopic-structural analyses reveal a significant increase of the chain mobility (glass transition temperature Tg) from -65°C to -55 °C after incorporation of cluster into polymer matrix (DSC analyses) and, interactions between the ether-type oxygen atoms of the PEO chains and the cluster compound (FTIR studies). The combination of a polyurea matrix and a molybdenum cluster salt demonstrate the feasibility to fabricate a rubber emitting device in the NIR region. Steady-state photoluminescence studies demonstrate that metal cluster emission properties are well retained within the host matrix whatever the loaded content. Upon irradiation in the UV-A region the loaded polyurea containing cluster salt can be produce reactive oxygen species (ROS) opening new perspectives as versatile membranes in the field of photodynamic therapy.

Acknowledgements: Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – (CAPES) – Finance Code 001, Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) – n° 306271/2017-6, Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP SPRINT grant n° 2017/50286-9) and CNRS (PRC Clustobrane).

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P047

ETHANOL DEHYDRATION OVER HYBRID ALUMINOSILICATE CATALYSTS PREPARED BY NON-HYDROLYTIC SOL-GEL

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The dehydration of (bio)ethanol to ethylene is an essential catalytic reaction in the perspective of the development of bio-based industry [1]. Traditional catalysts employed in this reaction are fully inorganic: alumina, silica-alumina, and HZSM-5 [2]. Each of these systems come with their limitations: only moderate activity in the case of Al_2O_3 and silica-alumina, and rapid deactivation by coking in the case of zeolite catalysts. Recently, we have shown, that non-hydrolytic sol-gel (NHSG) provides highly homogeneous and porous aluminosilicate materials exhibiting superior activity and long-term stability in ethanol dehydration [3]. The ethylene selectivity was improved by one-pot incorporation of organic groups [4].

In this follow-up study, the best performing NHSG-prepared aluminosilicate catalysts (fully inorganic) were post-synthetically modified by grafting with trimethysilyl groups. In such a way, the Brønsted acid sites (≡Si–O(H)···Al≡) were transformed into Lewis acid sites (≡Si–$OSiMe_3$ and Al≡). The number of reacted ≡Si–OH moieties and thus the trimethylsilyl groups loading and Brønsted/Lewis ratio was controlled via a temperature-vacuum pretreatment of aluminosilicate samples.

Structure, porosity, acidity, and hydrophobicity of NHSG-prepared catalysts were closely followed by MAS NMR studies, N_2 physisorption, IR-pyridine analyses, and water adsorption. Moreover, aluminosilicates were tested in a gas-phase fixed-bed catalytic reactor in ethanol dehydration. Lewis acid Al sites were found to exhibit a high ethylene selectivity even at relatively low temperatures (200–300 °C). These tailored NHSG-prepared aluminosilicate catalysts exhibited high ethylene productivities, markedly outperforming commercial silica-alumina (Figure 1).

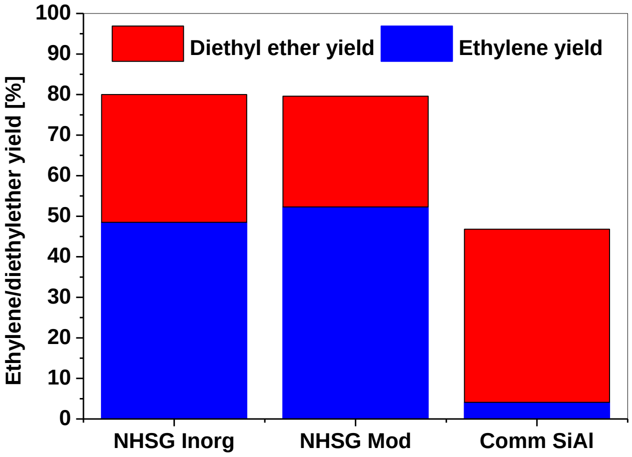

Figure 1 : Comparison of ethylene and diethyl ether yields exhibited by purely inorganic aluminosilicate catalyst prepared by NHSG (NHSG Inorg), organically modified aluminosilicate (NHSG Mod) and commercial siica-alumina (Comm SiAl).

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P048

An Investigation of the Influence of Organic Groups on the Structure and Properties of Polysiloxane Melting Gels

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ABSTRACT:

Polysiloxanes, produced by combined hydrolysis and condensation reaction of di- and trialkoxysilanes with methyl or phenyl groups build so-called melting gels.[1] They are rigid and transparent at room temperature, soften reversibly around 110 °C, and show irreversible curing above 150 °C. The glassy, transparent, and insoluble materials show extraordinary properties, like high transparency in a long wavelength region, low gas permeability and high thermal stability. A variable refractive index and adjustable viscosity of the precursor gel make the material interesting for many applications, especially in the optoelectronic field.[2]

The investigation of the acid-catalyzed solvent-free melting gel formation by various spectroscopic techniques, X-ray diffraction, thermal analysis, and chromatographic methods of a polyphenylsilsesquioxane show a defect rich structure with ladder-like domains. π-π-Interactions and hydrogen bonding initially cause the thermoplastic behaviour of the precursor gel. Condensation reactions initiated by higher temperatures lead to structural reorientation and irreversible curing.[3]

Based on these results we investigated the influence of further aryl compounds like 1-naphthyl-, 2-naphthyl and phenanthrenyl on the melting gel formation using organo di- and trialkoxysilanes. We study the influence of electronic effects and steric hindrance on the crosslinking, the built structures, and the OH-group stability to gain an understanding of the structural characteristics and their impact on the melting gel properties.

These investigations enable an adjustment of the properties as desired by varying the organic group generating melting gels that can be used for a wide range of applications.

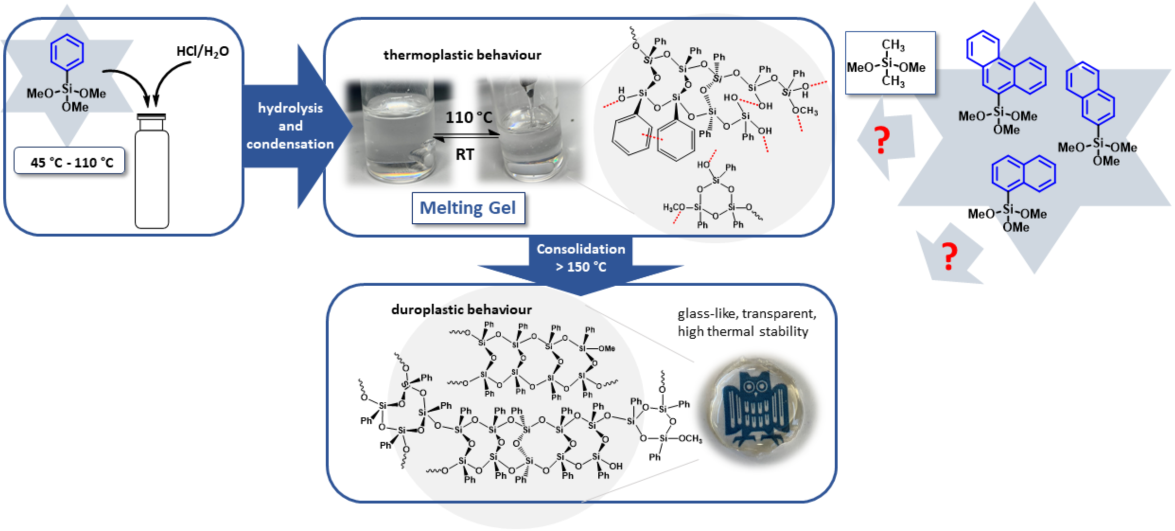

Figure 1 : Overview of the melting gel synthesis and the resulting structure of a polyphenylsilsesquioxane.

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TITANIA DOPED WITH IRON (III) AS PHOTOCATALYSTS FOR THE HYDROGEN PEROXIDE PRODUCTION

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ABSTRACT:

The demand for hydrogen peroxide is increasing worldwide. Although it is considered a "green" chemical, its synthesis is environmentally unfriendly. Direct hydrogen peroxide synthesis is the most effective way to overcome this issue, but factors such as risk of explosion and poor hydrogen peroxide stability prevent this process from being applied at the industrial level. Here, we have used sol–gel processes to prepare titania-based photocatalysts that can produce hydrogen peroxide directly, thus avoiding hydrogen peroxide deactivation and optimizing TiO_2 properties and advantages. More specifically, we have used a natural purified Brazilian kaolinite from São Simão to synthesize a new nanocomposite with $FeCl_3$ and Ti(IV) isopropoxide *via* a hydrolytic sol–gel route [1]. Kaolinite (10 g), ethanol (200 cm^3), acetic acid (1 cm^3), and Ti(IV) isopropoxide (2 cm^3) were mixed in a beaker at room temperature and stirred for 24 h. The solid was dried at 100 ºC for 24 h and split into four fractions: one was used as dried, and the other three were heated in air at 400, 700, or 1000 ºC, respectively, for 24 h. Drying did not modify the kaolinite basal spacing of kaolinite (7.14 Å). Anatase was formed at 400ºC. At higher temperatures anatase and rutile were formed, and kaolinite was amorphized and transformed into metakaolinite. Hydrogen peroxide was synthesized in glass reactors containing ethanol, in the presence of oxygen, and under photoirradiaton with a Xe arc lamp. The preliminary results showed the potential of the prepared photocatalysts for selective hydrogen peroxide production. Kaolinite promoted dispersion of the active phase on the clay surface, which promoted selective hydrogen peroxide production

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Synthesis and Functionalization of Dihydride-Substituted Laddersiloxanes

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Silsesquioxanes (SQs), consisting of an inorganic siloxane skeleton and organic moieties, are used to prepare organic-inorganic hybrid materials for various applications such as electronics, optics, coating materials, catalysis, medicine, etc.[1-3] Ladder-type SQs (laddersiloxanes) with highly ordered double chain structure exhibit highest refractive index among cage-type SQs and cyclic SQs, which is very interesting precursors for preparation of optical materials.[4,5]

In our laboratory, we are focusing on the synthesis of new laddersiloxanes bearing multiple reactive substituents and investigation of the reactivity of these compounds in order to introduce high functional moieties and to meet the demand as precursors for polymeric materials. Previously, a set of tricyclic laddersiloxanes (6-8-6-membered fused rings) with four substituents were synthesized.[6,7] At the beginning, vinyl and allyl groups were selected because numerous organic reactions can be performed with double bonds. The tetraallyl-substituted laddersiloxane exhibit excellent reactivity towards hydrosilylation and thiol-ene reaction, the reactions can proceed at four reactive sites. In this presentation, the synthesis of new laddersiloxanes with different reactive substituents, such as hydrido, hydroxy, or other groups will be shown.

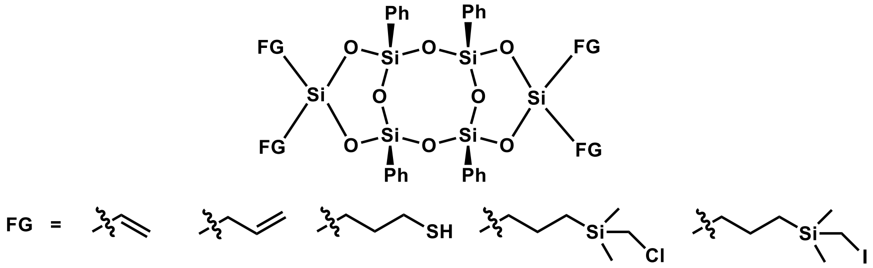
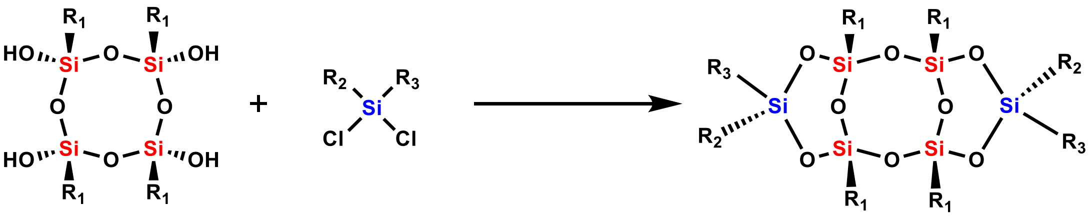


Figure 1. Tetra-substituted laddersiloxanes (previously reported).[6-7]



R_1=Ph,*i*-Bu

$R_2 \neq R_3$
R_2=alkyl
R_3=reactive group

Scheme 1 : Synthesis of functionalizable new laddersiloxanes.

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P051

SELF-ASSEMBLY OF FERRIA – NANOCELLULOSE COMPOSITE FIBRES

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An environmentally benign synthesis of a magnetically responsive, carboxymethyl cellulose based hybrid material has been reported. Under the reported aqueous synthetic conditions Fe(II) and Fe(III) co-precipitate to form magnetite nanoparticles with primary particle sizes in the range of a few nanometers when nucleation occurs between carboxymethyl cellulose nanofibers. Secondary particles with sizes ranging from 20-25 nm form when nucleation occurs in solution or at the solution – fibre interface, where the increase in particle size may be attributed to Ostwald ripening. Under reported conditions the composite is prone to aggregate. However, a fraction of the final product is capable of coordinating to carboxymethyl cellulose in such a manner as to form large fibre-like assemblies, with longitudinal dimensions far exceeding that of the individual starting components. The formation of these fibre-like assemblies is sensitive to small variations in synthetic conditions, requiring further attention. In addition, the composite was tested as a potential vehicle for topical drug delivery with the rate of drug release being controlled by day light. In order to test this, the adsorption and desorption of the broad-spectrum antibiotic Tetracycline was studied, revealing an dependence of daylight exposure on drug desorption rate in solution.

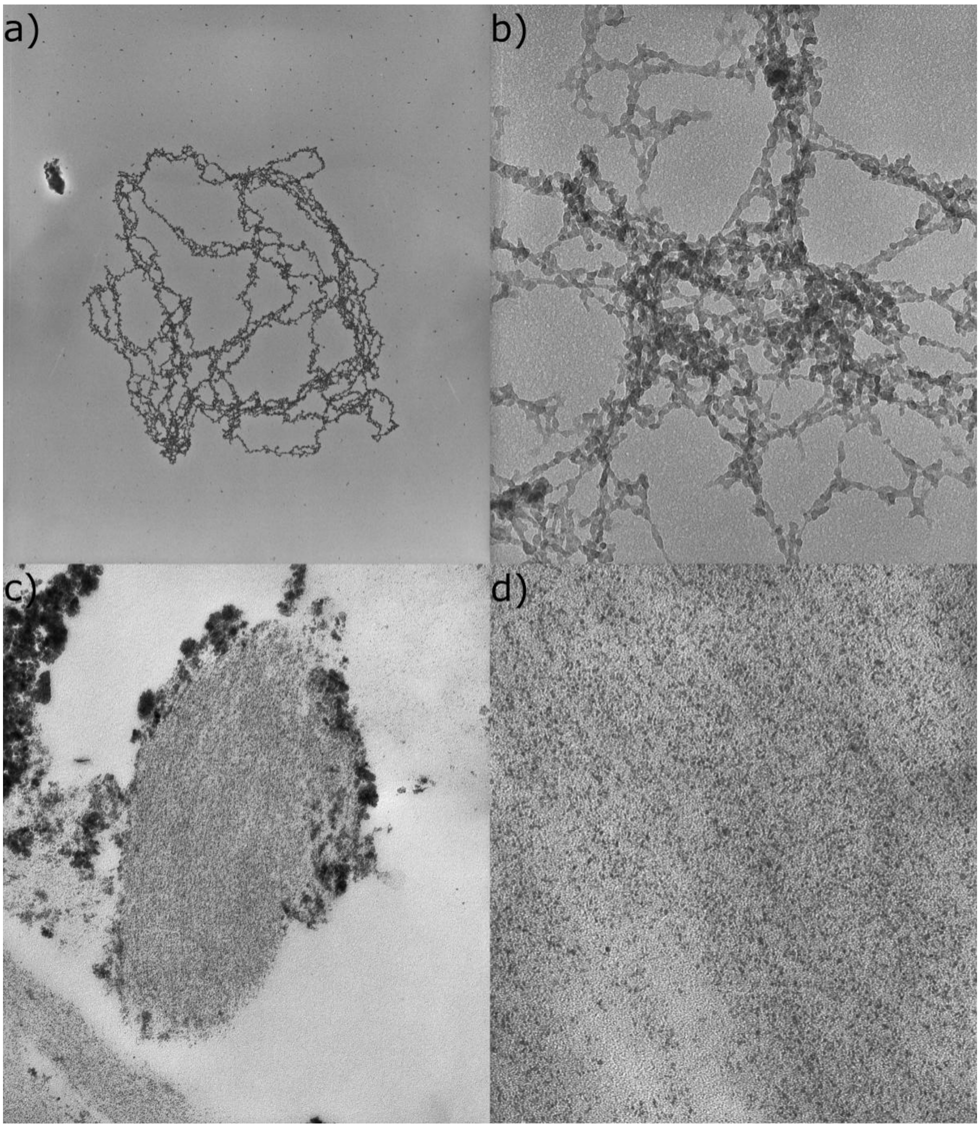

Figure 1: TEM images of a carboxymethyl cellulose iron oxide composite material showing the formation of assembled fibre-like structures a) 6.3k, b) 200k magnification and the cross-section of larger fibrous aggregates c) 75k, d) 200k

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1- To be published

POROUS COPPER AND COPPER HYBRID MATERIALS DERIVED FROM SOL-GEL TEMPLATES

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ABSTRACT:

The synthesis of porous metal structures produced fascinating results in the last decades. However, the creation of macroscopic objects with a high degree of control over 3D shape complexity and, at the same time, microstructural complexity is still a challenging task. State-of-the-art fabrication strategies towards porous metals share the same limitations, thus causing a lack of porous architectures that exhibit a complex tailored structure on the macro- and the microscale.[1]

Here, we propose a route to porous copper or copper hybrid materials with complex macroscopic shapes and a tailored microstructure with the aim to fill the above-mentioned gap and to develop fabrication approaches beyond state of the art. This offers potential for the creation of new metallic architectures with unique structures and special functional properties (e.g. electrical or thermal properties) that are unmatched by materials produced via conventional methods.

The fabrication of such porous copper or copper hybrid materials is based on a templating approach, using hierarchically structured resorcinol-formaldehyde or carbon monoliths from sol-gel synthesis with a defined microstructure as template.[2,3] These porous architectures are infiltrated with a copper precursor and subsequently coated with metallic copper via a wet-chemical deposition process. We present structural data of these novel morphologies, which have been investigated in detail by electron microscopy, X-ray diffraction and N_2 adsorption analysis.

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HYDROXYAPATITE AND β-TCP MODIFIED PMMA-SILICA COATINGS FOR BIOACTIVE CORROSION PROTECTION OF THE Ti6Al4V ALLOY

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Among the metallic biomaterials commonly used for orthopedic and dental implants is the Ti6Al4V alloy. However, its slow osseointegration and the release of toxic Al and V ions by the corrosive can delay the recovery and result in inflammation of the surrounding tissue [1]. One possible solution to this problem is a surface modification by organic-inorganic coatings, which can play a dual role as an efficient anticorrosive barrier and bioactive layer on Ti6Al4V [2,3]. Additionally, the incorporation of osteoconductive additives, such as hydroxyapatite (HA) and β-tricalcium phosphate (β-TCP) is promising for obtaining coatings with improved bioactivity and biocompatibility. Organic-inorganic PMMA-silica hybrids modified with HA and β-TCP at a concentration of 1000 ppm were obtained by combining reactions of the sol-gel process for tetraethyl (TEOS) with the radical polymerization of methyl methacrylate (MMA) and 3-(trimethoxysilyl) propyl methacrylate (MPTS). The structural properties of a few micrometers-thick films deposited by dip-coating on Ti6Al4V substrates were studied using infrared spectroscopy, X-ray photoelectron spectroscopy, X-ray diffraction, thermal analysis, and contact angle measurements. The prepared PMMA-silica-HA/β-TCP coatings are homogeneous, free of cracks, and have high adhesion (>14 MPa) to the substrate. The modified hybrids exhibit high thermal stability up to 260°C and an angle of contact with the water close to 80°. Electrochemical impedance spectroscopy assays performed during 60 days in simulated body fluid solution (SBF, ISO 23317) demonstrate the excellent anti-corrosion performance of the hybrid coatings with an impedance modulus of up to 130 GΩ cm^2, five orders of magnitude higher than that of the uncoated Ti6Al4V alloy.

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P054

MASTERING ELECTROLYTE PROPERTIES AND COMPATIBILITY: ORGANICALLY MODIFIED IONOGELS FOR SODIUM-ION BATTERIES

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Silica-based ionogels based on sol-gel synthesis are widely investigated to serve as solid electrolytes for sodium-ion batteries (SIBs). SIBs are more sustainable than lithium-ion batteries (LIBs) due to the high abundance of sodium. Ionogels, in which an ionic liquid electrolyte (ILE) is confined within a silica matrix, are attractive potential solid electrolytes because of their high ionic conductivity, thermal stability, and broad electrochemical window.[1] However, brittleness of such ionogels may adversely affect the performance of the final battery. Increasing the content of ionic liquid has been reported to improve the mechanical properties.[2-3] However, as the ionic liquid is an important cost factor of ionogels, due to the lack of a scalable synthesis, the content of ionic liquid should preferentially remain low.[4] Additionally, increasing the ILE content in silica-based ionogels synthesized through a non-aqueous process only results in a limited mechanical improvement. Therefore, it remains crucial to make further improvements based on organic modifications. It was hypothesized that this would allow lowering of the rigidity of the silica matrix by preventing full condensation due to the presence of an unreactive organic group attached to Si, whilst maintaining the electrochemical properties.

A non-aqueous sol-gel route with formic acid (FA) is used to obtain monolithic organically modified ionogels which are homogeneous, transparent, and depending on the phenyl content compliant. The hardness and storage modulus (nano-indentation) were improved upon organic modification whilst a slight reduction of ionic conductivity (electrochemical impedance spectroscopy, EIS) could be noticed as well. Besides, thermal stability (thermogravimetric analysis, TGA), chemical interactions (ATR-FTIR), and anodic stability (linear scanning voltammetry, LSV) were studied as well. These organically modified ionogels are finally researched in SIB full cells to demonstrate their performance as solid electrolyte and the cell's stability.

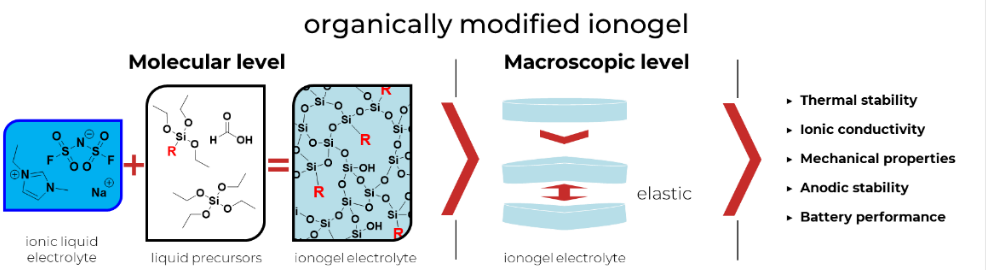

Figure 1: Graphical abstract of organically modified ionogels

Acknowledgments

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INORGANIC-ORGANIC SILICA COATINGS WITH ‘SELF-HEALING’ PROPERTIES

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Corrosion, despite of many methods of prevention, is still a global problem. Its costs are about 3.5% GDP [1]. Today science offers many solutions to corrosion mitigation i.e., coatings, inhibitors, cathodic/anodic prevention, etc. [2]. One of the most common, are coatings. However, modern materials for corrosion mitigation must be characterized not only as protective but also fulfill specific demands like no-toxic, no generate wastes, beneficial in terms of energy and environment. The sol-gel method provides an environmentally friendly product with controllable specific properties on a molecular level. Thanks to technological advancement and modernisation of the offered product, a sol-gel coatings market develops significantly. It is estimated that the sol-gel coatings market dedicated for corrosion mitigation will grow at a rate of about 11% for the period 2021-2028 [3]. Nowadays various modification of sol-gel oxide networks are offered, such as addition the active agents i.e. inhibitors or ZrO_2 [1].
Due to working environment of metallic products, the key issue is to search for the influence of the protection synthesis parameters and additives on the final properties, especially the long-term protection ability of coating materials. In this work, the silica sol-gel coatings modified by zirconia and active agents ($Ce(NO_3)_3$, CeO_2 and benzotriazole) were presented. Obtained silica coatings on metallic substrate (P265GH steel) were tested to corrosion protect in 0.05M NaCl, especially tested ‘self-healing’ ability by longing the time of exposure to corrosion agent (using EIS and LPR methods). Additionally, the SEM with EDX and Raman spectroscopy were used to characterize the morphology and chemical composition of coatings. The scratch test and multi-scratch test were conducted to determine mechanical properties like adhesion and friction.

The research was supported by the National Science Centre, Poland under the OPUS + LAP project ‘Research on the influence of self-healing, organic-inorganic sol-gel layers on the corrosion resistance and fatigue of steel in the VHCF range’ UMO-2020/39/I/ST5/03493

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P056

ION-IMPRINTED MATERIALS BASED ON TIO_2 INORGANIC MATRIX APPLIED FOR NI^{2+} ADSORPTION

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Remediation of wastewaters from the industrial pollutants is an essential question nowadays. Nickel strongly affects human health – it causes allergic reactions, nickel and several of its compounds are classified as carcinogens, may case spontaneous abortions, nausea, chronic asthma e.t.c.[1]. For the remediation purpose adsorption procedure is widely applied because of its simplicity and reliability, adsorption process allows to extract nickel from solution, collect it and reuse. Immobilization of N-containing ligands in the matrix of sorbent allows to get highly selective adsorbent and it may be conveniently performed via ion imprinting procedure. This approach was firstly developed in 1970s and implies complexation of target ion with subsequent immobilization of this complex in polymer matrix, after removal of target ion via regeneration step material is ready [2]. Ion imprinted materials are generally have disadvantages such as insufficient stability in different type of harsh conditions – for example they are prone to degradation under the UV irradiation – lack of robustness which is not sufficient to retain geometry of adsorption sites, and high cost [3]. To solve these problems it is possible, in the production of IIPs, to replace the organic polymeric resins with inorganic oxides such as SiO_2 and TiO_2.In the present work we made the novel type of adsorbents where organic resins were replaced by TiO_2 as a matrix and the support for chelating amino groups. Proposed materials demonstrate high values of adsorption capacity up to 150 mg (Ni^{2+}) per gram of adsorbent.

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P057

HYBRID ACID CATALYSTS PREPARED VIA TRIMETHYLSILYLATION OF ALUMINOSILICATES SYNTHESIZED BY NON-HYDROLYTIC SOL-GEL

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ABSTRACT:

Hybrid materials based on aluminosilicates are extensively studied for their enhanced catalytic performance. Organic groups can change acidity, hydrothermal stability, and porosity. First, we have shown, that non-hydrolytic sol-gel (NHSG) provides highly homogeneous and porous aluminosilicate materials exhibiting superior activity and long-term stability in ethanol dehydration [1]. Second, the ethylene selectivity was improved by one-pot incorporation of organic groups [2]. Interestingly, this approach did not display the direct influence of hydrophobicity on alcohol dehydration in contrary to other reports [3].

In this study, the NHSG-prepared aluminosilicate catalysts (fully inorganic) were post-synthetically modified by grafting trimethylsilyl groups onto their surfaces. Trimethylsilyl groups were attached to the surface using trimethylchlorosilane or trimethyl(methoxy)silane. The number of reacted ≡Si−OH moieties and thus the trimethylsilyl groups loading was controlled via a temperature-vacuum pretreatment of aluminosilicate samples. Trimethylsilyl groups loading was evaluated by ^{29}Si MAS NMR measurements (Figure 1). Structure, porosity, acidity, and hydrophobicity of NHSG-prepared catalysts were closely followed by MAS NMR studies, N_2 physisorption, IR-pyridine analyses, and water adsorption. Moreover, aluminosilicates were tested in a gas-phase fixed-bed catalytic reactor in ethanol dehydration and in a batch reactor in aminolysis of styrene oxide (liquid phase). These tailored NHSG-prepared aluminosilicate catalysts exhibited varying catalytic activity and selectivity in both catalytic reactions depending on trimethylsilyl groups loading in the samples.

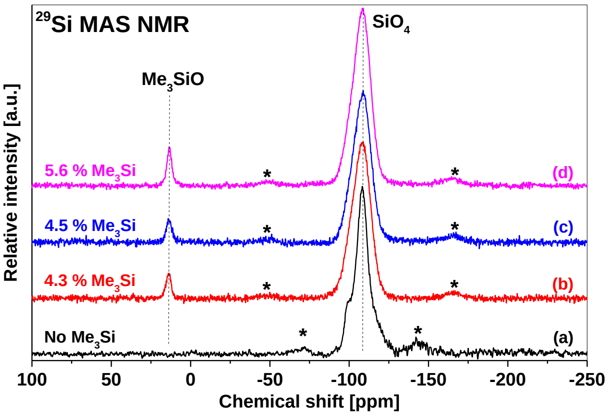

Figure 1: Comparison of pristine aluminosilicate with post-modified aluminosilicate samples. Trimethylsilyl groups loading was controlled by different conditions during temperature-vacuum pretreatment of pristine aluminosilicate. (a) Pristine aluminosilicate without Me_3Si groups; (b) Pretreatment at 500 °C under vacuum, then silylated; (c) Pretreatment at 150 °C under vacuum, then silylated; (d) Pretreatment at room temperature under vacuum, then silylated. Asterisks denote spinning sidebands.

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The work has been financially supported by the Czech Science Foundation under the project GJ20-03636Y.

P058

INFLUENCE OF ORGANIC GROUP ON STRUCTURE AND PROPERTIES OF ORGANOTRIALKOXYSILANE-BASED AEROGEL

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ABSTRACT:

Silica aerogel exhibits a revolutionizing potential for various applications, which is restricted due to its brittleness and expensive fabrication procedure. Organic-inorganic hybridization is a promising way to improve the mechanical properties of aerogels. Generally, there are three types of hybridization strategies used to modify aerogels: forming a composite with polymers or structural supports (e.g. fibre-reinforcement), surface modification, and employment of organoalkoxysilanes as a precursor. However, most of the polymer-reinforced aerogels exhibit coarsened microstructure and/or increased inhomogeneity leading to lower specific surface area and higher density. While aerogel surface modification requires additional steps, including tedious solvent exchange, increasing the time and chemical waste production [1-3].

Another approach to improve the mechanical properties is to use a trifunctional organoalkoxysilane. The synthesis of organic−inorganic hybrid aerogels only from organotrialkoxysilane is difficult due to hydrophobicity of the condensates and steric effect by the organic moiety [4, 5]. In particular, the hydrophobicity of siloxane condensates increases with the progress of polycondensation,[6] and phase separation between condensates and polar solvent takes place before gelation in most cases.

In this research, the condensation mechanism, which determines a specific aerogel internal structure and depends on the reacting mixture's chemical composition, is investigated utilizing a ternary system described on the Gibbs triangle. A series of methyl-, ethyl- and vinyltrimethoxysilane-based syntheses allow tracing the influence of the concentration of the precursor and the molar ratio of the solvent to the anti-solvent, determining the ranges of condensation to the form of a monolith (binodes), transitions between nucleation and growth and spinodal decomposition mechanisms (spinodes), and thus - understanding the effects associated with microscopic phase separation occurring during structure formation, is correlated with the final properties of the aerogel, such as secondary particle size, porosity and volume shrinkage during ambient pressure drying.

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P059

Waveguides processing by laser writing in organic-inorganic photoresists, for optofluidic platforms

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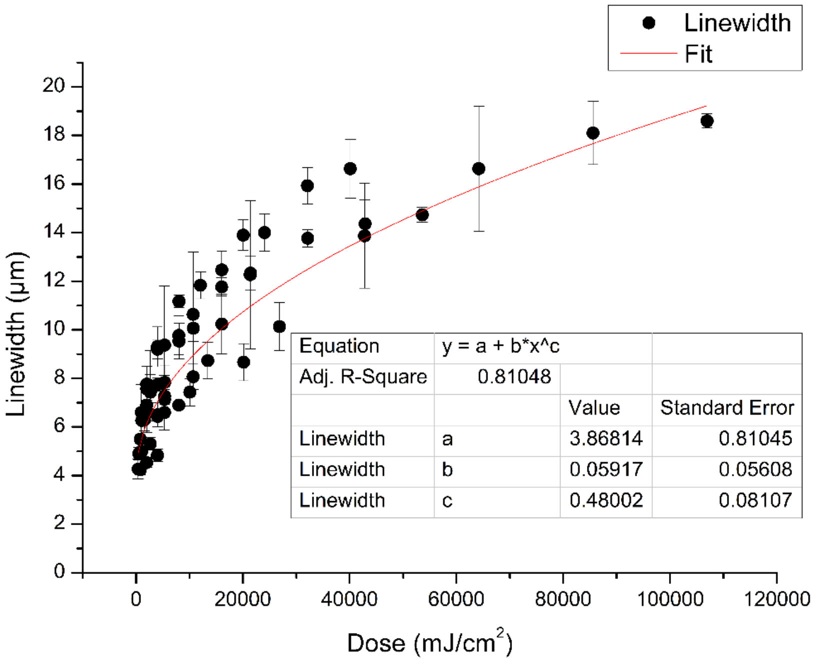
The interest in the fabrication of optofluidic platforms for sensing and manipulation applications is on the rise since the early 2000's [1]. As such there is a need for a new panel of materials enabling the fabrication of such miniaturised systems. The growing capability to use hybrid organic-inorganic materials for the fabrication of integrated optics components makes this class of material an ideal candidate for the fabrication of waveguiding structures for these systems. In this work a photosensitive composition based on two organically modified precursors: 3-(Trimethoxysilyl)propyl methacrylate (MAPTMS) and zirconium propoxide ($Zr(OPr)_4$) chelated with methacrylic acid (MAA) is investigated. This composition is extremely interesting because it allows the tailoring of the refractive index by changing the ratio of one precursor to another [2,3]. As such different compositions of these same precursors can be used to form the cladding as well as the guiding layer. The waveguides fabrication was done using 2D laser writing. The use of laser writing is beneficial on different levels: it allows for a flexibility in the waveguides design as it is a maskless technique, and it helps in overcoming the problem of oxygen inhibition in radically polymerizable resists as high localised laser powers can enable high radical generation[4]. We were able to fabricate waveguides in this photoresist by refractive index change and we were able to confirm light guiding in these structures at 635 nm with a refractive index step of 0.004. Revealed waveguide structures were also fabricated and characterised. The cured thickness of the waveguide was found to vary as the square root of the applied laser dose as seen in **Figure 1**, which makes the predictability of the waveguides lateral dimension easier. The optical losses in both revealed and unrevealed waveguide structures was found to be around

in the visible, which means that no scattering losses are further induced by the development step.



Equation	y = a + b*x^c		
Adj. R-Square	0.81048		
		Value	Standard Error
Linewidth	a	3.86814	0.81045
Linewidth	b	0.05917	0.05608
Linewidth	c	0.48002	0.08107

Figure 1 : The cured linewidth of written waveguides as a function of the applied dynamic dose.

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ICE-PHOBIC, LOW INTERFACIAL ENERGY, EROSION AND CORROSION RESISTANT SOL-GEL COATINGS APPLIED ON AA2024

Cecilia Agustín-Sáenz [1], **Olatz Adarraga** [1], **Usoa Izagirre-Etxeberria** [1], **Hugo Pervier** [2], **Marie Pervier** [2], **Fabiola Brusciotti** [1]

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ABSTRACT:

The interfacial energy of coatings is an important property that influences the material's wettability, adhesion and friction properties and therefore it may be modulated to contribute against adhesion of unwanted elements (ice, soiling, dust). Perfluorinated polymers are known for being materials with extremely low interfacial free energy, which results in an anti-adhesive behaviour for polar and non-polar substances. The high strength of the C–F bond grants excellent thermal, chemical, photochemical and hydrolytic stability. However, toxicological concerns surround these materials and their replacement is being pursued. Sol-gel approach offers a vast range of possibilities for coating design. Its ability to synergistically combine inorganic and organic moieties leads to the formation of hybrid materials with covalently bonded moieties linked to matrix by the non-hydrolizable and stable Si–C bond in organylalkoxysilanes. In this work, the development of ice-phobic solutions for aeronautic aluminium alloys has been accomplished by the functionalization of an anticorrosion hybrid sol-gel formulation with alkyl and polyfluoroalkyl moieties. The quantity and chain length of such moieties required to achieve hydrophobicity have been optimized. In this optimization, the morphology of the surface has been taken into account since the wetting of a surface by a liquid is affected by its topography. Therefore, the combination of topographical morphology and surface chemistry has been pursued to achieve super-hydrophobicity, considering this effect leads to improved icephobic performance.

The effect of the addition of alkyl and polyfluoroalkylalkoxysilanes in the sol viscosity, and in the thickness, roughness, interfacial free energy and hardness of the coatings has been studied. The corrosion performance has been analyzed by electrochemical impedance spectroscopy. The adhesion of two types of ice (rime and glaze) to the different surfaces prepared by the combination of coatings with different textures have been studied and correlated with the hydrophobicity and roughness of the treatments.

Acknowledgements

Clean Sky 2 European project **ERICE** "Super hydrophobic and erosion resistant coatings for turbine scroll and downstream pipe"

P061

Sol-gel hybrid coatings as primer varnish for enhancing adhesion and thermal resistance of copper magnet wire

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ABSTRACT:

The present work aims at developing a more sustainable and competitive production process with two main technical objectives: (i) Improve the energy performance and efficiency of electrical motors by 20% to 30% compared to the current situation by increasing the thermal class; (ii) Considerably reduce the consumption of (partly toxic) solvents and VOC emissions.

In this work, the preparation of sol-gel hybrid coatings, starting from metal alkoxides silica precursors, as primer varnish for enhancing adhesion, flexibility, mechanical, thermal and chemical resistance of magnet wire is investigated. The hybrid coatings were prepared and applied on coper wire using enamelling process by controlling both of sol-gel formulation (solvents, catalysts, pH, time of hydrolysis, miscibility of hybrid inorganic/organic precursors and the viscosity of the sol to avoid the gelation) and application process on enamelling prototype machine (speed fixed varied 7 m/min to 20 m/min; drying and annealing temperatures ranged from 200 °C to 500 °C; dry thickness, dry extract and viscosity adjustments of the varnish).

The microstructure, the morphology and the thickness of the obtained enamel were investigated by SEM-FEG analysis showing well continuity and free-cracks coatings. The characterization of the coated wires was investigated at laboratory scale in terms of mechanical resistance (flexibility, adhesion, elongation), chemical resistance to acidic and alkali agents, breakdown voltage resistance and thermal resistance. The obtained results show high resistance to breakdown voltages and promising thermal and mechanical properties. However, a very high mineral content decreases the resistance to the flexibility test and needs more investigation. The results and investigated solutions will be presented and discussed.

This work is carried out in the framework of HI-ECOWIRE project, funded by INTERREG NWE Programme. The project is based on an international consortium (SMEs, Industries, Research Centres and Universities) aiming at strengthening European competitiveness in the transport sector and energy production (wind turbine).

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P062

PROPERTIES OF POROUS METHYL-MODIFIED SILICA FILMS

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ABSTRACT:

Porous organosilicate glass (OSG) films prepared via EISA are promising materials for applications as anti-reflective coatings, membranes, solar cells, semiconductor manufacturing technology (low *k* - low dielectric constant dielectrics), etc. A high specific surface of porous film leads to water adsorbtion by silanols causing degradation of film's properties. For example, water adsorption deteriorates the electrical properties of the material, including increase of dielectric constant (water has k=81) and leakage currents, decrease of breakdown voltage, and so on. The methyl terminal groups placed on the pores surface can decrease adsorption of water molecules.

In this work we have studied an effect of different silicon alkoxide precursors contained methyl Si-CH_3 or dimethyl CH_3-Si-CH_3 bonds on the properties of porous OSG films prepared via EISA sol-gel techniques. Film-forming solutions with different methyl content (CH_3/Si ratio was varied from 0 to 1) were prepared by cohydrolysis of tetraethoxysilane (TEOS) and methyltriethoxysilane (MTEOS) or diethoxydimethylsilane (DEDMS). Brij® L4 surfactant has been used as a structure-directing agent in the the EISA method. The films were spin-on deposited on silicon substrates.

An increase of CH_3/Si ratio leads to an increase in the refractive index, water contact angle, pore size, and to decreasing k-value. TEOS/DEDMS films demonstrate higher value of refractive index and k than TEOS/MTEOS films due to higher silanol content.

Acknowledgments: the authors thank the Russian Foundation for Basic Research (RFBR Grant No. 18-29-27024 MK) and the Ministry of Science and Higher Education of the Russian Federation (No. 0706-2020-0022).

THE SUPERIORITY OF THE SOL-GEL METHOD FOR THE CREATION OF ADSORPTION MATERIALS WITH CONTROLLED SURFACE DESIGN

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Miroslava Vaclavikova[1], Gulaim Seisenbaeva[3], Vadim Kessler[3]

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ABSTRACT:

The study is devoted to the establishment of physicochemical principles of the one-stage production of silica microspheres, magnetically controlled carriers, and membranes with polysiloxane coatings bearing 3-aminopropyl, 3-mercaptopropyl, or thiourea groups. The synthesis of such silica carriers is conditioned by the facility of sol preparation and sol composition control, eco-friendliness of alcohol by-products forming during the sol-gel transformations, together with apparent advantages of the final materials (sorbents), such as hydrolytic stability, resistance to acidic media, the presence of specific functional groups, and the possibility of regeneration. Spherical particles are interesting objects for biotechnology, chromatography, and catalysis. Among the benefits of magnetic materials are their rapid removal from the reaction medium, which is crucial for biocatalysis, and the potential to enhance the process completeness. Membrane technologies can be used in the water treatment industry, especially membranes with specific properties for the removal of contaminants and maintaining their high performance. The synthesized materials proved to be effective in the adsorption of metal cations [1-4], dyes [3,4], filtration of water contaminated with heavy metals [5], and as biocatalysts [6,7].
The research was supported by Swedish Research Council grant DNr.2018-04841, APVV-19-0302, VEGA 2/0156/19, REA No. 734641-NanoMed.

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P064

CONFINEMENT EFFECTS OF IONIC LIQUID IN IONOSILICA BASED IONOGELS

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ABSTRACT:

Due to their unique physicochemical properties and their huge potential for a multitude of applications, ionic liquids (ILs) are nowadays among the most investigated systems in chemistry. However, one of the key issues that limit their applications is the fact that ILs are liquid. Therefore, ILs were immobilized within a solid host matrix forming a composite material also called ionogel (IG).[1] Indeed, IGs were thoroughly investigated in the last decade for their polyvalence that combines the properties of ILs with those of the host matrix

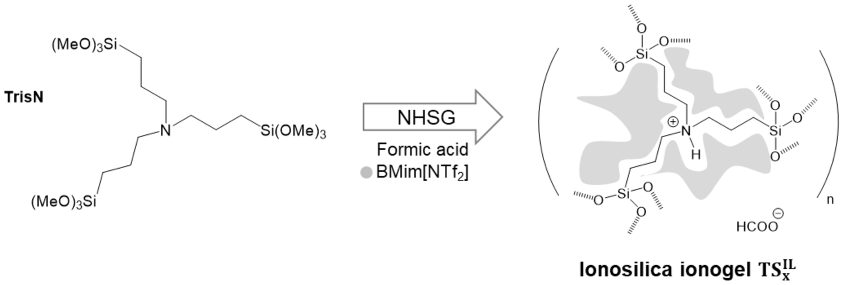

Figure 1. Synthesis scheme for ISIGs monoliths from the amine precursor TrisN.

In our ongoing effort to immobilize ILs into solid devices, we report herein the elaboration of all-ionic composites, *i.e.* ionosilica ionogels (ISIGs) (Figure 2), as a combination of ionic liquid guest confined in an ionosilica host (Figure 1, *left*). Indeed, Ionosilicas reported here are silica-based hybrid materials that are exclusively constituted of ionic fragments.[2] First, ISIGs monoliths were obtained *via* a non-hydrolytic sol-gel process (NHSG) starting from various silylated ionic amine and ammonium precursors in IL BMim [NTf_2] reaction media. We obtained all-ionic ISIGs as brittle and nearly colorless monoliths and focused on special confinement effects between the ionosilica host and IL guest using solid state NMR, Raman spectroscopy and impedance spectroscopy.

In a second time, we synthesized ionosilica ionogel thin films following hydrolytic sol-gel procedures, resulting in the formation of self-standing and flexible films.

Both systems, monoliths and thin films, can incorporate more than 80 *wt*.-% of IL while maintaining a mechanically robust morphology. The obtained ionosilica IGs are highly polyvalent materials with adaptable properties that may find applications in electrocatalysis, electrochemistry, gas sorption, and energy storage. Our work therefore opens the route to functional ionosilica ionogel combinations for specific applications in various domains.

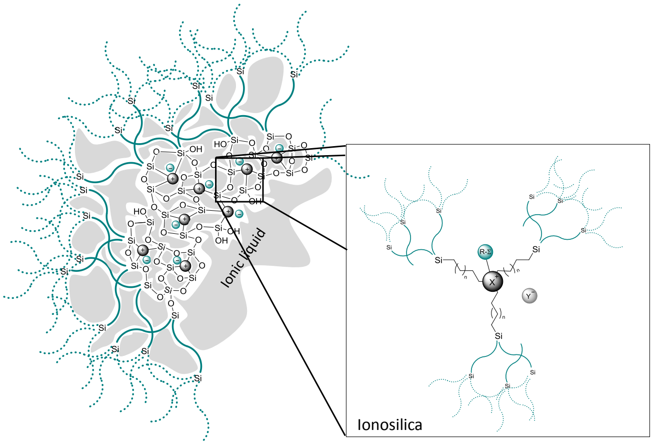

Figure 2. Ionosilica ionogel structure.

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ENLIGHTENMENT OF MULTICOMPONENT OXIDE POROUS MICROSPHERES GENERATION

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ABSTRACT:

Sol-gel derived silica-titania (SiO2-TiO2), and silica-titania-hafnia (SiO2-TiO2-HfO2) microspheres with tailored interconnected macroporosity (MICROSCAFS) have been developed by microemulsion techniques combined with polymerization induced phase separation, without the employment of a phase separation additive. The inherent gelation capability of the silanes involved, together with the action of the Ti and Hf precursors and the control of pH, water content and temperature, allow to well-master this technique, enabling a fine-tuning of the pore size morphology and reproducibility of the MICROSCAFS´ characteristics. These new products are being evaluated for solar-driven photocatalysis and are attractive for other applications in biomedical, energy, chromatography, etc.

However, the core phenomena occurring inside the water droplets of the microemulsion, critical for the interconnected macroporosity generation, such as the way macromolecules assemble in the sol and the phase separation evolves, are still not completely understood.

This work targets a mechanistic study of the sol-gel reaction in its first stages. For such purpose, cryo-scanning electron microscopy (cryo-SEM) was employed, i.e. aliquots of the reaction batch at specific times during the synthesis of the MICROSCAFS were taken, cryogenized and analyzed by cryo-SEM. This procedure was simultaneously combined with energy dispersive spectroscopy (EDS) to provide answers through the visualization of the phase separation and study of the chemical elemental composition at specific locations and reaction times. The oligomers form within the aqueous phase of the emulsion homogeneously and exhibit the theoretical elemental composition since the first stages of the MICROSCAFS´ synthesis. Next, they are shown to accumulate at the water/oil interfaces (Figure 1a), possibly to reduce the surface energy, which explains the presence of the thin layer that wraps the microspheres (Figure 1b). This is followed by the formation of the skeleton domains, which grow by gelation/phase separation until the MICROSCAFS achieve their final morphology (Figure 1b).

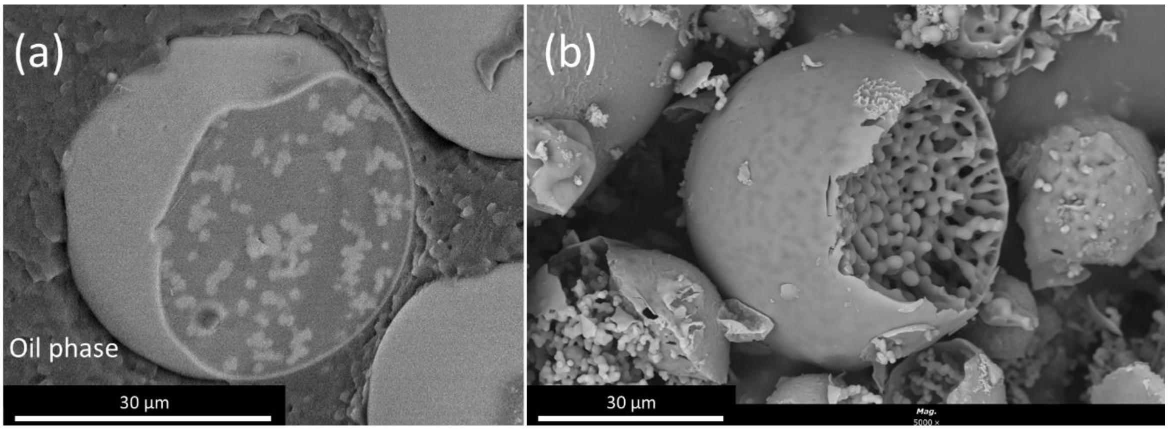

Figure 1: (a) Cryo-SEM image of a SiO_2-TiO_2-HfO_2 MICROSCAF during its synthesis; (b) SEM image of solid, dried SiO_2-TiO_2-HfO_2 MICROSCAFs after the synthesis.

MESOPOROUS ORGANOSILICAS FROM MULTIFUNCTIONAL DENDRIMERS: MODULATING POROSITY AND PORE FUNCTIONALIZATION

Mathilde LAIRD[1], Niklas HERRMANN[1], Carole CARCEL[1], Philippe TRENS[1], Erwan OLIVIERO[1], Guillaume TOQUER[2], Rozenn LE PARC[3], Jean-Louis BANTIGNIES[3], John R. BARTLETT[4], Michel WONG CHI MAN[1].

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ABSTRACT:

Dendrimers are well established as versatile precursors for diverse applications, including controlled drug delivery, catalysis, etc.[1] However, although they have been used to create dendrimer/silica hybrid materials,[2] their utilisation as template remains scarcely explored. Herein, we describe the synthesis of a new multifunctional dendrimer incorporating a poly(amidoamine) (PAMAM) core onto which linkers bearing acetylenic groups, together with cleavable ester and disulfide sites were grafted. Silylated groups were then anchored onto the intermediate acetylenic PAMAM G0 and G3 dendrimers via a Huisgen CuAAC cycloaddition Click reaction.

The PAMAM precursors were condensed in the presence of 1,4-bis(triethoxysilyl)benzene to form mesoporous organosilica gels or periodic mesoporous organosilicas (PMOs), with dendrimers embedded within the structure. The controlled cleavage of the inner part of the dendrimer enables pores with localized thiol groups to be generated on the pore surface. The cleavage of the dendrimer at the disulfide sites was achieved via treatment with dithiothreitol and the resulting intermediates and products were characterized by NMR, Raman, IR spectroscopy, N_2 physisorption, microscopy, etc. Further investigations of the pore properties by gold impregnation demonstrated the presence of polydisperse gold particles as well as well-defined gold/thiolate clusters with Au…S distances of 2.3 Å on both the gels and the PMOs. The influence of the dendrimer generation on the pore properties will be discussed.

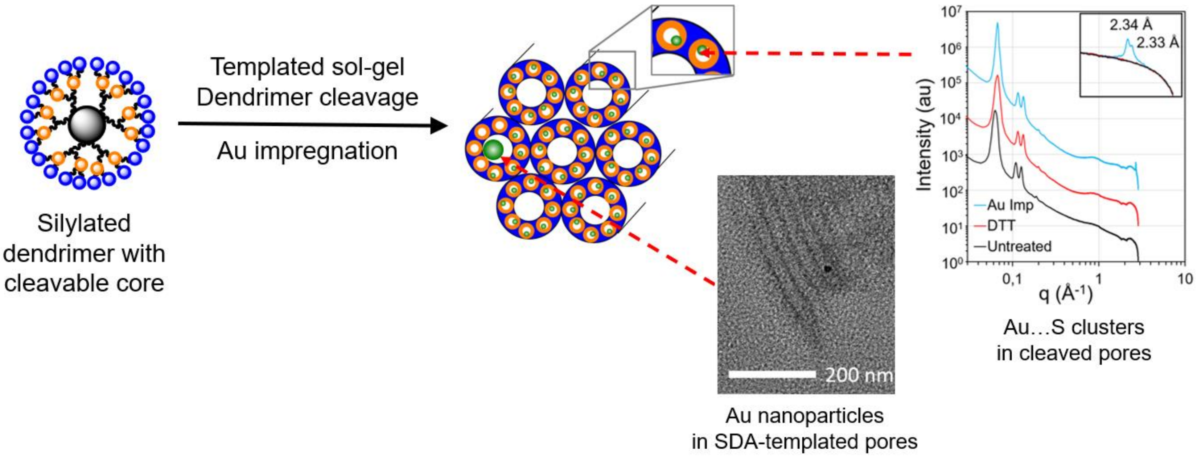

Figure 1: Gold clusters formation in thiol functionalized pore generated by dendrimer cleavage

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P067

SYNTHESIS AND STUDY OF MULTIFONCTIONAL NANOPARTICLES FOR IMAGING AND TREATMENT OF CANCER BY SPCCT

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ABSTRACT:

Cancer is one of the main cause of death in more than 130 countries [1]. In order to better treat this disease, the possibility to combine diagnosis and therapy has become a research field of growing interest [2].

Thanks to their optical, biological and chemical properties, rare earth fluoride nanoparticles (NPs) are relevant compounds for imaging and treatment in biomedical applications. Based on previous works on lanthanide fluoride nanocrystals [3] we developed terbium (III)-doped gadolinium fluoride NPs which act as contrast media for spectral CT scanner and show scintillation properties (emission of light under low energy X-rays excitation).

Spectral Photon Counting Computed Tomography (SPCCT) is a new imaging modality allowing energy discrimination with high spatial resolution. Its main asset is to map and quantify elements based on their K-edge. And it has been demonstrated that GdF_3 NPs have relevant characteristics to be used in the scope of such studies [4](**Figure 1**)

These scintillating systems, also allow treatment of deeply sedated tumors through a modern technique called X-ray photodynamic therapy (XPDT) (**Figure 1**). So, our objective is to functionalize these systems to have biocompatible agents with simultaneous imaging and treatment ability. This presentation will highlight the results obtained concerning the luminescent properties of NPs under UV and X-ray excitation and their behavior as a contrast agent. We will also describe the different strategies of multiple surface modification and their effects on these properties. Finally, the biocompability of the NPs will be discussed for further preclinical studies.

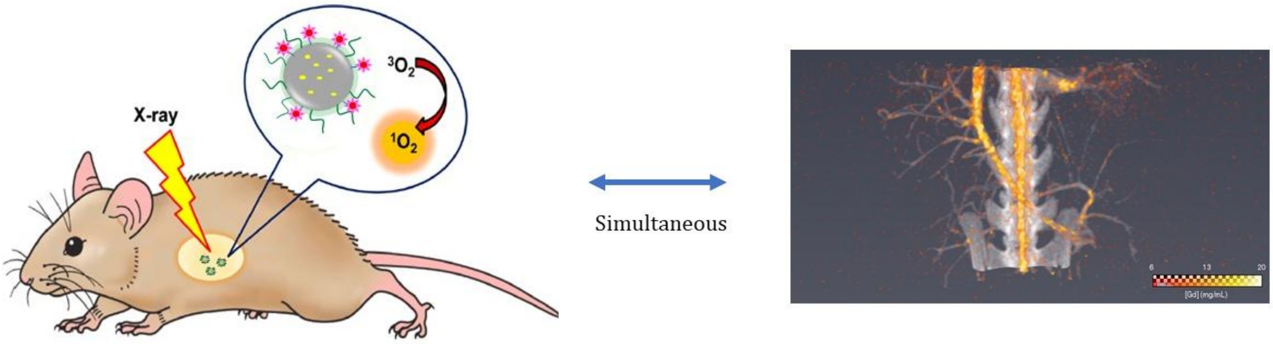

Figure 1 : XPDT principle : Low energy X-Ray provokes scintillation of the inorganic core of the NP. The radiation is absorbed by the photosensitizer to generate singlet oxygen combined with SPCCT imaging.

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METALLOPOLYMER HYBRID NANOCOMPOSITES: SYNTHESIS, STRUCTURE AND PROPERTIES

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ABSTRACT:

Organic/inorganic hybrid materials have rapidly become a fascinating new field of research in materials science. This interest results from unique combinations of organic and inorganic (metal, oxide, carbide and chalcogenide nanoparticles) component properties. These properties allow their use as magnetic materials for writing and storing information, heterogeneous catalysis, sensing devices, and also for medicine and biology [1–3].

We have developed several ways for producing metallopolymer nanocomposites: one-stage synthesis of metal nanoparticles and stabilizing polymer matrix – conjugated thermal (co)polymerization of metal-containing monomers and following thermolysis of forming polymers; in situ reduction of metal ions either in epoxy resins by curing agents or in thermoplastics by thermal decomposition of metal-containing precursor; and sol-gel synthesis [4-6].

Changing synthesis conditions (temperature, precursor ratio, stabilizing matrix) allows manufacturing nanoparticles of required size, shape and composition (for example, core-shell structures) with homogeneous distribution in stabilizing matrix, that is regulating functionality such as magnetic, catalytic, sensing, sorption properties.

The obtained metallopolymer nanocomposites exhibit improved mechanical and tribological properties, crack growth resistance, thermal stability, selective catalytic activity for hydrogenation of unsaturated organic compounds. Nanocomposites containing magnetoactive nanoparticles reveal ferro- and superparamagnetic properties. Their potential as effective magnetically tuned sorbents of heavy metals and radionuclides is being analyzed.

The reported study was performed in accordance with the state task, state registration No. AAAA-A19-119032690060-9

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P069

PORE-FILLING-DEPENDENT GUEST MOLECULE ALIGNMENT AND DEFECT FORMATION IN METAL-ORGANIC FRAMEWORK FILMS

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ABSTRACT:

The confined and well-oriented environment found in pores of metal-organic frameworks (MOFs) facilitates the alignment of guest molecules and provides unique interaction sites, thereby creating emergent properties beyond reach of either component in isolation. Thereby new applications for MOFs have opened up in the field of electronic, optics or sensing. The guest@MOF properties are strongly influenced by the degree of pore filling, i.e. the guest loading, the orientation of the guest as well as by structural changes of the host. However, a correlative study of these host-guest interactions as a function of the pore filling is required to further improve guest@MOF materials.

In this contribution, we present the simultaneous investigation of the pore filling, guest alignment and guest-induced structural changes in the three-dimensionally oriented $Cu_2(BDC)_2DABCO$ MOF film (BDC: 1,4-benzenedicarboxylate, DABCO: 1,4-diazabicyclo[2.2.2]octane; see Figure 1c and d for structure) using combined real-time polarization-dependent IR spectroscopy and gas adsorption measurements. The three-dimensionally aligned regular pores (along y-axis in Figure 1c) of $Cu_2(BDC)_2DABCO$ allowed to correlate the guest molecule's orientation and structural changes with the degree of pore filling at close to application conditions: Alignment of initially randomly oriented guest molecules is observed with increasing pore filling in a "sardine can" effect during adsorption from gas phase (compare Figure 1a). Simultaneously, the framework itself undergoes a reversible, guest molecule-dependent rotation of the aromatic linker and a linker detachment, which induces defects that are important sites for adsorption and reactivity.

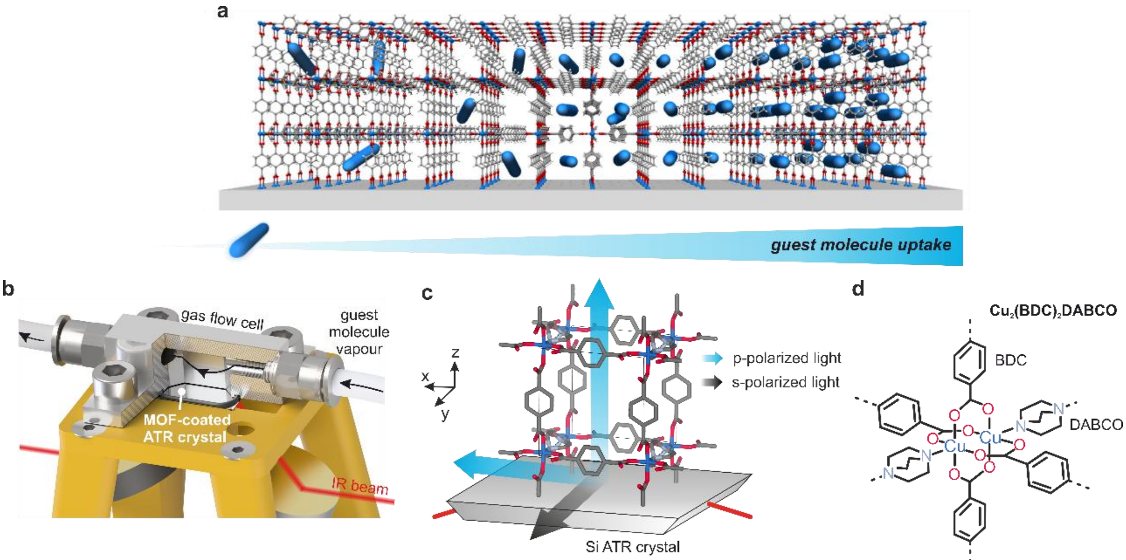

Figure 1 : Structure and orientation of guest MOF film during pore filling. a, The alignment of guest molecule in the framework is proportional to the degree of pore filling. b, FTIR-ATR spectroscopic setup. c, MOF film orientation on the Si ATR crystal and amplitudes of the evanescent wave interacting with the film. d, Cu paddle wheel surrounded by four BDC and two DABCO molecules form the $Cu_2(BDC)_2DABCO$ MOF substructure.

Deposition and Patterning of Metal-Organic Framework Thin Films via a Vertical Microfluidic Probe

Yujing Zhang[1], Victoria Chang[1], Hsin-Mei Kao[1], Tzer-Rurng Su[1], Eric Robert Rebarchik[1], Haori Yang[2], Cory Simon[1] and Chih-Hung Chang[1]

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Metal-organic frameworks (MOFs) have gained increasing attention due to their promising applications (e.g., gas storage/separations and catalysis) as nanoporous materials stemming from generally ultrahigh porosities and surface areas[1-4]. Recently, research has shifted to synthesize MOF thin films and micropatterns that enable new applications[5,6] (e.g., optoelectronics, smart coatings, and sensors). However, current deposition techniques could be improved by fine-tuning the reaction conditions, time, and temperature, all of which can be controlled using microfluidics.[7]

The present work describes developing an automated deposition system for MOF thin films onto various supports using a vertical microfluidic probe[8] (vMFP) directed by a pen-plotting instrument. Microfluidic devices take advantage of the physical and chemical properties of liquids at the microscale, allowing for less chemical volume and, therefore, lower cost while also shortening experiment time. MVPs enable us to take advantage of these benefits; they provide a non-contact, scanning microfluidic technology; used explicitly for chemical surface processing by confining nanoliter volumes of liquids between the head of the probe and the deposition surface. Using this system, MOF precursors' volumes can be confined through a reactor (i.e., the vMFP head) and onto support, reducing the reaction time for MOF thin film synthesis while increasing the yield. Attaching the vMFP to a pen-plotting device allows for precise deposition control, allowing for patterns and designs to be created with the MOF thin film, extending applications of the MOFs such as chemical sensors.

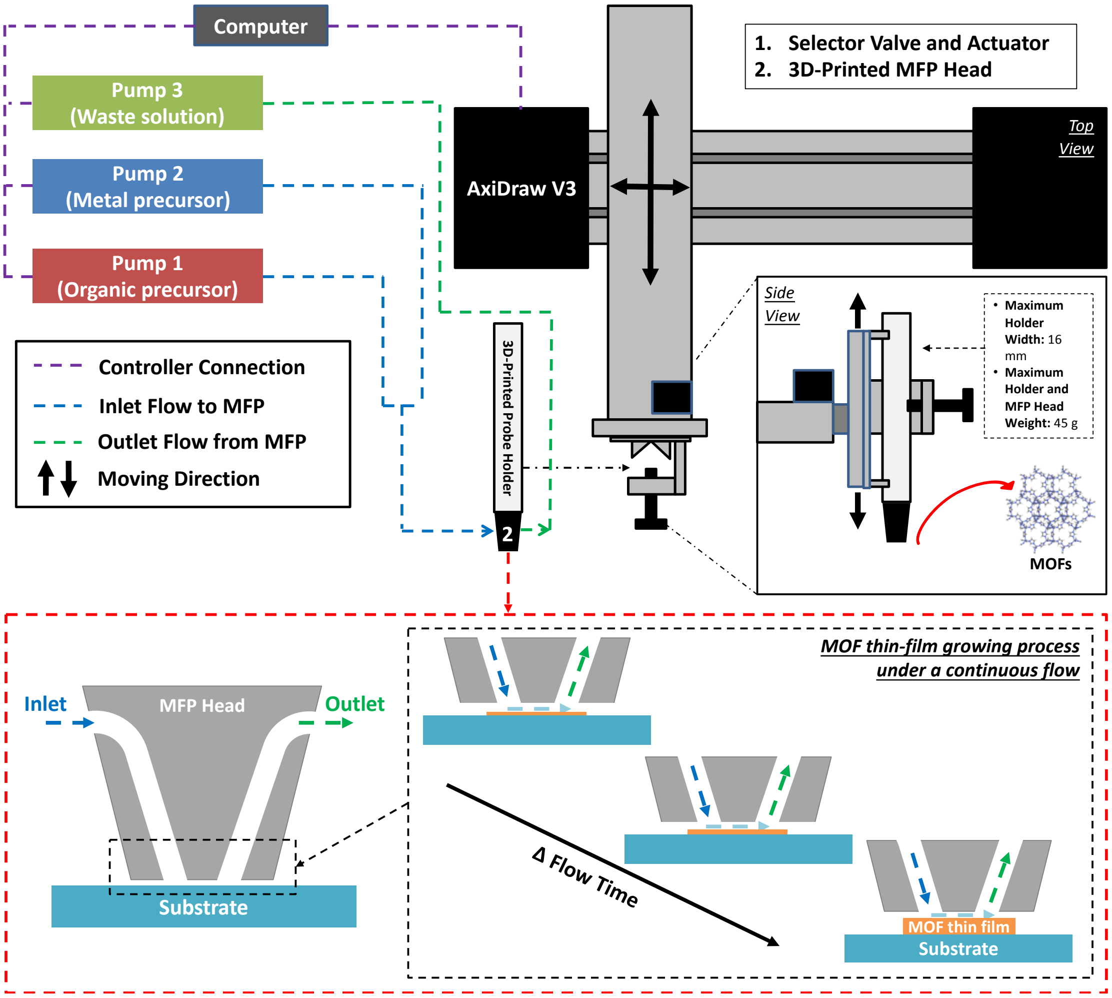

Figure 1 : Scheme 1 Illustration of the automated thin-film deposition system, assembled with a 3D-printed vMFP device in AxiDraw V3 pen plotter.

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P071

Synthesis of lead iodide hybrid perovskites: An In-Situ correlative study

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Ovidiu Ersen [1]

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ABSTRACT:

Hybrid Lead halide perovskites (HLHPs) of general formula APbX3 (A: organic cation; X: halogen) are one of the most studied classes of perovskites due to their great versatility and excellent performances in solar energy conversion[1]. Several synthesis methods allow obtaining LHPs including ligand-assisted reprecipitation (LARP)[2]. LARP approach is an easy pathway that presents the advantage of being done at room temperature by mixing two solvents with different polarities. The accurate knowledge of the formation process of these HLHPs, from the molecular precursors to the intermediate[3] and final 3D phases, is paramount to be able to optimize the performances of these very promising hybrid materials. In this framework, a correlative and in-situ study is required for shedding new lights on their formation and stability.

The first step is a classical analysis performed ex-situ (Figure 1-D). Using the LARP approach, we first obtained the presence of an intermediate (MAI-PbI_2-DMF) phase, identified by XRD, with a nanowire's morphology observed by TEM (Figure 1-E). After annealing at 80°C in ambient atmosphere, we observed a structural transition toward perovskite phase with a significant change in morphology, from nanowires to nanoplatelets (Figure 1-F). This transition was studied by in situ gas TEM and temperature-resolved XRD (Figure 1-G) which allowed us to directly assess the activation parameters and the kinetic of this structural transformation, as well as the subsequent decomposition of the perovskite phase into PbI_2. In addition, thanks to the recent development of the liquid phase TEM (LP-TEM), it is also possible to obtain a real time insight into the evolution of the reaction mixture and to observe what mechanisms occurs during the formation (Figure 1-C). Such dynamic information is particularly important for the monitoring of the nucleation and growth processes in which the structural characteristics of the final phase are very sensitive to subtle changes in the reaction conditions. The formation of the intermediate phase by LARP was thus monitored (Figure 1-B) which is, to our best knowledge, the first direct visualization at the nanoscale of such a metastable phase by TEM. By using experimental conditions which allow to mimic standard experiments achievable on a lab bench we were able, for example, to determine the influence of the toluene/DMF ratio on the synthesis (Figure 1-C). The as-obtained results will be correlated with synchrotron-based X-ray scattering data in order to obtain a phenomenological model able to explain all the observed phenomena.

P072

LP-TEM study + Synchrotron SAXS

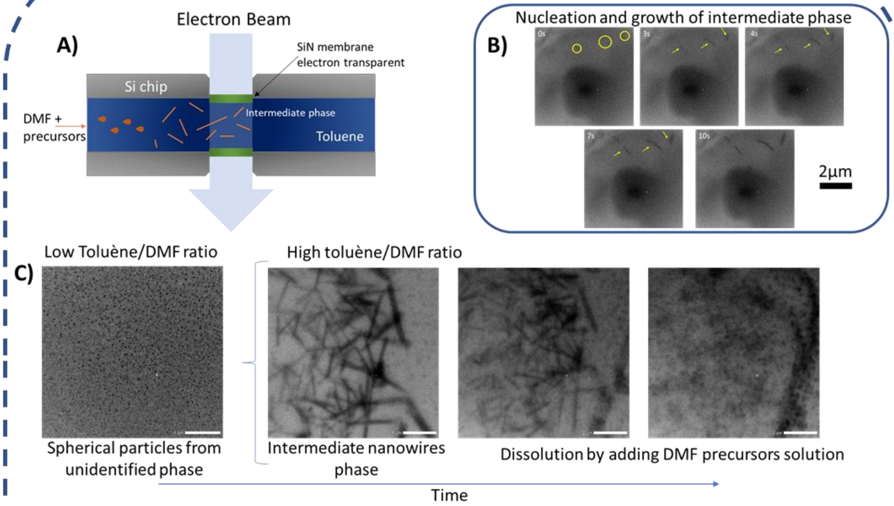
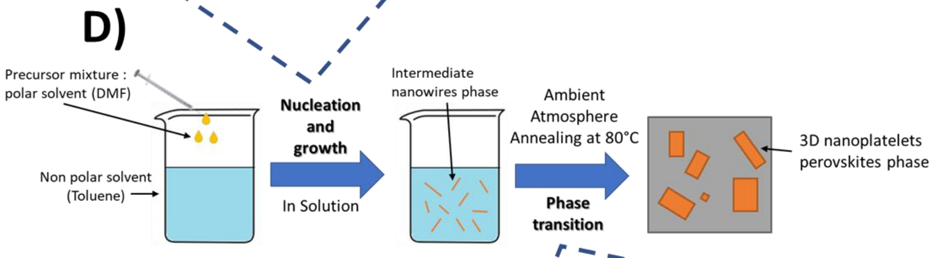


Figure. A) Scheme of the LP-TEM experimental cell. B) The box shows the fast nucleation and growth of the nanowires (10s). C) LP-TEM images. For a low Toluene/DMF we obtained spherical particles of unidentified phase. By adding a large amount of toluene, this ratio increases and allow us to get the nanowires in a dense liquid area. Adding more DMF precursors solution involve dissolution of these objects



Gas phase TEM study + Temperature-resolved XRD

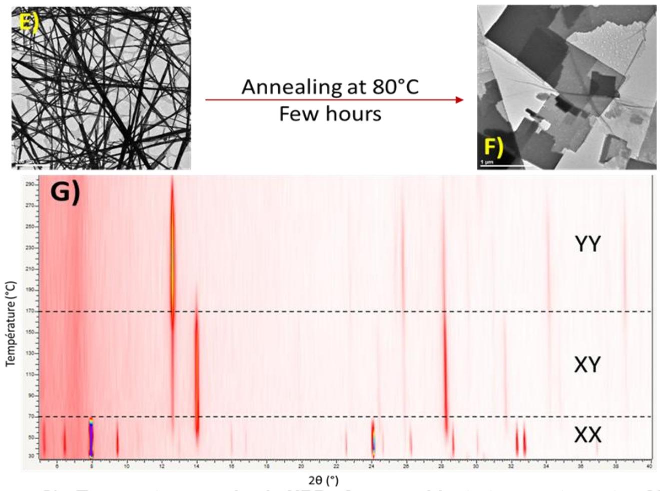


Figure. G) Temperature-resolved XRD from ambient temperature to 300°C. The intermediate phase peaks (area XX) disappear at 70°C to give way to the (110) and (220) perovskite peak (area XY). The disappearance of these peaks takes place in conjunction with the appearance of PbI$_2$ peaks (area YY), indicating the decomposition of the perovskite phase.

Figure 1: Correlative study of the nucleation and growth of the intermediate nanowires phase and the transition toward 3D nanoplatelets perovskites phase. D) Scheme of the LARP synthesis and phase transition for finally obtained the 3D perovskites.

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P073

RECYCLING OF HEAVY METALS BY USING AMINO-FUNCTIONALIZED MAGNETIC NANOPARTICLES

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ABSTRACT:

In this paper, specific and selective binding of heavy metal ions on stabilized amino-functionalized magnetic nanoparticles (γ-Fe_2O_3@NH_2 NPs) was performed. For this purpose, γ-Fe_2O_3@NH_2 NPs were characterized by thermogravimetric analysis (TGA), FT-IR spectroscopy, specific surface area (BET), transmission electron microscopy (TEM), EDXS analysis and zeta potential measurements. The adsorption of heavy metal ions was evaluated by determining adsorption efficiency (%) and capacity (mg/g) based on the atomic absorption spectroscopy (AAS) measurements for CrT, Pb^{2+} and Co^{2+} and inductively coupled plasma optical emission spectrometer (ICP-OES) measurements for Hg^{2+}. Effect of different adsorbent amounts (m_{ads}=20 / 45 / 90 mg) and the type of anions (NO_3^-, Cl^-, SO_4^{2-}) on adsorption efficiency was also tested. The desorption process of heavy metal ions was performed with 0.1 M HNO_3 and evaluated with AAS. Results show improvement of adsorption efficiency for CrT, Pb^{2+} and Hg^{2+} ions at pH 7 by 45 mg γ-Fe_2O_3@NH_2 NPs, and the sequence is as follows CrT > Hg^{2+} > Pb^{2+}, with the corresponding adsorption capacities 90.4 mg/g, 85.6 mg/g, 83.6 mg/g respectively. The adsorption of CrT ions was not affected by different anions. The desorption results show the possibility for reuse of γ-Fe_2O_3@NH_2 NPs with HNO_3, as the obtained desorption efficiency was 100% for Hg^{2+} ions, 96.7% for CrT, 91.3% for $Pb^{2+}$and 9.5% for Co^{2+} ions.

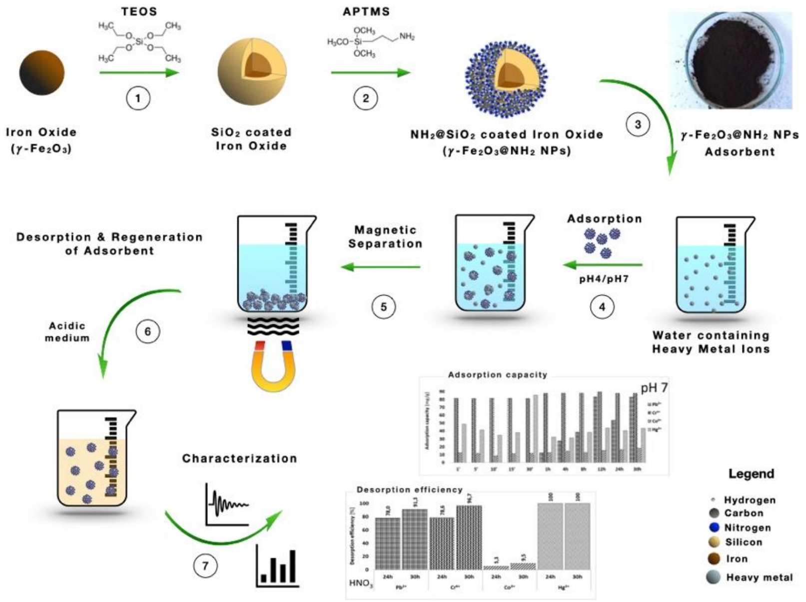

Figure 1 : Graphical Abstract

P074

CHARGE TRANSFER COMPLEXES IN POLYSILSESQUIOXANE GELS: A SUPRAMOLECULAR APPROACH

Thaisa B.F. Moraes [1, 2], **Gregoire J.-F. Demets** [2], **Denis Frath** [1], **Thomas Gibaud** [3], **Eduardo R. Triboni** [2], **Floris Chevallier** [1] **and Christophe Bucher** [1]

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Gels are made of large amounts of solvent trapped within a 3D molecular network. The structure and strength of the 3D network are the most critical parameters in determining the properties of the gel and their applications. [1-4] Physical gels are formed by self-assembly of low molecular weight gelators (LMWG) into a 3D supramolecular network. As the structure of the gel relies on dynamic non-covalent bonds, supramolecular gels are inherently very sensitive to stimuli and their properties can be easily modulated by external stimulations of a chemical or physical nature. [1,2] On the other hand, chemical gels, also referred as polymeric gels, are produced from monomers capable of structuring 3D networks by means of covalent cross-linked bonds leading to irreversible gels. [1-4]

Polysilsesquioxane gels based on naphthalene diimides (**NDI-PS**) exhibit unique electrochemical, photochemical and binding properties towards π-donor molecules (**D**). [3,4] The latter can potentially be entrapped within the 3D-network of **NDI-PS** gels through hydrogen-bonding and/or charge transfer (**CT**) interaction from the π-donor guest to the **NDI** π-acceptor units. [4] Herein, we show the general properties of **NDI-PS** gels towards different π-donors such as naphthalene ($\mathbf{D_1}$), 1,5-dihidroxynaphthale ($\mathbf{D_2}$), 1,5-diaminonaphthalene ($\mathbf{D_3}$), 1,5-alkoxynaphthalene ($\mathbf{D_4}$). The incorporation of donor guest ($\mathbf{D_n}$) has been developed at different stage of the sol-gel process to understand their influence onto the structural organization of the 3D-network and on the mobility of the guest through the gel. The photo- and electrochemical reduction of the **CT** gels were used as a strategy to produce multi-responsive systems.

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P075

ALTERING SILICA SURFACE PROPERTIES FOR SELECTIVE ADSORPTION TOWARDS REE AND LTM

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ABSTRACT:

With the EU's efforts to decarbonize its economy to increase renewable energy generation and the onset of e-mobility, the demand for various high-tech applications, including wind turbines and electric motors, is growing[1]. The primary component in these applications are strong magnets, i.e., FeNdB and CoSm, where rare-earth elements (REE) are present together with the late transition metals (LTM)[2]. Adsorption has gained scientific interest in separating those two groups of metals using different nano adsorbents with high adsorption capacity and selectivity. These properties arise from increased surface area compared to their macroscopic counterparts and the ability of surface modification with ligands to target specific metals.

We have successfully prepared silica nanoparticles by modified Stöber synthesis. Particles were functionalized using two different ligands under reflux conditions. Iodine-containing ligand served as an intermediate to produce aminated product to bind REE and polysulfide ligand to bind LTM. Adsorption and desorption tests were conducted, and reusability was calculated. These adsorbents forecasted an excellent potential for selective metal separation and purification.

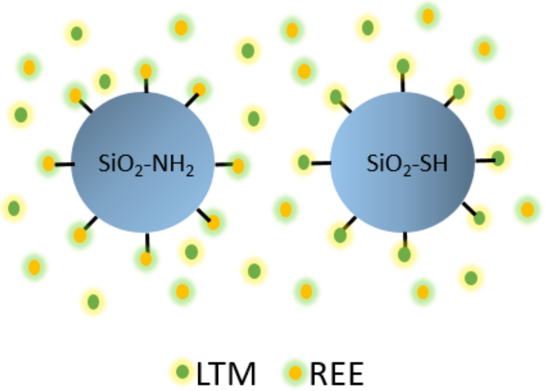

Figure 1 : Selective removal of REE and LTM using functionalized silica adsorbents

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P076

SOL-GEL APPROACHES FOR ELABORATION OF POROUS TITANIA-SUPPORTED TRANSITION METAL CATALYSTS

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Chemical reactions catalyzed by metal complexes have become one of the central tenets and instruments in the arsenal of modern organic synthesis. However, the homogeneous catalysts are expensive, difficult to separate from the products and cannot be easily reused, which is a major drawback for their industrial applications. Therefore, the immobilization of catalysts onto solid supports attracts growing interest.

This work is focused on the development of sol-gel approaches to reusable titania-supported catalysts with potential interest for industrial productions of fine chemicals. The immobilization of air-stable metal complexes with nitrogen ligands such as 1,10-phenanthroline and porphyrin was investigated by reason of their remarkable catalytic and photocatalytic properties (Fig. 1).[1-3] We explore different routes for immobilizing these complexes using titania as support and phosphonic acids as anchoring groups. This strategy combines several advantages including the strong covalent linkage of phosphonates to TiO_2 networks and excellent mechanical, thermal and chemical properties of titania. In particular, we were interested to control the porosity of the materials and prepare cost-effective catalysts with surface characteristics that are relatively close to those of mesoporous materials commonly used as heterogenized catalysts such as functionalized ordered silicas. In this regard, the immobilization of phosphonate-substituted 1,10-phenanthroline ligands and their copper(I) complexes was investigated in detail. First, materials were prepared by reacting ligands or their complexes with titanium isopropoxide according to the sol-gel process (Routes C and D, Fig. 1). Alternatively, these ligands and complexes were grafted onto the surface of mesoporous titanium oxide (S_{BET} = 650 $m^2\ g^{-1}$) (Routes A and B, Fig. 1). Then immobilization of Ru^{II} and Pd^{II} complexes with 1,10-phenanthrolines and Zn^{II}, Mn^{III} and In^{III} porphyrins was carried out to prepare porous heterogenized catalysts. Finally, the catalytic performance of the most porous materials was examined in the Huisgen cycloaddition, Sonogashira-type reactions and the photocatalytic oxidation of sulfides by molecular oxygen.

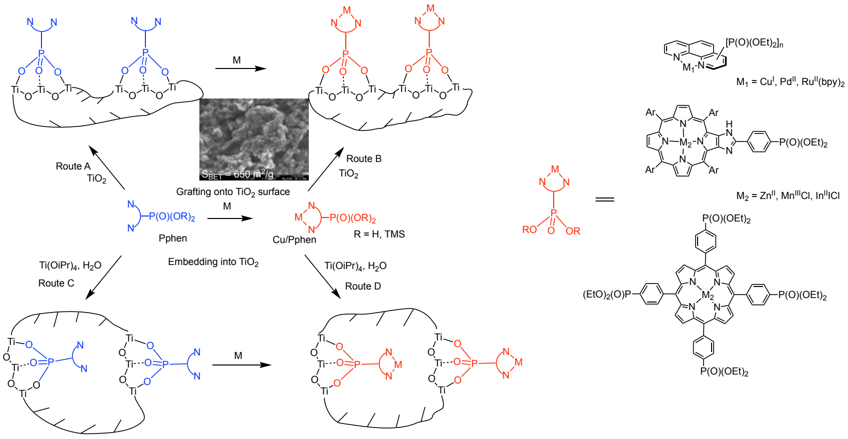

Figure 1 : Schematic representation of the immobilization of metal complexes with 1,10-phen-anthroline or porphyrin ligands according to the surface modification reaction (routes A and B) and direct sol-gel processes (routes C and D).

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Main Menu

Nano- and micro-structured materials

EFFECT OF CERIUM DOPED HYDROXYAPATITE NANOPARTICLES ON THE BIOLOGICAL PROPERTIES

Alina-Mihaela Prodan[1,2], Simona Liliana Iconaru[3], Steluta Carmen Ciobanu[3], Mihai-Valentin Predoi[4], Stefania Raita[5], Cristian Catalin Petre[6], Mircea Beuran[1,2], Daniela Predoi[3,*]

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ABSTRACT:

In the last years the cerium doped hydroxyapatite (Ce:HAp) coatings were very little investigated. The Ce:HAp composite coatings was obtained by dip coating method. The $Ca_{10-x}Ce_x(PO_4)_6(OH)_2$ with x_{Ce}=0.05, stable suspensions were obtained at room-temperature by an adapted sol-gel method. This research presented the stability of Ce:HAp gels from which the coatings were made were obtained. The stability of suspension was evaluated by dynamic light scattering, zeta potential and ultrasound measurements. Zeta potential and ultrasound measurements on the suspension of Ce-HAp composite coatings revealed a good stability. The value of stability parameters of Ce:HAp suspension obtained by ultrasound measurements was in good agreement with the value of bidistilled water used as reference fluid. The complex studied such as transmission electron microscopy, scanning electron microscopy, Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy were conducted on suspension and coatings. A uniform distribution of all the constituent elements on the surface Ce:HAp coating was observed. The optical spectroscopy, atomic force microscopy and metallographic examination on Ce:HAp composite coatings were also performed. Cell culture and MTT (3-[4,5-dimethylthiazol-2-yl]-2,5-diphenylte-2H-tetrazolium bromide) assay and antimicrobial studies were also conducted on Ce:HAp suspension and coating. The biological studies such as cell culture and MTT assays highlighted that the Ce:HAp suspension and coating have no negative effect on the cell viability and proliferation. The antimicrobial assays have demonstrated that both Ce:HAp suspension and 5Ce-HAp coating have successfully inhibited the development of CFU for gram-positive *Staphylococcus aureus* ATCC 25923, gram-negative *Escherichia coli* ATCC 25922 and fungal *Candida albicans* ATCC 90029. More of that, the antimicrobial assays showed that the Ce:HAp suspensions had a biocide effect against *E. coli* and *C. albicans* microbial strains after 72h of incubation.

Acknowledgments: This work was supported by the Romanian Ministry of Research and Innovation through the project PN-III-P2-2.1-PED-2019-0868 contract no. 467PED ⁄ 2020 and project PN-III-P2-2.1-PED-2019-1375 contract no. 331/PED/2020.

P078

FUNCTIONAL BLOCK COPOLYMERS FOR *IN-SITU* FUNCTIONALIZATION OF MESOPOROUS SILICA FILMS

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Nature provides the ultimate inspiration – able to direct, gate and selectively transport through pores and channels with technologically unreached performance. To approach this performance, the precision in nanoporous material design has to be significantly improved. For example, material architecture and structural as well as functional hierarchy have to be precisely designed. To do so nanoscale layer-wise material build up, e.g. using printing techniques for nanoporous structure formation in combination with *in-situ* functionalization approaches, is envisioned to allow precise structural and functional hierarchy design at the nanoscale.

Specifically, stimuli-responsive mesoporous silica films were prepared by evaporation-induced self-assembly through physical entrapment of functional block copolymers as structure directing agent, which simultaneously serve as functionalization of the mesopores. By this way highly filled pores with e.g. PS-*b*-PAA that exhibit remarkable gating ionic permselectivity with changes in pH[1], enabling the switching between cation- and anion-selectivity under basic and acid conditions, were achieved. Stimuli-responsive transport characteristic can also be observed in partly filled pores. Different examples of functional templates for *in-situ* functionalization and the resulting ionic permselectivity will be presented. Mesoporous films are characterized regarding their porosity and film thickness using ellipsometry, TEM and SEM. Ionic permselectivity is determined using cyclic voltammetry and correlated to porous structure and *in-situ* functionalization. Using functional templates for *in-situ* functionalization of mesoporous layers bears the potential for localized stimuli-responsive polymer functionalization within a precisely designed architecture[2] and fabrication of *in-situ* functionalized porous silica films by high throughput printing methods[3]. This direct and simple approach of *in-situ* functionalization of mesoporous silica using functional block copolymers is expected to be highly relevant for a variety of technologies based on molecular transport in nanoscale pores, such as sensing, separation, catalysis and energy conversion.

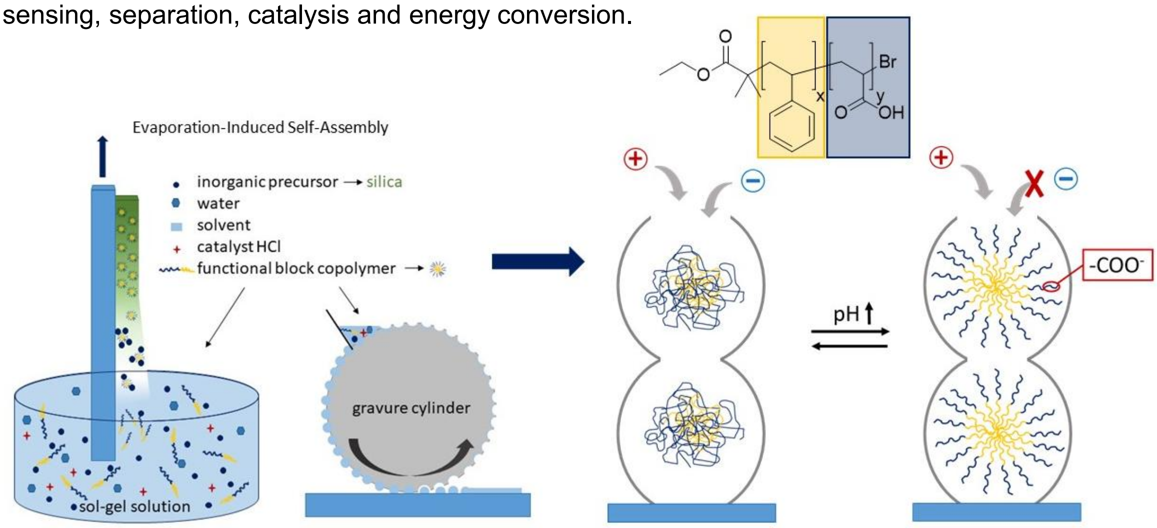

Figure 1 : Stimuli-responsive mesoporous silica thin films prepared in an one step procedure by Evaporation-Induced Self-Assembly (EISA) have achieved tunable ionic permselectivity, thereby demonstrating their high potential for developing multifunctional, complex architectures with to date unreached transport performances.

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P079

MESOPOROUS BIOACTIVE GLASS NANOPARTICLES AND HETEROSTRUCTURES FOR BONE REGENERATION

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ABSTRACT:

Bioactive glass nanoparticles are a promising material for bone tissue regeneration because when implanted, a carbonated hydroxyapatite (HAp) layer is quickly formed onto their surface, bonding them to natural bone tissues.[1] This mineralization process is accelerated by a large specific surface area and a high quantity of calcium ions inside the silica network, which are the main factors impacting the particles reactivity with body fluids.[2]

Mesoporous bioactive glass (MBG) nanoparticles obtained by soft chemistry are ideal for such application because of their large specific surface area. However, it is a challenge to synthesize them with both optimized porosity and calcium content, calcium ions being known to disturb the surfactant assembly during the synthesis and thus the final material porosity.[3] Therefore we systematically studied the impact of different synthesis parameters on MBG particles specific surface area and composition. Then, their bioactivity was assessed after immersion in Simulated Body Fluid (SBF) at 37°C. A faster HAp growth was found for the sample with the highest Ca content and the smallest specific surface area, indicating that the composition might predominate over the specific surface area when it comes to bioactivity kinetics.

Based on these results, γ-Fe_2O_3@MBG heterostructures have been synthesized by encapsulating magnetic nanoparticles within a MBG shell, in order to design a material suitable for simultaneous magnetic hyperthermia treatment[4] and bone regeneration in the case of bone cancer.

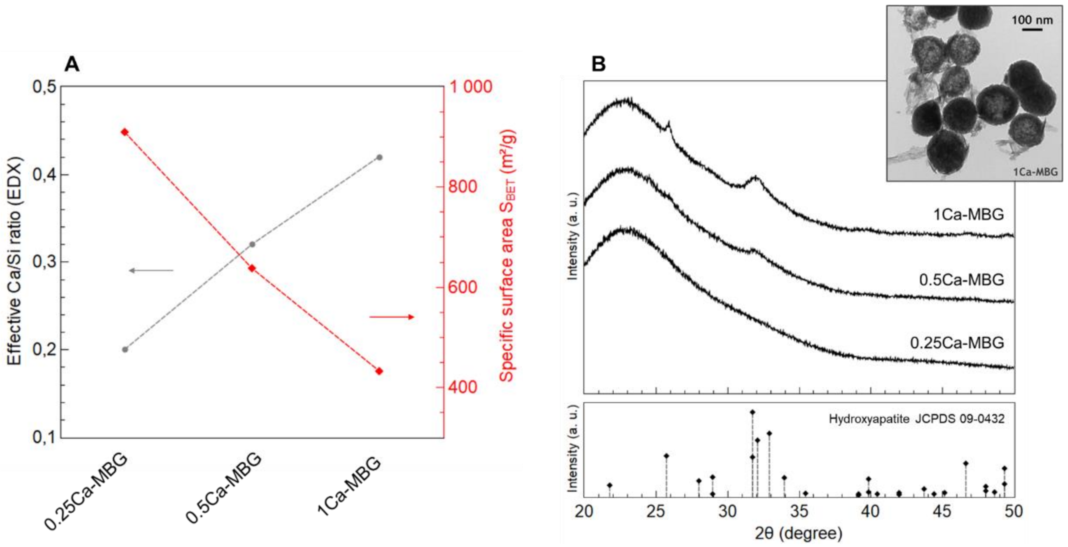

Figure 1 : Effective Ca/Si ratio and specific surface area for MBG nanoparticles synthesized with an initial Ca/Si ratio of 0.25, 0.5 or 1 (A) and XRD patterns of the MBG nanoparticles after immersion in SBF for 1 day, along with a TEM picture of the 1Ca-MBG sample (B)

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3D Printing of Ceramic Nanostructures by Two-Photon Lithography

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ABSTRACT:

Two-photon lithography is a potential route to produce high-resolution inorganic and hybrid materials at the nanoscale. Two-photon lithography has shown interesting potential on silica-based materials including hybrid functional structures[1]. In the case of ceramics nanofabrication, the large shrinkage due to the elimination of an important organic counterpart of the printed material during debinding/sintering remains a lock to further development of this technology. To limit this phenomenon, an original approach based on a composite resin incorporating 45 wt% ultrasmall (5 nm) nanoparticles is proposed[2]. Example illustrating the approach is to use zirconia nanoparticles and a zirconium acrylate precursor to process 3D zirconia microlattices and nanostructured optical surfaces. Interestingly, the nanoparticles are used both as seeds allowing control of the crystallographic phase formed during the calcination process and as structural stabilizing agent preventing important shrinkage of the printed ceramic. After 3D photolithography and pyrolysis, the weight and volume loss of the microstructures are drastically reduced as compared to similar systems processed with the reference resin without nanoparticles, and stable 3D microstructures of cubic zirconia are obtained with high spatial resolution. In the case of a patterned surface, the refractive index of 2.1 leads to a diffraction efficiency large enough to obtain microfocusing with linewidths of 0.1 µm, and the demonstration of a microlens array with a period as small as 0.8 µm.

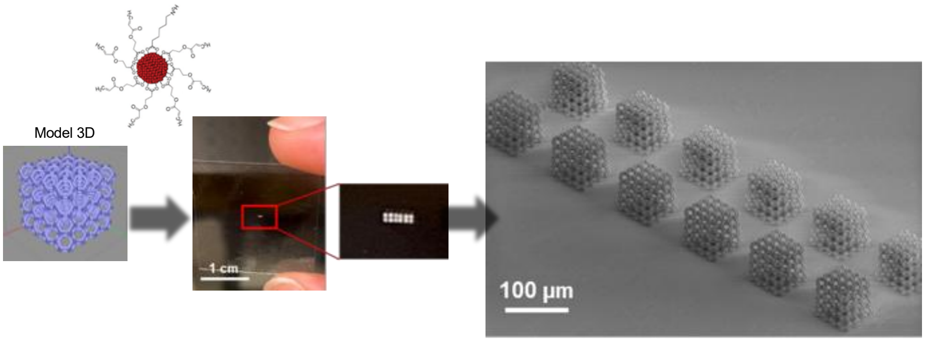

Figure 1 : Pure zirconia nanostructures obtained by two-photon lithography from functional nanoparticles

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Microstructure and colloidal stability of humic acids-bonded Fe_3O_4/APTES nanoparticles: effect of ambient conditions

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Nowadays, numerous researches are being performed to formulate nontoxic multifunctional magnetic materials possessing both high colloidal stability and high magnetization, but there is a demand in the prediction of chemical and colloidal stability in water solutions. Herein, for the first time, a series of silica-coated magnetite nanoparticles (MNPs) has been synthesized via sol-gel method with and without establishing an inert atmosphere during synthesis and then tested in terms of humic acids (HA) loading. The influence of ambient conditions on the microstructure, pH-dependent charging and HA loading of different silica-coated magnetite nanoparticles has been established. The XRD patterns show that the content of stiochiometric Fe3O4 decreases from 78.8% to 42.4 % at at inert and ambient atmosphere synthesis respectively. The most striking observation was the shift of MNPs isoelectric point from pH~ 7 to 3 with increasing HA up to reaching the complete reversal of zeta potential sign. This is result when the MNPs surface is completely covered by HA molecules, so this phenomenon is closely related to HA adsorption. The zeta potential data of MNPs can be used to predict the loading capacity for HA polyanions and hepls to understand way for new materials development with complexation ability of humic acids, with magnetic properties of nanoparticles and with the insolubility of silica gel.

P082

DIRECT DEEP UV MICRO- AND NANOSTRUCTURATION OF ZINC OXIDE THIN FILMS FROM NANOCRYSTALS COLLOIDS

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ABSTRACT:

Deep UV photolithography (193 nm) is a reference technique for micro/nanopatterning. The photoresists used, which are exclusively organic, have only a sacrificial role and do not contribute to the final properties of the material. This also adds a significant number of steps and the use of corrosive products in the process. In the case of metal oxides, several studies have already made it possible to considerably reduce the number of steps by directly structuring the material using hybrid photoresists [1, 2]. The produced oxide is however amorphous and a high-temperature annealing step is necessary to obtain the crystalline phase, ruling out the application to flexible substrates. A possible solution is to start directly from the oxide in the form of nanocrystals (NCs) and to assemble them. This approach has already been successfully tested in the case of quantum dots (CdS, CdSe) and for micrometric resolutions [3] but always involving toxic products. The objective is to propose an original direct nanopatterning approach using colloidal NCs as "building blocks" that assemble under the effect of DUV light, while being more environmentally friendly (abundance, toxicity).
Using FTIR and XPS spectrocopies, ellispsometry and XRD characterizations, it has been observed that the assembly of NCs results from a spatially controlled aggregation following the degradation of ligands on the surface without modification in size of the NCs. The study focuses mainly on ZnO but the wide variety of oxides that can be synthesised in the form of NCs by the sol-gel route encourages a generalisation of the process to other oxides.

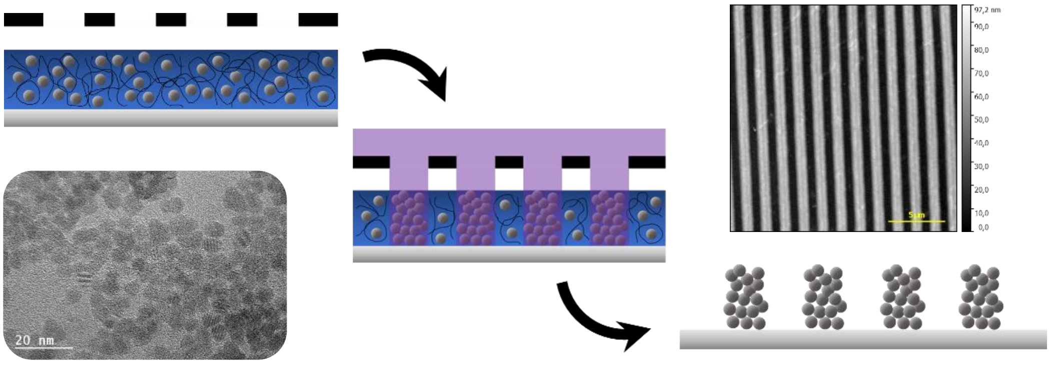

Figure 1 : Using sol-gel ZnO NCs as building blocks to pattern microstructures by DUV-induced ligand removal

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OPTIMIZATION OF FABRICATION OF CRYSTALLINE 3D MICRO/NANOSTRUCTURES BY LASER ADDITIVE MANUFACTURING

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In recent years, ceramics play an important role in science and industry as it can withstand immense thermal, mechanical, chemical, and other hazards. Therefore, the interest in suitable methods for the production of advanced free form 3D ceramics by combining laser lithography with calcination has been growing rapidly.

In this work the focus was on the study of an advanced method for transforming silicon and zirconium metalorganic 3D nano/micro-structures into pure crystalline 3D objects, by combining laser multi-photon lithography and calcination. We synthesized a series of organic-inorganic polymer precursors via the sol-gel method varying the molar ratio of silicon (Si) and zirconium (Zr) complexes (Si:Zr, where Si=9; 8; 7; 6; 5 and Zr=1; 2; 3; 4; 5) [1] and investigated the prospects of 3D fabrication of these materials. We have demonstrated that the phase purity of obtained structures is tunable and ranging from amorphous glass to polycrystalline phases (cristobalite, t-ZrO_2, m-ZrO_2, $ZrSiO_4$ (Figure 1)) depending on the initial precursor composition and annealing protocol. Furthermore, the study has shown that the crystalline structures retain their shape without any distortion. The sizes of single features in these objects vary from around 60 nm [2] to tens of micrometers with overall size going to cm scale. This puts laser direct writing and calcination combination as a viable methodology for 3D mesoscale structuring.

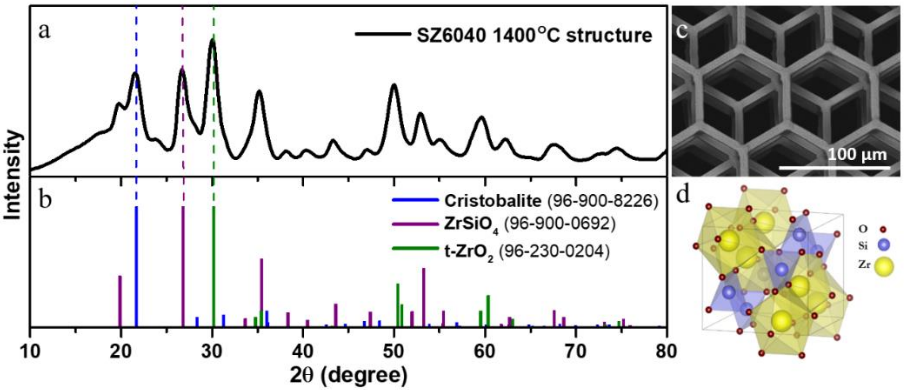

Figure 1 : (a) X-ray diffraction (XRD) analysis of the SZ6040 material heat-treated at 1400 °C for one hour in air at an ambient pressure; (b) reference patterns; (c) SEM image of SZ6040 material heat-treated at 1400 °C for one hour in air at an ambient pressure; (d) lattice structure of the $ZrSiO_4$.

Overall, results show multi-photon lithography and thermal post-processing as a powerful tandem for creating ultra-resilient multifunctional 3D micro-/nano-scale ceramic crystalline structures.

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P084

THE MODELING OF INFORMATION SINTESIS IN SILICA PRECIPITATION WITH CHIRAL MATRIX COMPOUND UNDER CONSTENT MAGNET

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ABSTRACT:

Attempt of obtaining the sorbent selective with respect to biologically active components of essential oil Eucalyptus dives has been made. The shifting of optical activity of Eucalyptus dives liquid oil under the chiral selective SiO_2 is observed, wich was obtained under chiral matrix. It is concluded that chiral selective effect is growing for the systems adsorption synthesis under the magnetic influence. The growth of magnetic field induction for 100 times (lg 100=2) leads to growth of nano-particle size approcsimality 2 – 3 times. The growth of chiral selective adsorption activity more than 2 times was observed. Obviously, there is a decrease in chiral-selective adsorption stereochemical difficulties.

This phenomenon can be identified as informational synthesis with a decrease in entropy. The growth of magnetic field is connected with growth of nano-size chiral pores by logarithm like quantity of information with number of selecting objects. The self-organization of chiral-selective adsorption centers is comparable with formation of active centers in enzyme.

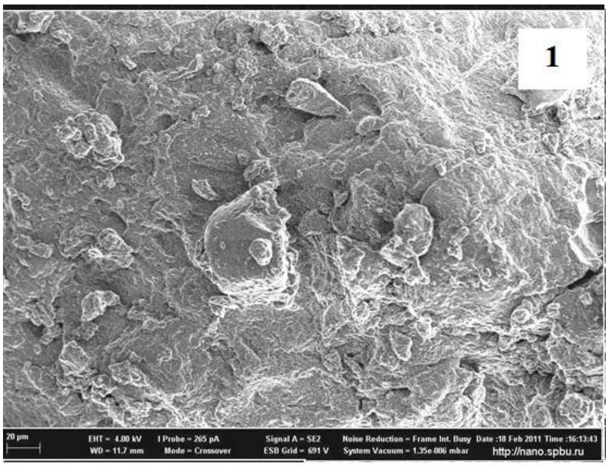

Figure 1 : Non-magnetic precipitation.

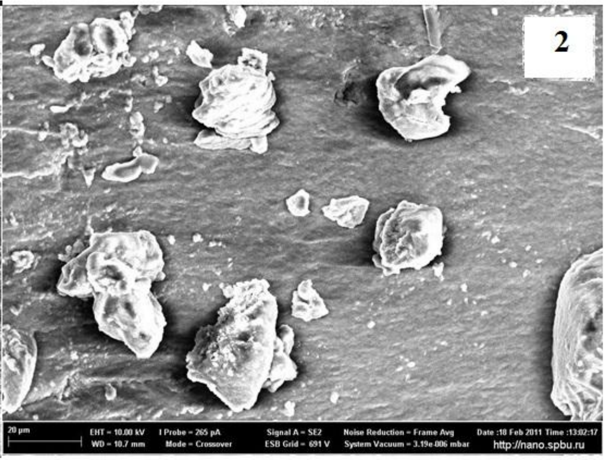

Figure 2 : Magnetic precipitation

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MODIFIED STÖBER PROCESS TO SYNTHESIZE SILICA PARTICLES OF CONTROLLED SIZE WITHOUT ORGANIC SOLVENT

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ABSTRACT:

One of the most studied processes to synthesize spherical silica nanoparticles of controllable sizes is the Stöber method [1]. An important drawback of the method is the large amount of organic solvents that is consumed.

In this presentation we investigate the role of ethanol in a typical Stöber method. Ethanol was found to improve the hydrolysis efficiency of tetraethyl orthosilicate (TEOS) and aids in dispersing the particles, which can increase the particle size of the obtained silica spheres and allows the reaction to form monodispersed silica particles rather than forming a gel.

In an attempt to circumvent the use of ethanol, we discovered a two-phase synthesis method to produce silica spheres in a controllable size without organic solvent. As long as the amount of reactants is controlled within a certain range, gels will not be formed, even without the organic solvent, allowing monodisperse silica spheres to be obtained. Similar to the Stöber method, the particle size of the silica spheres synthesized by this solvent-free method is controllable between tens of nm and 1 µm, and this modification has great potential to be extended to those synthesis processes of other advanced materials based on the Stöber process.

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MICROSTRUCTURED TiN LAYERS USING A ONE-STEP TiO_2 SOL-GEL LITHOGRAPHY PROCESS AND NITRIDATION PROCESS.

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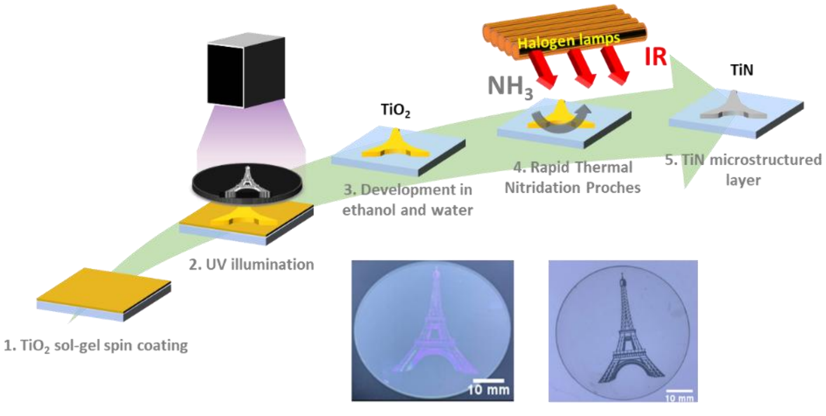
ABSTRACT:

The TiN patterned layers have a high number of applications, one of them being the miniaturization of optical components to control and manipulated light amplitude, phase and polarization [1]. By combining its plasmonic properties in the visible and infrared regions [2] with a microstructuration, a good metasurface is obtained to applications in plasmonic resonances, wavelength filtering, etc.

Fabricate TiN micro or nano structured surfaces is a challenge : the high melting point (>2900°C) [2], the good chemical stability [3] and the hardness [4] of this material make the patterning difficult. Some authors were realized TiN microstructured surfaces using the bottom-up technique that required a lot of sacrificial layers and etching process [5]. This method use multiple steps which make the process difficult to implement and time-consuming.

In this work, the authors show another recent method which consists in a direct fabrication process to give a TiN micro/nanostructured surface. In a first step, a TiO_2 sol-gel photo-patternable thin film is microstructured before a conversion into TiN using a rapid thermal nitridation process in an ammonia atmosphere. The microstructured films were characterized by Raman Spectroscopy, X-ray diffraction and atomic force microscope (AFM).



TiO_2 TiN

Figure 1: Microstructuration and nitridation process to fabricate TiN microstructured surface.

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P087

Interplay of solid-liquid interactions and anisotropic aggregation in solution. The case study of boehmite.

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ABSTRACT:

Nanoscale anisotropic materials appear in a wide variety of applications (photocatalysis, liquid crystals, …). The design of these objects is also key for tuning the texture of porous materials, since the aspect ratio of the involved nanoparticles is known to affect their stacking in the final material and thus the porosity formation. A very well-known example of this is the preparation of boehmite based alumina supports in catalysis: the stacking of nanorods allows for the formation of alumina carriers with high surface area and pore volumes. However, the initial anisotropic object is not always easy to obtain and synthetic strategies must be specially developed when selected structures do not naturally (thermodynamically) lead to anisotropic particles. In this work we carried out a combined experimental and theoretical study on the formation of boehmite nanorods in aqueous hydrothermal conditions[1]. Boehmite nanorods with a width of about 10 nm and more than 100 nm in length were obtained from Al(**III**) molecular precursors at 170 °C. Electron diffraction studies show that the crystallites are oriented in the nanorods with a [001] preferential growth direction, and from DFT calculations we infer that differences in interface solid-liquid stabilization energies, computed for each nanocrystal facet, are the driving force of this anisotropic aggregation. Besides, the solid-liquid interface energies in this work are computed as a function of the solvent dielectric constant. In our work, this enabled us to analyze our results obtained at different hydrothermal conditions. Moreover, in this presentation, we show proof that this descriptor can be used to rationalize similar results obtained with different solvents. Therefore, the conclusions from our study are worth the attention of other fields, as we manage to propose a consolidated mechanism of γ-AlOOH boehmite nanorods formation with concepts and descriptors that may be invoked in a wide variety of synthesis methods.

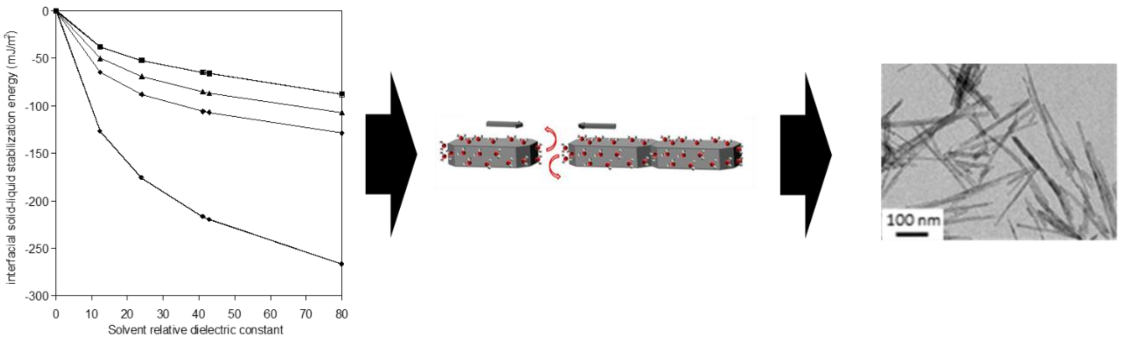

Figure: Relationship between computed solid-liquid interface energies (left), the inferred aggregation mechanism and the observed nanoparticles. Adapted from reference 1.

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P088

POLYUREA XEROGEL FOR PRECISE CONTROL OVER DICLOFENAC DRUG RELEASE

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ABSTRACT

The class of polymers known as polyurea have been widely used in the fields for building, packaging, and coatings due to their exceptional properties. Polyureas have been demonstrated high mechanical performances and are commonly used as foams, coating, fibers, elastomers, adhesives, and sealants because the wide polymeric/poliisocyanates precursors allow to obtain distinct materials presenting intermolecular interaction between polyurea chains.[1,2] In this study, a polyurea xerogel (PolyU) was synthesized and applied as a versatile drug carrier. The PolyU matrix provides a high drug loading and offers a tuning over diclofenac drug (DCF) release profile. A simple one-pot reaction of an amino-terminated-polyether-PEO and a crosslinker hexamethylene diisocyanate trimer-HDI allow us to obtain the polymeric networks. The gelation time during the sol-gel reactions (hydrolysis and condensation) can be modulated from minutes to hours by using solvent to achieve a decrease of reactivity between amine groups from PEO with isocyanate from HDI crosslinker. The interactions betweem PolyU networks and DCF was in depth evaluated by Fourier Transform Infrared Spectroscopy (FTIR), small angle X-ray scattering (SAXS) and computational studies. Analysis performed by differential scanning calorimetry (DSC) have confirmed the inhibition of crystalline moities of PEO by drug interactions with the xerogel. Citotoxicity assay (XTT) demostrated that PolyU did not causes changes in CHO-K1 cell response. A precise control over DCF was demostrated by the judicious choice of the drug loaded into PolyU matrix. The use of this class of polyurea containing drug open positive perspectives finding applications from drug delivery systems, encapsulation for food formulation, beverages and cosmectics.

Acknowledgements: Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – (CAPES) – Finance Code 001, Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) – n° 306271/2017-6, Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP n° 2019/17860-9.

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P089

HYDROTHERMAL SYNTHESIS OF Sr-Cr-Fe HYDROGARNET POLYHEDRA AND THEIR CONVERSION TO POROUS $SrCr_{1-x}Fe_xO_{3-\delta}$ PEROVSKITE

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ABSTRACT:

Simultaneous control of the crystal phase and materials morphology is important to develop new functional ceramics. In view of the morphological control, the solution processes have been extensively studied for a variety of ceramics. In the previous research, the $Ca_3Al_2(OH)_{12}$ hydrogarnet microcubes were prepared via a solution process, which were subsequently calcined in air resulting in porous mayenite particles via the topotactic conversion.[1] It was also revealed that the porous $SrFeO_{3-\delta}$ perovskite particles can be obtained from the $Sr_3Fe_2(OH)_{12}$ hydrogarnet precursor by the same approach. Upon heating under inert atmosphere, however, $SrFeO_{3-\delta}$ perovskite transforms into brownmillerite structure which has the lower ionic and electronic conductivity than perovskite.

In this study, we have performed the partial substitution of Cr^{3+} for Fe^{3+} in the perovskite aiming at the improvement of thermal stability.[2] For this purpose, we have prepared the polyhedral $Sr_3(Cr,Fe)_2(OH)_{12}$ hydrogarnet crystallites with varied Cr/Fe ratios via the hydrothermal reaction. Figure 1 shows the SEM-EDX elemental mapping images of the sample prepared with Cr/Fe=1/9, which confirms the well-defined polyhedral crystallites with relatively narrow size distribution of approximately 10 μm as well as the homogeneous distribution of Cr. The hydrogarnet precursors were phase-separated into the perovskite phase and $SrCO_3$ as shown in Figure 2. The following extraction process of $SrCO_3$ from the calcined sample resulted in the single-phase perovskite. In addition, the mesopores were formed by the extraction while the polyhedral morphology remained intact. The porous Cr-substituted perovskite polyhedral showed the improved thermal stability under N_2 atmosphere up to 600 ºC.

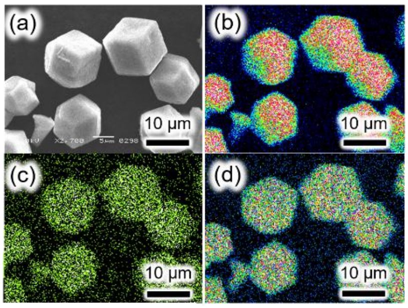

Figure 1: (a) SEM and (b-d) EDX elemental mapping images of the $Sr_3(Fe,Cr)_2(OH)_{12}$ hydrogarnet particles: (b) Sr, (c) Fe, (d) Cr.

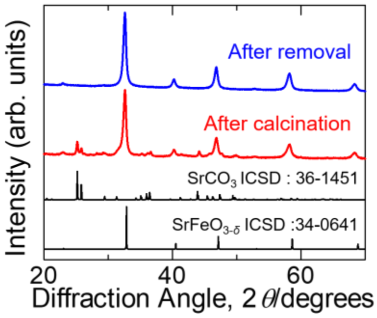

Figure 2 : XRD patterns of the calcined hydrogarnet particles (red) and the particles with $SrCO_3$ removed (blue)

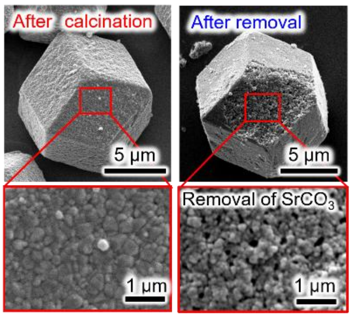

Figure 3: SEM images of the calcined hydrogarnet particles (left) and the $SrCO_3$-extracted particles (right).

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P090

Preparation and application of photothermal responsive photonic gels

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ABSTRACT:

Photonic crystals are composed of two or more materials with different refractive indices in an orderly arrangement of micro-nano structures. Photonic materials have received extensive attention due to their brilliant structural colors and unique photonic band gaps. In recent years, researchers have introduced smart responsive materials into photonic crystals to obtain responsiveness photonic materials. When stimulated by the external environment, the photonic structure changes, causing the structural color to change. Therefore, it has broad prospects in the fields of pigment [1], sensing [2], anti-counterfeiting [3], and so on. However, the angle dependence of traditional photonic crystals limits its accuracy in the field of chromaticity sensing and detection. In addition, although the angle-independent structural color can be obtained by destroying the long-range order structure, there are still problems such as photobleaching and color saturation. Therefore, the development of responsive amorphous photonic materials is of great significance. In this paper, a photothermal responsive amorphous photonic gel is prepared. As shown in Figure 1a, the photothermal responsive building blocks takes silica nanoparticles as the core, and sequentially covers the melanin layer with photothermal conversion and absorption of incoherent scattered light, and the temperature-sensitive hydrogel layer, and finally assembles into an amorphous photonic crystal. When irradiated by near-infrared light, the melanin layer of photonic gels converts light energy into heat energy (Figure 1b), the temperature-sensitive hydrogel layer shrinks by heat, the spacing of the building blocks changes (Figure 1c), and finally, the photonic band gap shifts. The photothermal responsive photonic gel has been successfully constructed, and it is hopeful that it will be widely used in the field of sensing and anti-counterfeiting.

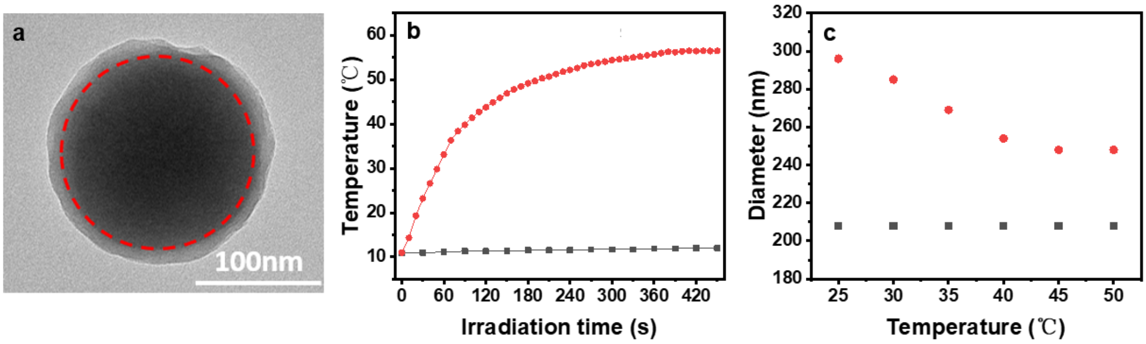

Figure 1 (a) TEM images of photothermal responsive building blocks; (b) Temperature change trend of photothermal responsive photonic gels (red dot) and ordinary photonic gels (black dot) under near-infrared light (1W/cm^2); (c) The size change trend of photothermal responsive building blocks (red dot) and silica nanoparticles (black dot) at different temperatures.

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The spontaneous supramolecular chiral inversion caused by thioether bond activated transformation between J- and H-aggregation

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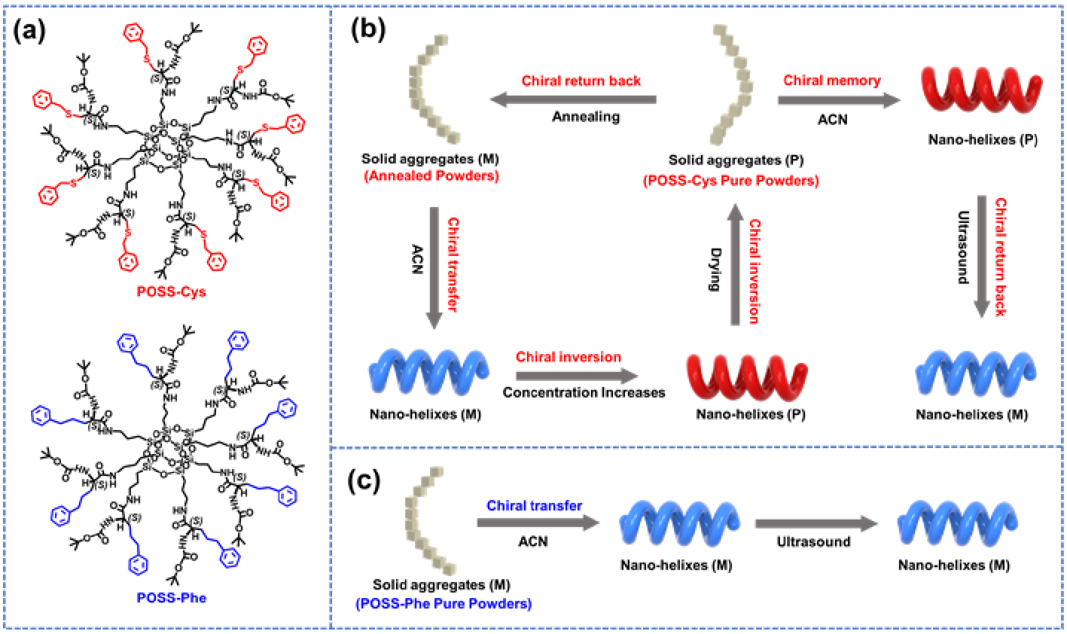
ABSTRACT:

The transformation between H- and J-aggregations in supramolecu-lar chiral self-assembly could induce variable helical nanostructures with unintentional chiral inversions, which is uncontrollable and on a superficial understanding in non-isomerization systems. Herein, we report a controllable supramolecular chiral inversion through a thi-oether bond activated transformation between J- and H-aggregation in polyhedral oligomeric silsesquioxane (POSS) based dendrimers. In dendrimer, the flexible inactive chromophores linkage thioether bond promotes the predictable transformation of π- aggregation and cause the chiral inversion with ultrasound, densify or annealing applied. What's more, the inversed chirality can be memorized and transferred from solutions to solid powers and further assembled nano-helixes even after heating-cooling self-assembly, which is attribute to the close-knit per-aggregation of dendrimers impede the transfer of inherent molecular chirality. Only apply the ultrasonication to assemblies or annealing process to solid powders, the J-aggregation could exchange to H-aggregation with the inversed handedness return back to inherent chirality. This research allows decipher the chiral assembly rules in π-conjugated building blocks and accelerates the development of controllable self-assembly.



Scheme 1. (a) The chemical structure of POSS-Cys and POSS-Hpy. (b), (c) are the schematic illustration of the supramolecular chiral assembly of POSS-Cys and POSS-Phe: the chiral inversion, chiral transfer and chiral memory.

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P092

ANTI-COUNTERFEITING LASER PRINTING ON PLASMONIC METASURFACES

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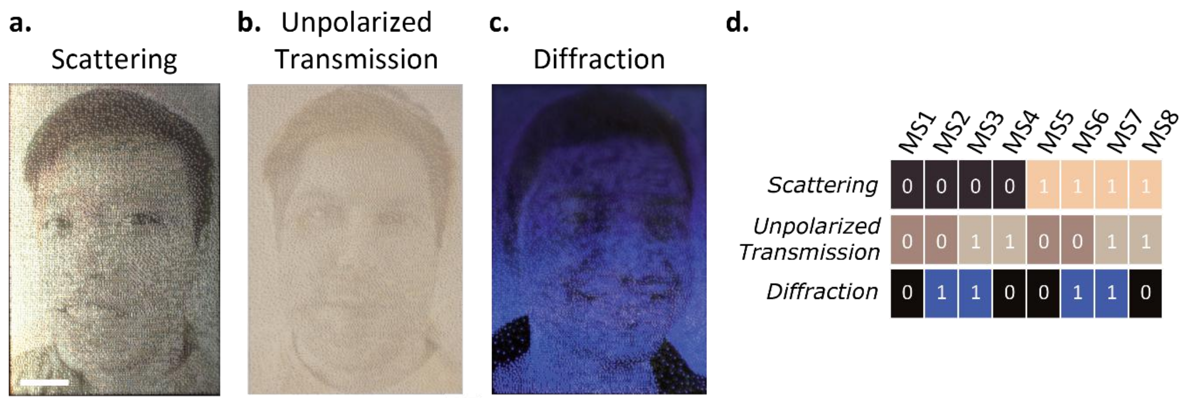
ABSTRACT:

Plasmonic metasurfaces enable image multiplexing by displaying different images when altering the conditions of observation. Continuous and femtosecond laser irradiations of Ag:TiO2 nanocomposite films have been shown to produce a wide range of visual effects, from plasmonic absorption colors with reflection/transmission dichroism, to diffraction by embedded nanoparticle gratings and polarization-dependent dichroism. Nanosecond laser scanning enables faster processing of large areas while offering the same kind of visual effects. Here, ns laser processing is used to produce centimeter-sized images that can be used as anti-counterfeiting security features [1]. The latter are based on multiplexed image printing and relies on the ability to identify metasurfaces that form logical color trees between different modes of observations within databases of thousands of metasurfaces (Fig. 1d). This enables us to produce several proofs of concept demonstrating different kinds of multiplexing. Fig.1 shows 3 demultiplexed images observed under white light in “scattering”, “unpolarized transmission” and “diffraction” on a single metasurface printed by ns laser.



	MS1	MS2	MS3	MS4	MS5	MS6	MS7	MS8
Scattering	0	0	0	0	1	1	1	1
Unpolarized Transmission	0	0	1	1	0	0	1	1
Diffraction	0	1	1	0	0	1	1	0

Figure 1 : Three-image multiplexing allowing naked eye observation (a) Color photograph of the sample taken in mode “scattering”. (b) Color photograph of the same sample taken in mode “unpolarized transmission” (d) Color photograph of the same sample taken in mode “diffraction” (d) Corresponding logical color tree found by the color-search algorithm. The length of the scale bar is 2.5 mm and is the same for all images.

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P093

Evaluation of thermal sensitivity as a function of phonon energy in Nd^{3+}/Yb^{3+} codoped oxide materials produced by modified Pechini method

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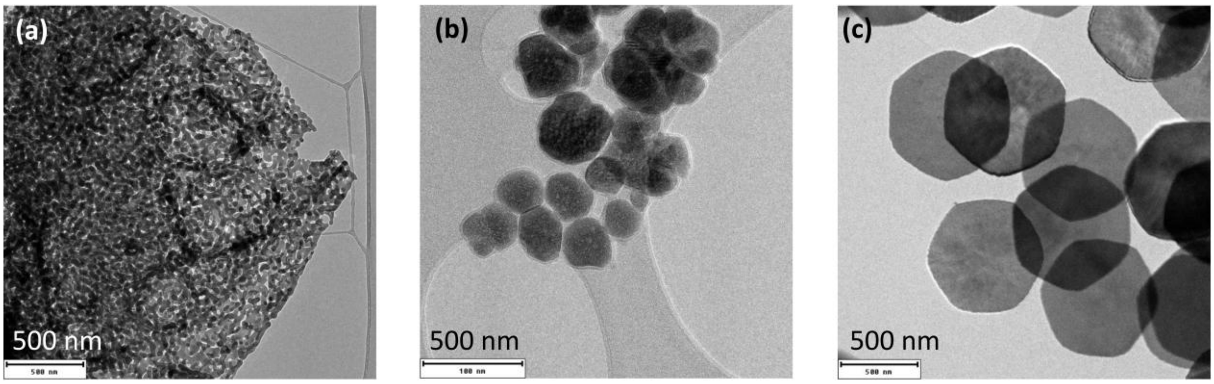
ABSTRACT:

The research on lanthanide-doped luminescent nanocrystals has great relevance in biomedicine thanks to the capacity of such nanomaterials to emit light in the near-infrared range allowing bio-imaging and potentially in thermal sensing. In this latter field, systems doped with Nd^{3+} and Yb^{3+} stand out as they have possibility for down- and up- conversion energy luminescence and accentuated and discriminated emission and excitation lines within the biological windows (i.e. in the near-infrared range) and thermally coupled emission levels, essential for thermal sensing [1,2,3]. This work aims to investigate how the thermal sensitivity of different oxide materials is affected by the host matrix when codoped with Nd^{3+} and Yb^{3+} ions.

First, due to its generic nature and synthesis flexibility, the polymeric precursor method – modified Pechini method - was chosen to synthesize several nanostructured compounds in order to screen the thermometry properties of several oxides at the nanometer scale: Y_2O_3, $Y_2Ge_2O_7$, $Y_3Al_5O_{12}$, Y_3BO_6, YBO_3 and $YAl_3(BO_3)_4$ (Figure (a)). Typically, the annealing conditions of the dry resins obtained by calcination under a controlled oxygen atmosphere were adjusted in time (between 3 and 10 min) and temperature (around 900-1100 °C), as evidenced by Differential Thermal Analysis (DTA), X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM). The luminescence signal of the different matrices, studied first in single Nd^{3+}-doped samples, was found optimal between 0.25 and 1 mol.% Nd^{3+} according to the crystal structure. Samples codoped with Nd^{3+}, Yb^{3+} were then synthesized according to the same process and their luminescence properties were measured, in particular with temperature variation, to assess their thermal sensitivity. This study allows us to understand the effects of cross-relaxation and lattice vibration involved in the temperature-dependent energy transfer process between the Nd^{3+} and Yb^{3+} doping ions.

Second, after this screening, the compounds with the most promising thermal sensitivity were elaborated by solvothermal method to obtain individual nanocrystals that can be used for *in vivo* measurements [4]. Well-crystallized 50-nm sized $Y_3Al_5O_{12}$ and larger YBO_3 nanocrystals have been obtained under mild pressure (200 bar) and temperature (200-300 °C), Figures (b)-(c), while their luminescence properties and thermal sensitivity are under study.



High magnification TEM images of nanoparticles of a) $Y_3Al_5O_{12}$ obtained by modified Pechini method and b) $Y_3Al_5O_{12}$ and c) YBO_3 particles by solvothermal method.

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PREPARATION AND INVESTIGATION OF OXIDE SYSTEMS BASED ON MAGNESIUM OXIDE FOR REDOX PROCESSES

Timofey M. Karnaukhov[1,2], Aleksey A. Vedyagin[1], Svetlana V. Cherepanova[1,2], Vladimir O. Stoyanovskii[1], Grigory B. Veselov[1,2]

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Sol-gel prepared magnesium oxide is perspective support for catalysts, sorbents, and oxygen carriers due to its high dispersion, developed mesoporous structure, and noticeable thermal stability. These features allow maintaining the desired properties of the active component introduced into the MgO-based matrix during prolonged redox and thermal treatments [1]. Moreover, magnesium oxide can form joint phases with oxides of many metals in a wide concentration range. This feature provides ample opportunities for a controllable modification of the redox behavior of these two-component oxide systems. The sol-gel method allows introducing the precursors already at the gel-forming stage, which provides a uniform distribution of the components within the sample [2].

In the present study, nanostructured M_xO_y–MgO samples (M = Co, Fe, Ni, Cu, Ni+Mo) were synthesized using a sol-gel approach [3-6]. The phase composition and texture of the samples were carefully studied and characterized using a complex of physicochemical methods: nitrogen adsorption, electron microscopy, XRD, EDS, and Mössbauer spectroscopy.

Redox properties of the prepared oxide samples were investigated by TPR and in situ XRD techniques. Magnesium oxide affects the properties of the second component significantly. On the one hand, the MgO matrix retains the particle size of the second component. On the other hand, the strong interaction of the oxides significantly modifies the redox behavior of the samples.

Thus, this work presents several new oxide materials based on a highly dispersed MgO support. We carefully characterized textural, structural, and phase features of the samples. Redox behavior of the prepared samples has been studied in detail, and the accompanying structural and phase transformations have been revealed and described. The used physicochemical methods provide essential information to establish the relationship between the phase composition, textural features, and redox properties of the prepared oxide materials.

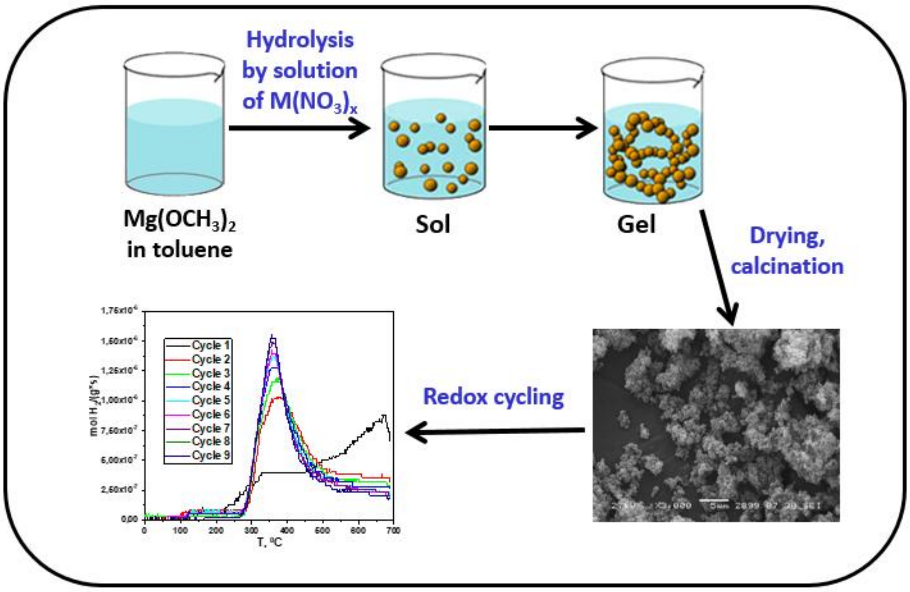

Fig. 1. Graphical abstract.

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Metal and metal oxide nanoparticles for biogas culture applications

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Biogas is an interesting resource towards the path of a sustainable society. Metal derived nanoparticles (NP) have been investigated as a potential aid for the biogas producing microbial cultures (1). In this work we produced a library of gold and metal oxide nanoparticles and also hybrid gold-metal oxide materials. The particles were evaluated for the possibility to enhance methane production using specifically syntrophic acetate oxidising culture. For the latter, the synthesis exploited a seed mediated growth approach. The starting material was composed of spherical gold nanoparticles produced with the Turkevich method (2). The "green" water-based metal oxide precursor solutions were applied as reducing agents in conjunction with auric acid and amino acid surfactants as shape-directing agents following the ideas expressed in the work of Avila-Alejo *et al.*(3). The nanoparticles were then characterized with techniques such as SEM-EDS, NanoSight, DLS, AFM, UV-Vis spectroscopy etc. Evaluation of the effects of NP on biogas production demonstrated possibility to enhance greatly the productivity of the process.

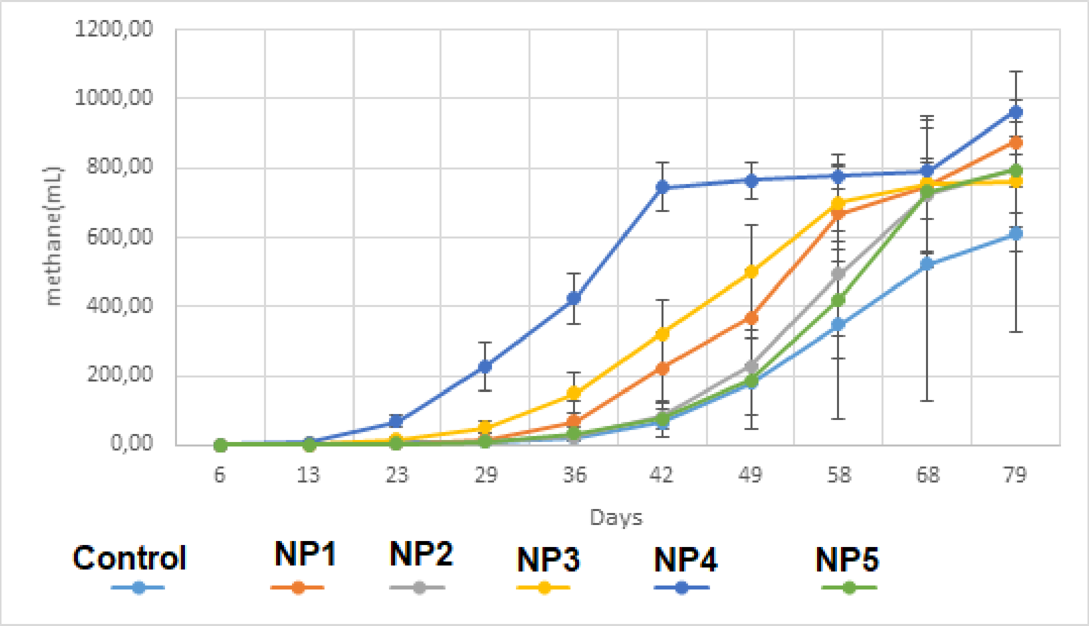

Figure 1 : Accumulate methane production from cultures grown without and in presence of NP, light blue is the control, the rest is different NP-treatments.

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PROPERTIES OF THE Cu-TiO_2 NANOSTRUCTURES OBTAINED BY SOL-GEL AND MICROWAVE ASSISTED SOL-GEL METHODS

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ABSTRACT:

In the present work the results of obtaining Cu doped TiO_2 nanostructures by the sol-gel (SG) and the microwave-assisted sol-gel (MW) methods are presented. The comparative investigations of the structure and morphology of the as-prepared gels and of the nanopowders obtained by annealing was realized by Fourier-transform Infrared Spectroscopic (FTIR), Raman Spectroscopy, UV-Vis Spectroscopy, Simultaneous Thermal Analysis coupled with Mass Spectrometry (TG/DTA-MS), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), X-ray Diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS). Thermal analysis studies have shown substantial differences in the decomposition of gels depending on the method of preparation and on the amount of the dopant (2.0 and 5.0 mol % CuO). The thermally treated gels at 450 ^{o}C showed for the samples obtained by the sol-gel method the formation of TiO_2 anatase phase, while in the case of samples obtained by the microwave-assisted sol-gel method beside anatase phase, the presence of small amounts of rutile was observed. The different crystalline structure of the mentioned samples could be correlated both with method of preparation and with the presence of cooper ions with different valence.

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Multimodal $Fe_3O_4@SiO_2$-NH_2-Ag nanocomposites as a tool for contactless temperature stimulated processes

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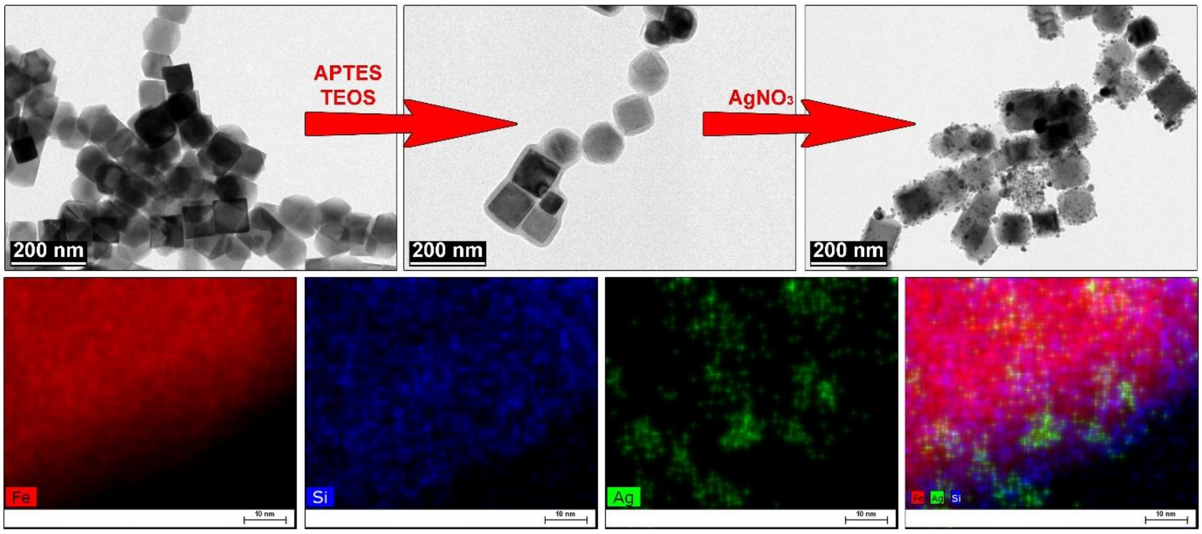
ABSTRACT:

Cubic Fe_3O_4 nanoparticles were synthesized via thermal decomposition of iron acetylacetonate in organic solvent (dibenzyl ether). Morphology and size were controlled using optimized synthetic parameters such as temperature, time, additives type, additives ratio, monomer concentration. Subsequently, magnetic nanoparticles were coated with porous silica and Ag nanoparticles were deposited on the silica surface through the reduction process. Physicochemical properties were characterized by TEM imaging (TEM, HR-TEM, SAED) X-ray powder diffraction (XRD) and FTIR-ATR spectroscopy. The composition of multimodal nanocomposites was confirmed using STEM EDX mapping. The dynamic light scattering technique (DLS) was used to evaluate the hydrodynamic size and zeta potential. The efficacy of the energy conversion was measured under contactless stimulation with alternating magnetic field and laser radiation within 1st and 2nd optical biological window.

Figure 1 : TEM images of the Fe_3O_4 (left top), $Fe_3O_4@SiO_2$-NH_2 (middle top), $Fe_3O_4@SiO_2$-NH_2-Ag (right top) and STEM EDX mapping of the $Fe_3O_4@SiO_2$-NH_2-Ag (bottom).



MANGANESE AND VANADIUM DOPED ZnO NANOSTRUCTURES OBTAINED BY MICROWAVE ASSISTED SOL-GEL METHOD

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ABSTRACT:

ZnO is a semiconductor belonging to the II-VI group and has several interesting characteristics, such as high electron mobility, wide band gap, strong luminescence at room temperature, so on. These attributes make ZnO an attractive compound for various emerging applications. By adjusting the properties of ZnO with transition metal (TM) ions, new functions can be developed. Among the different transition metals (TM) selected for doping ZnO, Mn and V are the most promising. Different methods are available for preparation of doped ZnO nanostructure, among these methods sol-gel technique is an efficient and versatile procedure. In the recent time to combine the sol-gel method with microwave irradiation started to be of interest for preparation of oxide nanostructures. In the present work, microwave (MW) assisted sol-gel (SG) method was used in order to obtain 2% Mn and 2%V doped ZnO nanostructures, which were compared with the ones obtained by classic sol-gel method. The characterization of the samples was carried out by X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and X-ray fluorescence (XRF). As compared with the samples obtained by sol-gel method, the MW assisted sol-gel samples have presented TG/DTA curves with similar thermal effects, but with different intensity. In the same way, in the case of both type of samples, many similar FT-IR vibration peaks were recorded, but with different intensities. The differences could be correlated with the influence of the MW on the sol-gel reactions. The thermally treated samples will be tested as sensors.

SYNTHESIS AND CHARACTERIZATION OF SILICA-BASED MESOPOROUS NANOPARTICLES: THE PH STUDY

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ABSTRACT:

Mesoporous silica nanoparticles (MSNs) are considered promising drug carriers due to their ordered pore structure that allows high drug loading and release capacity. Si and Ca represent important components of bone biology and bone metabolism. The dissolution of such ions from MSNs can lead to osteogenic differentiation of stem cells in the direction of extracellular matrix calcification[1]. Moreover, Ce ions have received a lot of attention due to their desirable properties, such as antioxidant, anti-inflammatory, and antibacterial properties, which are considered to be prerequisites for tissue regeneration[2]. The aim of this work was to study the effect of different pH values on the physicochemical properties of sol-gel derived MSNs. The synthesis of pure silica MSNs and Ca/Ce-doped MSNs MCM-41 type was performed via the CTAB-assisted Sol-Gel method. The synthesis of the MSNs was conducted via the Sol-Gel method using tetraethyl orthosilicate (TEOS) as the silica source and Cetyltrimethylammonium bromide (CTAB) as the pore directing agent in an alkaline environment (for pH values=11.00, 11.75, 12.22, and 12.50). For the synthesis of Ca/Ce-doped MSNs, the ions were added to the solution as nitrate salts ($60SiO_2$, 35CaO, $5CeO_2$ % mol). The physicochemical properties of MSNs were investigated by S.A.XRD, SEM/EDS, TEM, FTIR, and N_2 porosimetry. Different pH values affected the particle size and the mesoporous structure. As it is shown in the isotherm plots (Fig.1), pH 11.75 is the ideal value for the formation of both neat and doped-MSNS with tubular meso- and micro-pores.

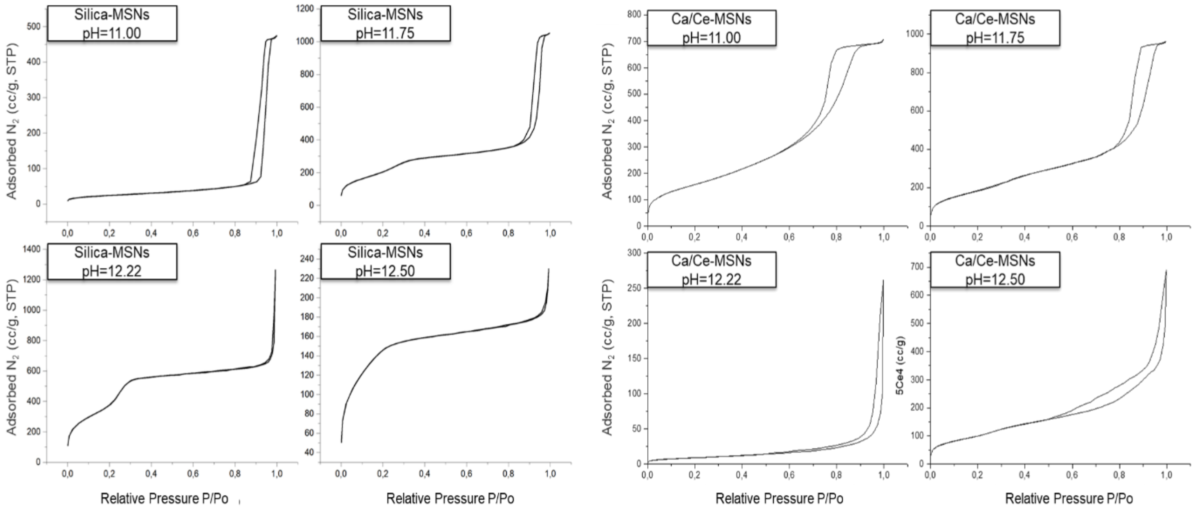

Figure 1: N_2 adsorption/desorption isotherms of Silica-MSNs (left) and Ca/Ce-doped MSNs (right)

Acknowledgments: This work is supported by European Union's Horizon 2020 research and innovation programme under grant agreement No 953128, project: Smart, Multifunctional Dental Implants: A solution for peri-implantitis and bone loss.

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P100

SYNTHESIS AND CHARACTERIZATION OF AKERMANITE SCAFFOLDS TOWARDS BONE TISSUE REGENERATION

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ABSTRACT:

Various glass ceramics have been used as scaffold materials, especially Si-based ceramics doped with Ca and Mg. Akermanite ($Ca_2MgSi_2O_7$) has attracted interest for bone regeneration due to its controllable biodegradation rate, improved mechanical properties, and high apatite forming ability[1,2]. The aim of this study was to produce Akermanite scaffolds through the Foam Replica Technique combined with the Sol-Gel method to improve the overall effectiveness towards potential hard tissue regeneration. The methodology followed was similar to the one proposed in the literature[1]. Briefly, tetraethyl orthosilicate (TEOS), d.d.H_2O, and HNO_3 were mixed for 30min. Then, Mg and Ca were added to the solution as nitrate salts and stirred for 5h. The solution was aged and dried to produce a xerogel, sieved, and heated up to 700°C. The powder was thermally characterized before the fabrication of the scaffolds with TGA/DSC. The scaffolds were produced by the immersion of PU foams to Sol-Gel solution several times, then dried, heated up to 700°C, and sintered at 1300°C. The scaffolds were loaded with Moxifloxacin, an antibiotic with antimicrobial activity. The characterization was performed by FTIR, XRD, and SEM/EDS. The bioactivity, degradability, and mechanical properties were also investigated. Drug loading/release profiles were assessed with HPLC. The fabricated highly-porous scaffolds presented a high drug loading capacity (84%) and controlled release rate, while the *in-vitro* bioactivity evaluation indicated the formation of a Ca-P layer on the surface of the samples after 14days of immersion.

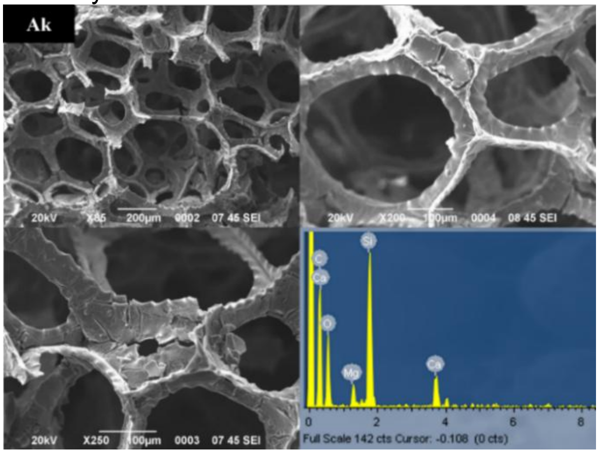

Figure 1: SEM microphotographs of the synthesized Akermanite Scaffolds and EDS analysis.

Acknowledgments: This research is co-financed by Greece and the European Union (European Social Fund- ESF) through the Operational Programme «Human Resources Development, Education and Lifelong Learning» in the context of the project "Strengthening Human Resources Research Potential via Doctorate Research" (MIS-5000432), implemented by the State Scholarships Foundation (IKY).

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MESOPOROUS SILICAS WITH VARYING PORE SIZE AND SURFACE FUNCTIONALITY AS CARRIERS OF BIOACTIVE MOLECULES

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ABSTRACT:

Mesoporous silicas are nano- or microparticles with large surface areas and pores with diameters between 2 and 50nm. Due to their unique properties, they are used in many applications, such as catalysis, adsorption, and drug delivery[1-2]. In this study, sol-gel chemistry was applied to synthesize SBA-15 mesoporous silicas, that were tested for their effectiveness as bioactive molecule carriers. The syntheses were conducted via the cooperative self-assembly route, in acidic environment, using tetraethyl orthosilicate (TEOS) as Si-source and Pluronic® P123 as the pore directing agent. Three SBA-15 variants were produced: i) SBA-15(8) with large (8 nm) and long pores, ii) SBA-15(4) with small (4 nm) and short pores, and iii) SBA-15(sc, *short channel*) with large (8 nm) and short pores. Additionally, the surface of SBA-15(8) was organically modified with amino or phenyl moieties. SBA-15 silicas were loaded either with *artemisinin*, a lactone able to stimulate the generation of reactive oxygen species (ROS) or with *rhBMP-2*, a bone morphogenic protein. The biocompatibility and haemolytic activity of neat and drug-loaded mesoporous silicas, as well as the bioactive molecule release profiles, were evaluated and the results were correlated with the morphological, structural, and textural properties of SBA-15 silicas. The N_2 adsorption/desorption isotherms of the samples are presented in Fig.1. All samples had Type IVa isotherms with Type H1 hysteresis loops. The surface area values of SBA-15(8), SBA-15(4), SBA-15(sc), p-SBA-15(8), and a-SBA-15(8), were 820, 650, 800, 716, and 474 m^2/g, respectively.

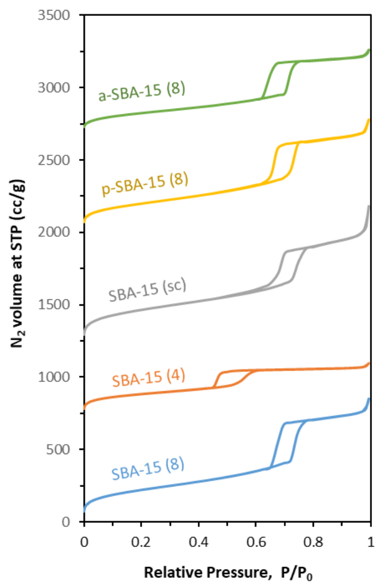

Figure 1: N_2 adsorption/desorption isotherms of SBA-15 mesoporous silicas

Acknowledgments: This work is supported by European Union's Horizon 2020 research and innovation programme under grant agreement No 953128, project: Smart, Multifunctional Dental Implants: A solution for peri-implantitis and bone loss.

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MICROSTRUCTURE AND COLLOIDAL STABILITY OF HUMICS-SILICA COATED Fe_3O_4 NANOPARTICLES: EFFECT OF SYNTHESIS CONDITIONS

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ABSTRACT:

Nowadays, numerous researches are being performed to formulate nontoxic multifunctional magnetic materials possessing both high colloidal stability and high magnetization, but there is a demand in the prediction of chemical and colloidal stability in water solutions. Herein, for the first time, a series of silica-coated magnetite nanoparticles (MNPs) has been synthesized via sol-gel method with and without establishing an inert atmosphere during synthesis and then tested in terms of humic acids (HA) loading. The influence of ambient conditions on the microstructure, pH-dependent charging and HA loading of different silica-coated magnetite nanoparticles has been established. The XRD patterns show that the content of stoichiometric Fe3O4 decreases from 78.8% to 42.4 % at inert and ambient atmosphere synthesis respectively. The most striking observation was the shift of MNPs isoelectric point from pH~ 7 to 3 with increasing HA up to reaching the complete reversal of zeta potential sign. This is result when the MNPs surface is completely covered by HA molecules, so this phenomenon is closely related to HA adsorption. The zeta potential data of MNPs can be used to predict the loading capacity for HA polyanions and help to understand way for new materials development with complexation ability of humic acids, with magnetic properties of nanoparticles and with the insolubility of silica gel.

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HYDROPHOBISATION OF SOL-GEL MICROPOROUS ORGANOSILICATE FILMS

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ABSTRACT:

This study analyses the surface modification of sol-gel microporous organosilicate films via treatment in hexamethyldisilazane (HMDS) vapour for their hydrophobisation [1]. Three different film-forming solutions were prepared using (co)hydrolysis and (co)condensation reactions of 1,4-bis (triethoxysilyl) benzene (BTESB), a mixture of tetraethoxysilane (TEOS) and methyltriethoxysilane (MTEOS), a mixture of TEOS and diethoxydimethylsilane (DEDMS) to obtain the silica films with different organic bonds. Molar ratio MTEOS/TEOS = DEDMS/TEOS = 1/5. Brij® L4 was added to form a porous structure via the EISA process. The films were formed by spin-on deposition and then subjected to soft baking at 120–200°C. After that, each sample was split into two parts. Both parts of each sample were annealed at 390°C. Subsequently, the films were cooled to 100°C. Then one part of the samples was put through treatment in HMDS vapour. Heat treatment with HMDS leads to a decrease of silanols and an increase of methyl groups content. As a result, the water contact angle is increased, the dielectric constant and loss tangent are decreased. Thus, relatively large HMDS molecules (0.775 nm) can penetrate the open microporous structure (≥0.66 nm in diameter) and react with surface silanols. However, analysis of the FTIR spectra showed temperature-limited and time-dependent stability of the created surface methyl groups. Silylation with HMDS slightly reduces porosity but appears to slightly increase pore size. Annealing after HMDS vapour treatment leads to micropore wall strengthening. In the case of porous BTESB film, annealing at 390°C in N_2 causes aromatic ring destruction.

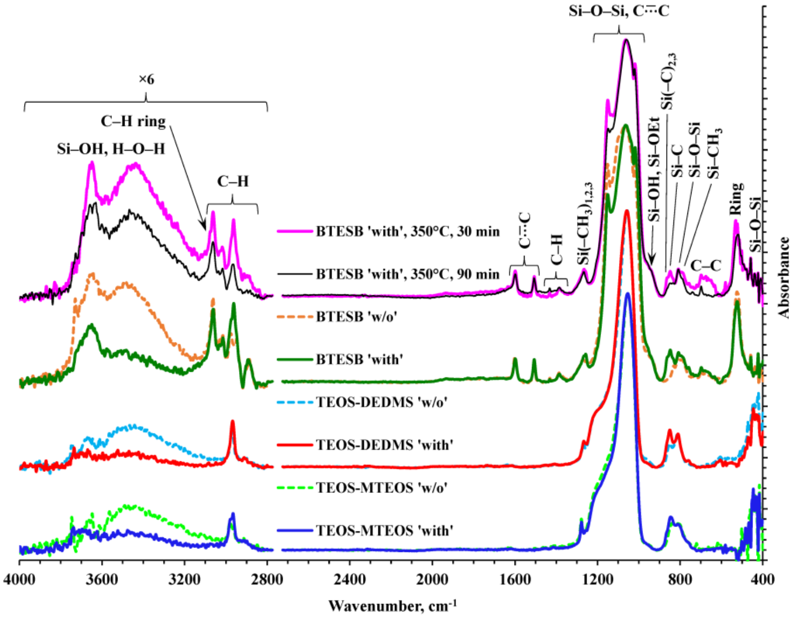

Figure 1 : FTIR spectra of different samples under study with (‘with’) and without (‘w/o’) HMDS treatment. All spectra are normalised to the amplitude of the wide Si–O–Si band and shifted

Acknowledgement: This work was supported by the Ministry of Science and Higher Education of the Russian Federation, project No. 0706-2020-0022 and RFBR grants Nos. 18-52-27022, 18-52-27024.

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IMPACT OF CORE-SHELL NANOSTRUCTURE ON THE DIELECTRIC PROPERTIES OF $CaCu_3Ti_4O_{12}$

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ABSTRACT:

In recent years, a lot of interest has been devoted to the so-called colossal dielectric permittivity materials. The use of high k oxides as dielectric material is technologically attractive to reduce the size of capacitors while keeping or increasing their properties. The titanate $CaCu_3Ti_4O_{12}$ (CCTO) was the first material exhibiting an exceptionally high permittivity (up to 10^5) with a very weak frequency and temperature dependence [1]. It has been established that the origin of this high permittivity values comes from extrinsic polarization induced from internal barrier layer capacitance (IBLC), which is described by a structure composed of semi-conducting grains and insulating grain boundaries [2, 3]. Unfortunately, the CCTO ceramics with giant permittivity exhibits higher dielectric loss and conductivity, which limits its practical applications.

The grain boundaries play an important role in the dielectric behavior [4-5]. To solve this problematic and improve the properties of CCTO, a core shell microstructure is proposed in our work. This technique consists of coating the grains with elements like SiO_2, TiO_2, Al_2O_3 (figure 1). The shell allows a better control of the microstructure of the grain boundaries and attempt normally to increase the resistivity and reduce the dielectric losses, while keeping a high permittivity. To realize the coating two different methods are used : the first one is chemical method with, either the modified Stöber method [6] or ultrasonic sol-gel reaction [7]. The second one is a physical method, which consist in depositing the shell by a non-equilibrium cold plasma [8]. The microstructure of the compounds obtained are studied by SEM and TEM. Dielectric properties are studied by complex impedance. Results show an improvement in resistivity and dielectric losses. The embedding carried out by the two methods is shown in Figure 1.

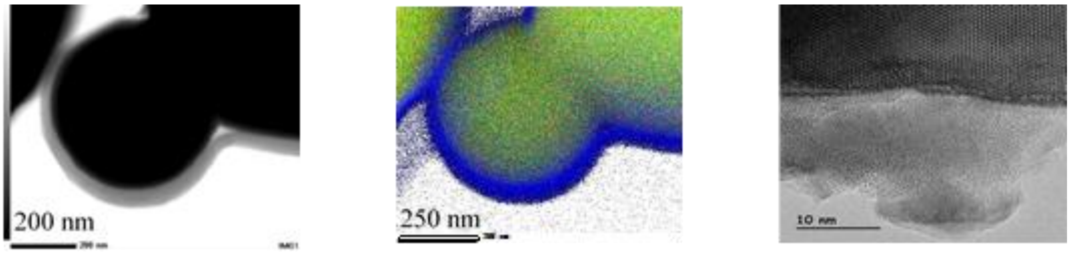

Figure 1: On the left and the middle, TEM picture of CCTO coated by SiO_2 by plasma method and its cartography of elements. On the right, TEM picture CCTO coated by a mixture of Al_2O_3 and TiO_2.

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Photo-patterned metal-oxide thin films obtained by laser curing and their application in opto-electronics

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ABSTRACT:

Metal oxide thin films are widely used in optics and photonics[1], for their transparency in the visible range, high refractive index and dielectric or semi-conductive properties. To obtain these materials, a possible approach is sol-gel chemistry, but their integration on polymer substrates is limited due to the required thermal treatment. We developed an alternative method by performing a Deep-UV (193nm) curing process at room-temperature, starting from thin films of oxo-clusters from transition metals[2]. The structuration of such films was also achieved successfully by different photolithography approaches at micro and nanoscale. The thickness of these materials is precisely controlled by the dilution rate and the deposition parameters of spin-coating, while their refractive index can be partly adjusted through irradiation.

Here, we present a study of two different metal-oxide (TiO_2 and ZrO_2) materials curable by Deep-UV. We investigated their chemical and physical composition by performing XPS, XRD and FT-IR measurements, and their optical properties by spectroscopic ellipsometry. Then, we present their applications in opto-electronics. They include plasmonic properties obtained either by nitridation or coupling with gold nanoparticles or gold thin films[3]. Sensing applications are also shown, such as photo-detection or gas sensing abilities.

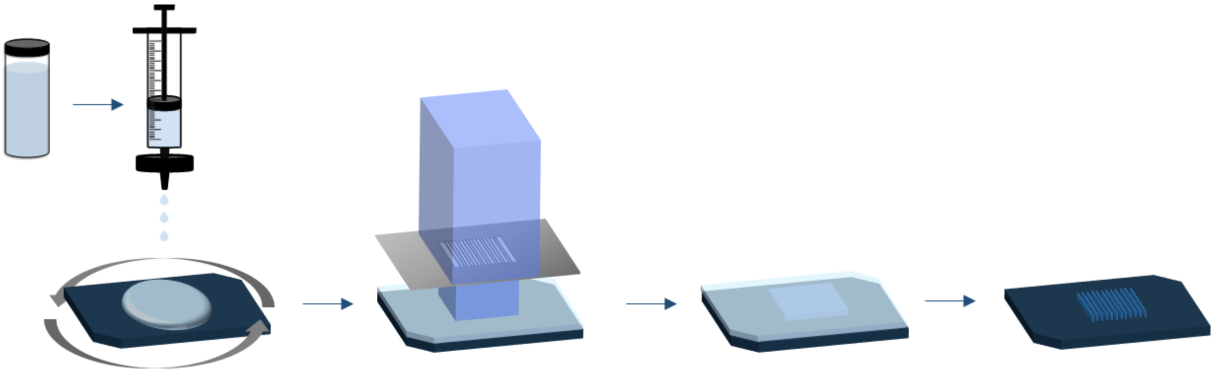

Figure 1: Schematic structuration by photolithography

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INVERSE MATERIAL SEARCH AND SYNTHESIS VERIFICATION BY HAND DRAWINGS VIA TRANSFER LEARNING AND CONTOUR DETECTION

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ABSTRACT:

Nano- and micromaterials of various sizes, shapes, and morphologies and composition have an extensive use in many different areas. However, search for the synthesis procedures giving custom nanomaterials with the desired pre-defined surficial structure, shape, and size remains a major challenge and is often implemented by manual research articles screening. Here, we develop for the first time scanning and transmission electron microscopy (SEM/TEM) inverse image search and hand drawing-based search *via* transfer learning (TL), namely, VGG16, convolutional neural network (CNN) pre-trained on millions of the images from the Internet, repurposing for image features extraction (FE) and image similarity (IS) determination. Moreover, we demonstrate the case use of this platform on calcium carbonate system, where the data (>200 unique samples) was acquired by random high throughput experimental synthesis and subsequent evaluation by SEM, and on gold nanoparticles (Au NPs) TEM data extracted from the research articles. This approach can be used for advanced nanomaterials search, synthesis procedure verification, and nanomaterial morphology quantitative descriptors generation, which can be further combined with machine and deep learning (ML/DL) solutions to provide data-driven nanomaterials discovery.

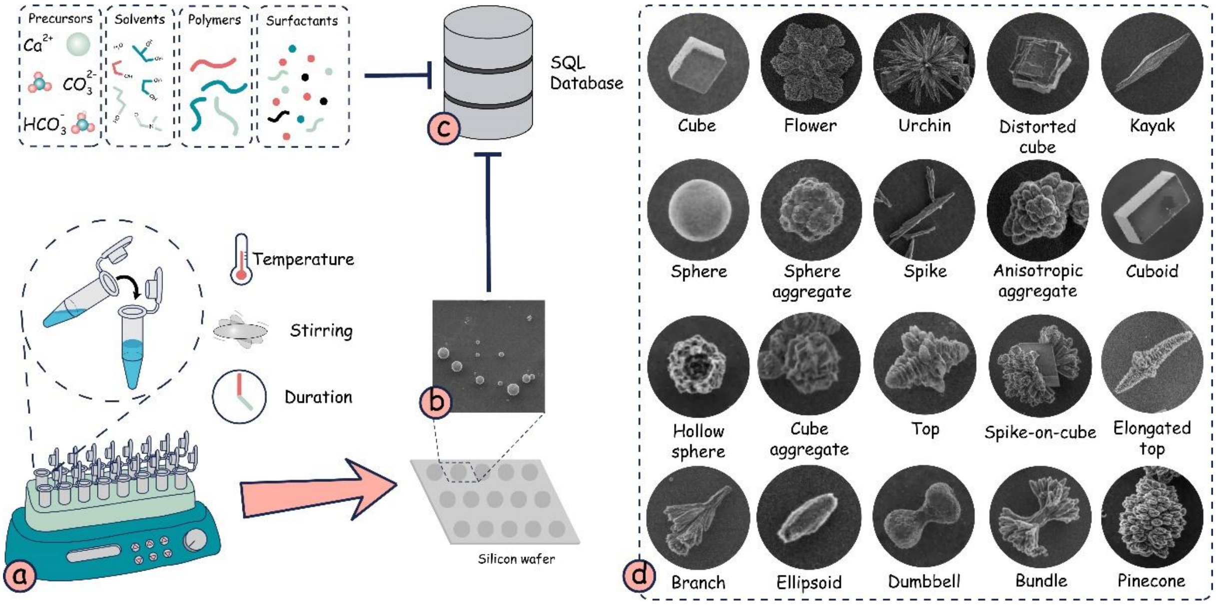

Figure 1: Calcium carbonate database collection *via* random high throughput synthesis.

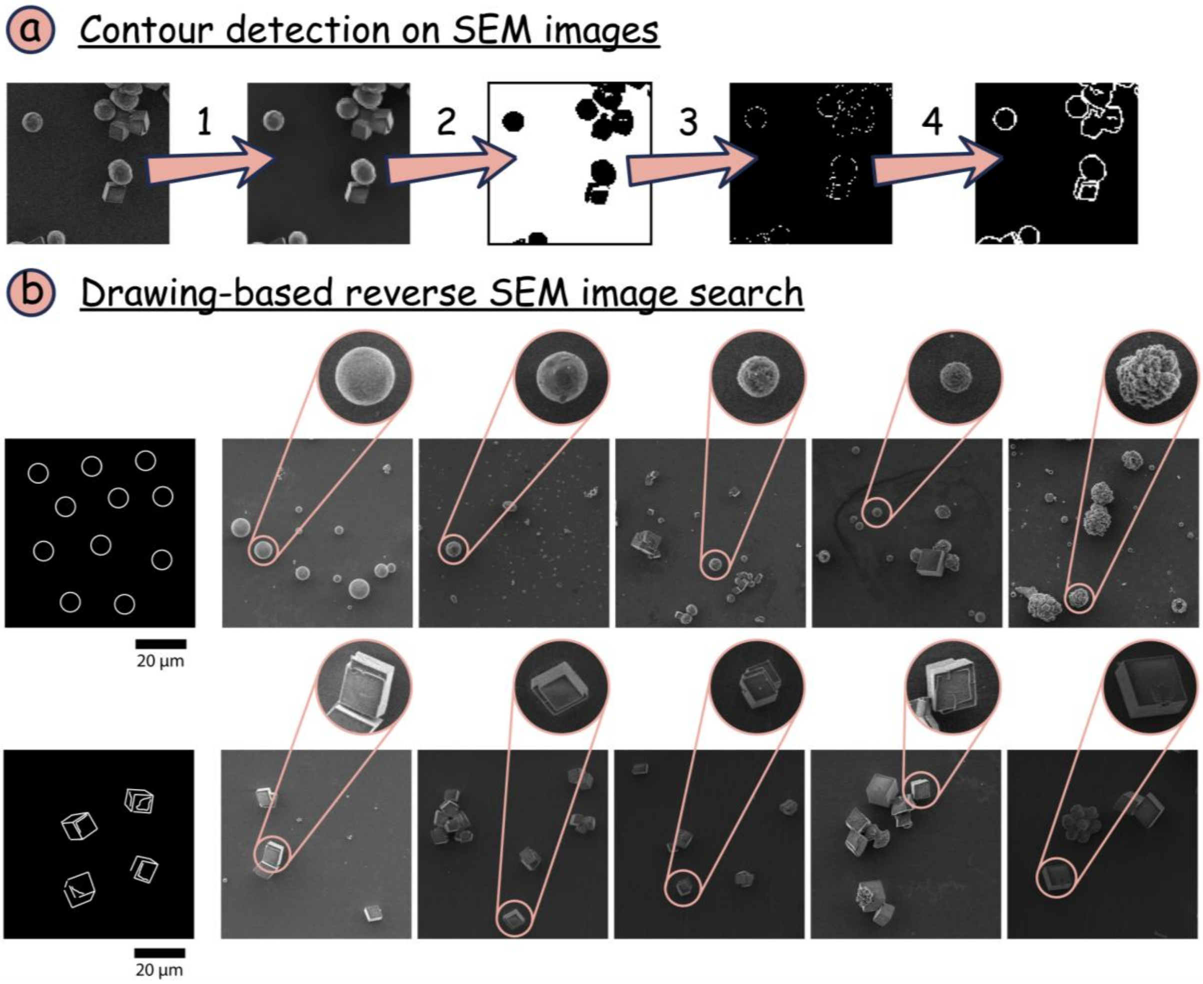

Figure 2: Hand drawing-based material search.

VANADIUM-BASED NANOMATERIALS BY SOL-GEL TECHNOLOGY FOR ENERGY STORAGE

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ABSTRACT:

Nanomaterials have received great attention for large-scale energy storage devices with high power-density and ultralong life energy storage. A series of vanadium oxides and its derivates were prepared by sol-gel technology and modified with oxygen vacancies and conductive materials such as conductive polymers including polypyrrole, polyaniline and poly(3,4-ethylenedioxythiophene). When applied as electrode materials for aqueous supercapacitors, vanadium-based supercapacitors demonstrated excellent electrochemical performance (over 600 F g^{-1} at a current rate of 0.5 A g^{-1} and excellent cycling stability (over 15 000 cycles at a rate of 10 A g^{-1}) due to their significantly enhanced kinetics by the synergistic effects of oxygen vacancies, conductive materials and the special nanostructure. These results suggest that sol-gel technology have great potentials in nanomaterial design and preparation for energy storage devices.

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CONCENTRATED MXENE SOL AS A PRECURSOR FOR PREPARING HIGHLY CONDUCTIVE THIN FILMS

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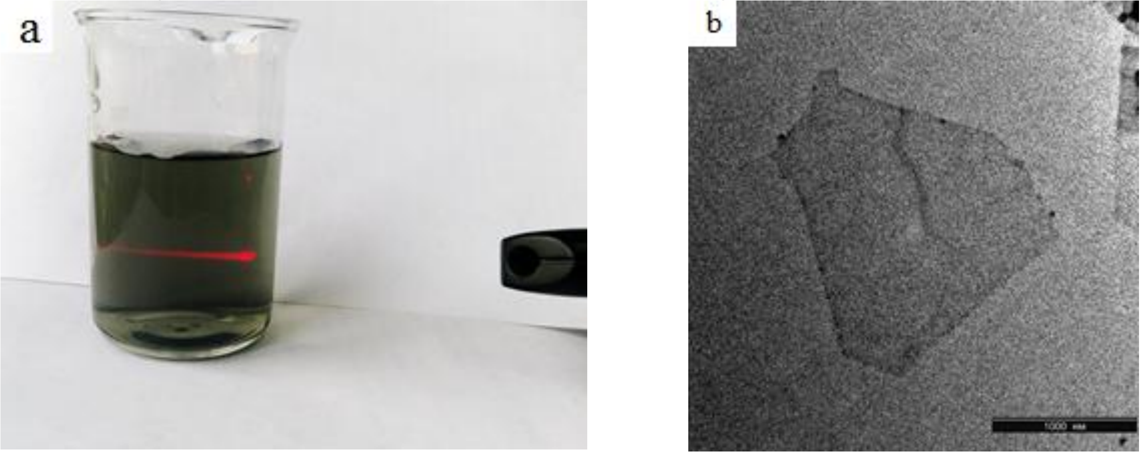
ABSTRACT:

Two-dimensional (2D) materials such as graphene, metal oxides and hydroxides, and others, are currently amongst one of the most intensively studied classes of materials that hold great promise for future applications in many technological areas [1]. MXenes are a new family of 2D nanomaterials characterized by uncommon combination of metallic conductivity and hydrophilicity that is the key to the promise and excitement these materials have engendered.

2D MXene nanosheets (Ti_3C_2) was prepared by etching bulk MAX phase powder (Ti_3AlC_2) in solution containing HCl and LiF [2]. A method for obtaining a concentrated stable MXene sol was developed. Concentration of MXene sol reached 5 g/L. MXene sol has a green color (fig. 1, a). A characteristic peak due to plasmon absorption is observed at 755 nm in the UV-Vis spectrum. The TEM data show that prepared 2D MXene particles are characterized by a lateral size of 2–3 μm (fig. 2, b). The high concentration of MXene colloidal solution makes it possible to obtain high-quality conductive thin films. The films were prepared on glass substrates by vacuum drying under heating. The prepared thin films are characterized by a metallic luster with a violet tint. The film thickness was up to 2 μm. The specific electrical conductivity of the thin films reached 3×10^5 S/m. It has been established that the films are highly sensitive to the moisture content in air. Resistance of the films increases up to 60 times when humidity changes from 25 % to 98 % RH. This makes it possible to use the films as humidity sensors.

Figure 1 : Photo fo MXene sol (a) and TEM image of 2D MXene nanoparticle



Acknowledgments

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Synergic temperature effect of star-like monodisperse iron oxide nanoparticles and their biological impact on MDA-MB-231 cells

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ABSTRACT:

Magnetic nanoparticle anisotropy has been tailored by preparation of different shape MNPs (star-like, cubic, and polyhedric) using a self-modified rapid hot-injection process. The surface of the nanoparticles was modified by anchoring the etidronic ligand (ETI) containing phosphonate groups with a strong binding affinity that ensured sufficient colloidal stability, surface protection, and minimized particle aggregation. The heating conversion was measured using contactless external stimulation through the action of alternating magnetic field and NIR laser radiation (808 nm) separately and in synergy mode to increase the thermal effect in a function of particle shape (shape anisotropy) as well as MNPs concentration. The structural properties were characterized by X-ray powder diffraction and analyzed employing Rietveld refinement (cell parameters); morphology, particle size, and element mapping were performed using transmission microscopy (HRTEM, STEM, and EDS).

Figure 1 : Title 1

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SOL-GEL THIN FILM MORPHOLOGY MODEL

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Sol–gel thin film morphology is explained by a model based on diffusion, convection, and evaporation during thermal annealing. According to Fick’s law, the solution diffuses from a region with a larger solvent fraction toward a region with a smaller solvent fraction. An extremely small difference between the solvent fraction at the bottom interface and at the free surface creates a convective roll. It carries solvent from bottom to top and then from top to bottom, after partial evaporation at the free surface. We show that the roll size increases with temperature. Moreover, the evaporation time is inversely proportional to the temperature and to the solvent fraction difference between the bottom interface and the free surface. This model may explain the difference in morphology (columnar/granular) observed in thin films elaborated by sol-gel. The columnar morphology in sol–gel thin films is linked to the complete removal of organic constituents in the previous deposited layer, otherwise the morphology is granular. Moreover, when the dilution of the precursor solution increases, the surface roughness decreases, facilitating grain coalescence. In this case, the film is dense without pores. To conclude, this general flow model based on the physics of fluids gives a deep insight into sol–gel thin film elaboration.

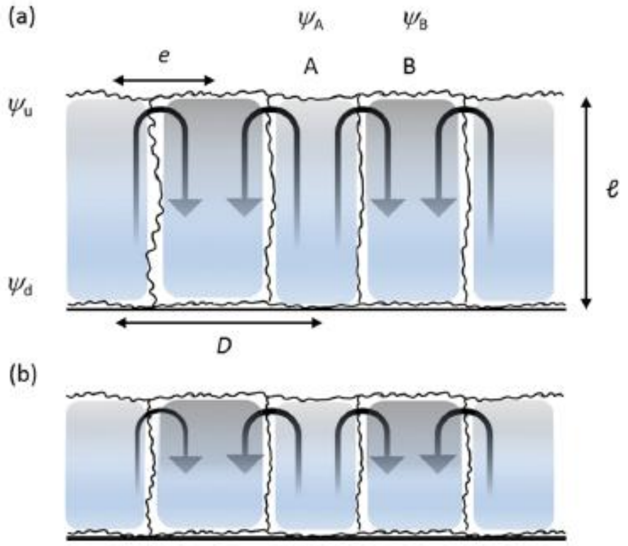

Figure: Loops, represented by black arrows, occur in the thin film due to convection and evaporation at low annealing temperatures. The inorganic fraction (respectively solvent) is represented by gray (respectively blue) shading. The inorganic fraction increases slightly from bottom to top as well as from domain A to domain B. (a) Beginning of the convective process, (b) advanced process of evaporation and convection. The layer thickness decreases due to evaporation.

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SPRAY PYROLYSIS-ASSISTED SYNTHESIS OF CuCl/ γ -Al_2O_3 MICROSPHERES AND THEIR PROPERTIES FOR CO ADSORPTION

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In this study, we developed a facile and scalable preparation method of CuCl@γ-Al_2O_3 composite microspheres for CO storage and separation by combining sol-gel and spray pyrolysis methods, followed by metal salt impregnation. γ-Al_2O_3 microspheres were first prepared by spray pyrolysis of a mixture containing various ratios of boehmite sol and citric acid (CA). Pore-size distribution analyses indicated that the mesopores that are generated inside of the γ-Al_2O_3 microspheres and their pore volumes could be fine-tuned by adjusting the CA/boehmite ratio. Importantly, the newly formed pore structures have been identified to accelerate the thermal dispersion of CuCl species into the γ-Al_2O_3 matrix, resulting in improved CO sorption. Gas-adsorption experiments showed that CO-adsorption capacity and CO/CO_2 selectivity were strongly affected by the CA/boehmite ratio, CuCl-dispersion temperature, and CuCl-loading amount. The optimized adsorbent exhibited a maximum CO-adsorption capacity of 1.69 mmol/g and CO/CO_2 selectivity of 84 (at 25 C and 100 kPa), exceeding the benchmarks for CO-selective adsorbents. Moreover, the spherical CuCl@γ-Al_2O_3 adsorbent showed good regenerative ability after a number of adsorption–desorption cycles. This study provided facile and scalable synthesis method for low-cost CO-selective material with high CO performance.

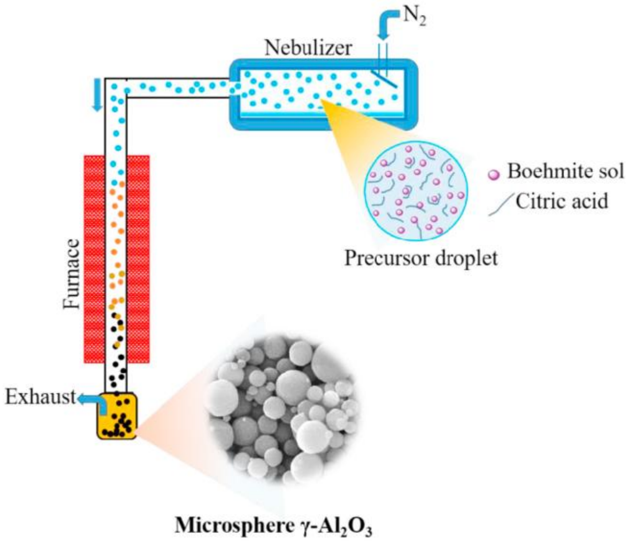

Figure 1 : Schematic of spray pyrolysis-assisted synthesis of γ-Al_2O_3 microspheres

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Synthetic pathways towards morphology-controlled Lu- and Hf-halide double perovskites and hydroxy-halide nano and micro-particles

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Advanced synthetic methods to generate nano- and microparticles hold great promise for controlling their properties and enable improved fabrication processes of functional materials and composites bridging several size ranges. Luminescent particles are relevant for many types of applications such as lighting, display, or scintillator technologies, provided their efficiency and density is sufficiently high. Here, we present syntheses of high-density caesium hafnium halide double perovskites and lutetium hydroxy chlorides. For generating Cs_2HfF_6 (CHF), Cs_2HfCl_6 (CHC), and $Lu(OH)_2Cl$ (LHC) particles, three different synthetic approaches were chosen: a heating-up synthesis, an emulsion synthesis, and a microwave assisted solvothermal synthesis, respectively. A heating-up approach was suitable to generate colloidal CHF nanocrystals at a temperature of 160 °C.[1] The obtained nanopowder shows no intrinsic band to band recombination due to the large bandgap of Cs_2HfF_6. However, defect-related emissions are observed in pure CHF particles, which are enhanced by incorporating dopants (Mn(**II**) and Eu(**III**)). Secondly, Cs_2HfCl_6 is an intrinsically fluorescent and radioluminescent material. A microemulsion synthesis was chosen to generate micron sized CHC. The low solubility of the precursor salts in organic solvents prevents the use of classical heating-up synthetic methods. The microparticles produced show the same absorption and emission profiles as reported bulk samples.[2] Lastly, $Lu(OH)_2Cl$ microparticles were obtained *via* a microwave assisted route with sizes ranging from 200 nm to 10 µm depending on the parameters temperature and time. Eu-doped samples show typical europium emission profiles.[3] All the obtained particles' structure and morphology were analysed by X-ray diffraction (XRD), scanning electron microscopy (SEM) while their optical properties were characterised by photoluminescence spectroscopy (PL). We discuss how various high-density materials can be obtained as nano- and/or micropowders. Based on these results, the appropriate synthetic route can be selected to ensure suitable properties like luminescence, dispersibility, morphology, or size, depending on specific applications.

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USE OF PHOTO-CROSSLINKABLE SOL-GEL FILMS FOR TEXTURING SUPERHYDROPHOBIC SURFACES

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Living organisms have evolved many strategies to change their color and appearance. Some of these characteristics rely only on physical and topographical properties and allow to create color and optical effects without chemical modifications. Indeed, the material structuration can provide visual aspects such as: diffractive, glossy or matt effect, or tribological behavior such as superhydrophobic or omniphobic surfaces [1]. For example, patterned surface can bring an antireflective effect by mimicking moth eyes patterns or the hydrophobic behavior of the lotus leaf.

Although biological structuration process is a bottom-up approach, it can be replicated using top-down microelectronic production techniques. However, a core challenge is the size of the patterning area (from cm² to m²) and the patterning of complex areas (2.5-3D geometries). The most recent developments around sol-gel type processes [2] have allowed to propose alternative routes to replace resins commonly used in nanoimprint lithography processes.

Thus, we propose a process that is simple to implement to produce super hydrophobic patterned surfaces. The process consists in the synthesis of a tailored silica or oxide-based sol-gel system used to coat the substrate, then a stamp is applied on the latter before thermal or photo crosslinking. Examples of as-obtained patterned surfaces are depicted in figure 1.

To test the hydrophobic behavior of the sample, water contact angle measurements have been carried out. Preliminary results are satisfactory since they show a contact angle around 140° as shown in image 2. Work is in progress to optimize the sol-gel solution to obtain a superhydrophobic behavior (corresponding to a water contact angle higher than 150°). Finally, further investigations will be considered to characterize the water repellency and the topography of the surfaces as well as mechanical and wetting equipment's such "Alpin", a homemade anti-adhesion test equipment that provides complementary information on the contact angle, scratch-test, goniometer, etc.

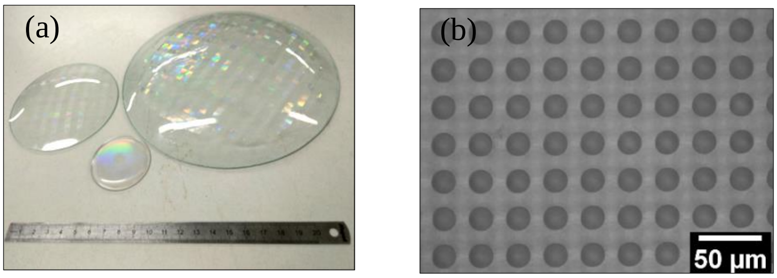

Figure 1: (a) Hemispheric surfaces (b) Surface functionalized by nano-micro patterning.

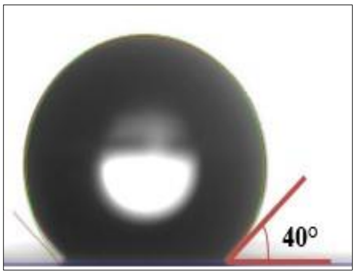

Figure 2: Contact angle of the dropped drop.

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METAL OXIDE NANO MATERIALS FOR BIOCONTROL APPLICATIONS

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ABSTRACT:

Nanoparticles of metal oxides (NP) identical to natural widespread minerals are attractive instruments in bio-control applications. They have been proved to contribute to improved growth and attachment of biocontrol bacteria bio-films on plant roots, causing improved resistance to plant stress.[1] Another important bio-control mechanism is the redox catalytic action exerted by NP containing easily reduced transition metal cations.[2] In particular, the destruction of peroxide species, generated through drought stress, could be initiated by stabilized Fe(III) containing phases.[2]

In this study we investigate how NP with thoroughly controlled size, shape and composition can be generated by a variety of sol-gel approaches, including application of single-source precursors for uniform doping, and how their characteristics can potentially guide their biological activity. Special focus is set on Mn-containing oxide phases because of their proved biocompatibility and the versatility of redox transformations.

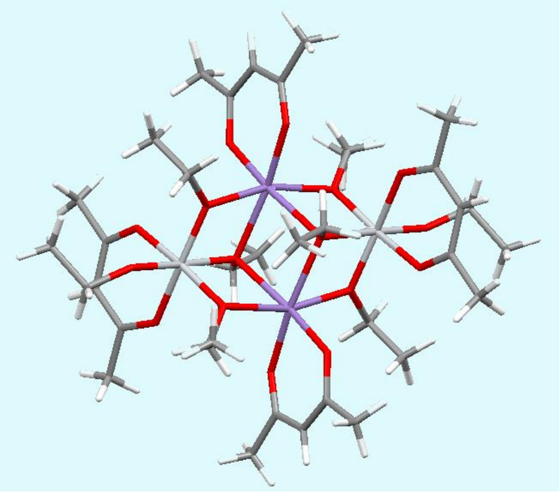

Figure 1 : Molecular structure of the $Ti_2Mn_2(acac)_4(\mu\text{-}OEt)_8$ precusor.

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Cellulose Nanocrystals in Spherical Titania-sols Microdroplet: From Dynamic Self-assembly to Nanostructured Microsphere Synthesis

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ABSTRACT:

Cellulose nanocrystals (CNCs) are spindle-like rods derived from a variety of natural resources via strong acid hydrolysis,[1] which can spontaneously organize into a cholesteric structure, called chiral (Ch) nematic structure.[2] Self-organization of CNCs into well-ordered Ch nematic liquid crystals are ubiquitous in nature,[3] inspiring widespread interest in the development of green functional materials with versatile applications, such as biomimetic nanomaterials, soft nanotechnology, optoelectronics and photocatalysis technology.[4] Typically, studies have focused on obtaining long-range ordered Ch nematic structure in planar functional films by using evaporation-induced self-assembly (EISA) technology. Only a few attempts have been dedicated to investigating the Ch nematic structure of CNCs aqueous suspension in spherical microdroplets. The direct observation of the self-organization of CNCs in spherical microdroplet is challenging, in particular with regard to the involvement of inorganic precursors.

In this study, we encapsulated CNCs in spherical titania-sols microdroplets using an inverse micro-emulsion method. We monitored the self-assembly process from seconds to hours with the aim to determine the key steps that drive the self-organization of CNCs from isotropic to Ch nematic phase in such aqueous sol. Polarized optical microscopy (POM) provides a unique perspective to witness the evolution process of CNCs tactoids from nucleation, growth and migration to equilibration in spherical microdroplet. Simultaneously, growth mechanisms as well as the induced structural defects during different evolution stages have been identified during the process. Moreover, the impact of temperature on the Ch nematic structure was investigated and a proof-of-concept of the transfer of such structure into solid TiOx/C microspheres by hydrothermal method was demonstrated. This study therefore provides insights into the self-assembly process of CNCs in spherical confinement, favoring further comprehension of growth mechanism as well as opening up a new approach to transfer the Ch nematic structure into spherical nanostructured materials.

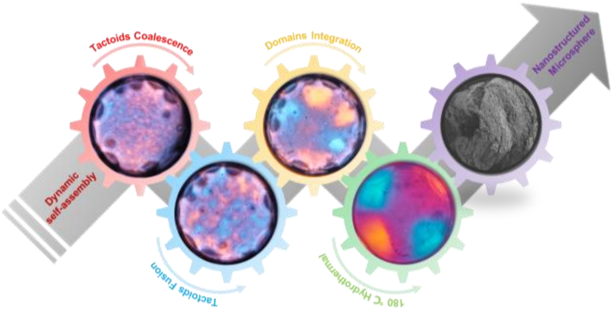

Figure 1: The evolution process of CNCs in spherical microdroplet.

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Nanoparticles synthesis, self-assembly

Precise control of size and morphology of Co-Al layered double hydroxide nanoparticles via dialysis process.

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ABSTRACT:

Layered double hydroxides (LDHs) are ionic lamella clays and have unique properties such as anion exchangeability, surface basicity, adsorption capability. Precise control of size and morphology of LDHs is crucial for their application in anion exchange, catalysts, drug delivery and so on[1][2][3]. Here, we found a method to control the size and morphology of Co-Al LDH nanoparticles by dialysis.

The colloidal suspension of Co-Al LDH nanoparticles was synthesized via alkalization reaction using an epoxide[4]. The LDH suspension was sealed in a dialysis tube and dialyzed at room temperature with water (pH = 5.8) for 24 to 120 hours. The homogeneous red-coloured LDH colloidal suspensions were obtained in all conditions. These suspensions were dried to powder for X-ray diffraction (XRD) measurements to identify the crystal phase. In all samples, the full width at half maximum (FWHM) of 003 and 110 peaks were almost unchanged and the position of 110 peak was almost unchanged, which indicate that the composition of Co-Al LDH remained unchanged. However, a transmission electron microscope (TEM) observation revealed that the size and morphology of LDH nanoparticles changed with dialysis time (Fig. 1). This result was attributed to the dissolution-reprecipitation reaction of LDHs nanoparticles by dialysis with water.

LDH thin films were prepared by spin coating using LDH suspensions with different particle sizes. XRD measurements were carried out on the fabricated LDH thin films. FWHM of the 003 peak of the LDH thin film decreased with increasing dialysis time. The decrease in the FWHM indicates the orientation of the 003 face of LDH, and an orientation of LDH nanoparticles was realized by controlling the morphology.

This study showed that the dialysis process under mild conditions was effective in precisely controlling the size and morphology of Co-Al LDHs nanoparticles.

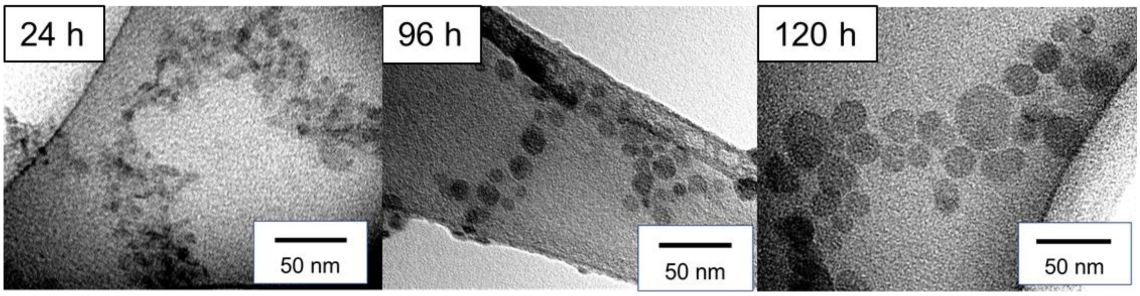

Figure 1: TEM images of Co-Al LDH nanoparticles with varying dialysis

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SILVER MELAMINE SELF-ASSEMBLEY FOR SERS ANALYSIS

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ABSTRACT:

The new detection SERS[1,2] platform is applicable for the quick and easy formation of sensing devices for food, agriculture, and environmental science. We design films using an adopted Liesegang rings formation process that includes the reaction-diffusion of silver nitrate and melamine followed by precipitation of different intermediates and their reduction by light in pectin medium. These films are flexible, resistant and can be prepared without effort in large surfaces. Surprisingly, presence of melamine provides an excellent substrate for the extraction of pollutants at the solid liquid interface. It is giving rise to a powerful but easy and fast method for the quantification of, for example, thiram in fruits. Moreover, melamine allows minimize the silver concentration for the formation of thin film as flexible platform for SERS analysis. The optical properties of the structured samples were investigated by Raman spectroscopy using benzenethiol (BT). To check the signal intensity homogeneity through the radial cross-section of the sample, a large map was carried out on the film. The surface of an apple was contaminated with thiram. After airdrying, a piece of the film was placed on the apple and sprayed with ethanol (into the uncover side) to transfer the thiram to from the apple surface to the film. Then, the films were studied by SERS. The vibrational pattern is clearly recognized for concentrations less down to the nM regime; and, by correlating the peak area with concentration, a linear relation can be stablished from 10^{-5} to 10^{-6} M. These detection limits are competitive with those provided by classical.

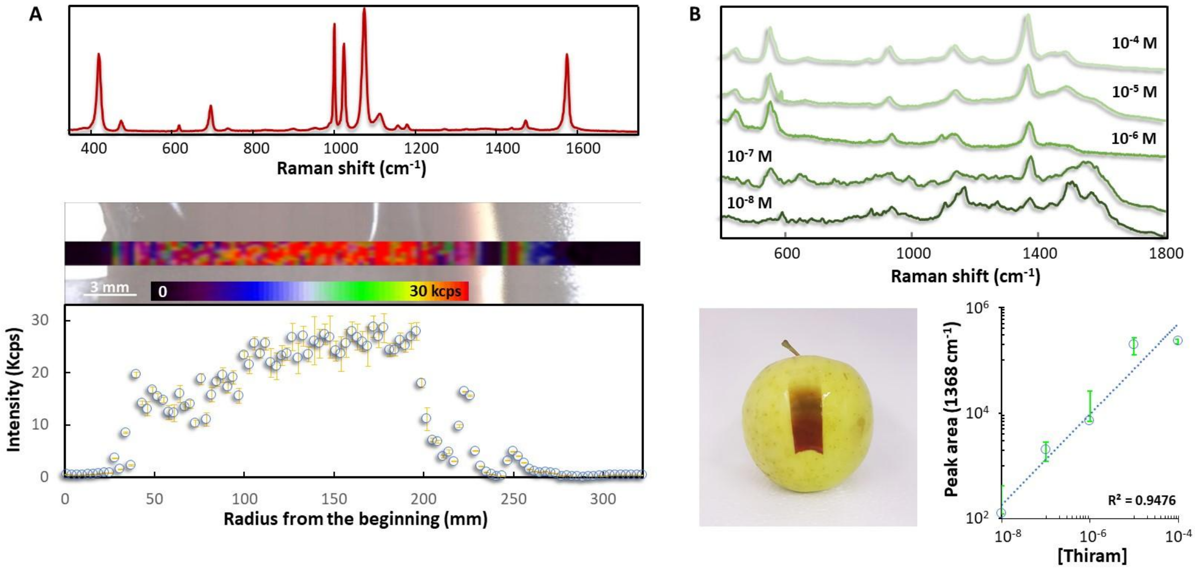

Figure 1 : A) SERS spectrum of benzenethiol on the film acquired with a NIR laser (785 nm) and SERS mapping of a large area of the film and the intensity of the 1072 cm^{-1} (in plane CH deformation). B) SERS spectra of thiram at different concentration after transfer the pesticide from the apple surface to the film by spraying ethanol. Correlation of the peak area of the CS stretching with the thiram concentration.

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ENHANCED ADSORPTION OF NAPROXEN BY β-CYCLODEXTRIN-IMMOBILIED REDUCED GRAPHENE OXIDE

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ABSTRACT:

Naproxen is one of the most widely employed nonsteroidal anti-inflammatory drugs (NSAIDs), and consequently is widely distributed in soil and water at a very low concentration. Unfortunately, naproxen itself and its byproducts are harmful to living organisms even humans. Therefore, developing strategies for removing naproxen from aquatic environments is urgent.

In this study, a one-step hydrothermal method synthesized β-cyclodextrin-immobilized reduced graphene oxide composite (β-CD/rGO) was employed to remove naproxen from aquatic environments. The β-CD/rGO had a porous structure with abundant hydroxyl groups, and acetalization between the β-CD and rGO provided a more stable three-dimensional structure. The maximum equilibrium adsorption capacity of naproxen on β-CD/rGO at 313K was 361.85mg g^{-1}. The adsorption of naproxen onto the β-CD/rGO fit well with the pseudo-second-order kinetics and the Langmuir adsorption model. The ΔH was higher than 40kJ mol^{-1}, which indicated that this adsorption was chemisorptive and endothermic. Host-guest interaction, hydrogen bonding, and π-π interactions were uncovered as three main mechanisms involved in binding between naproxen and the β-CD/rGO. Moreover, used β-CD/rGO could be regenerated with ethanol, making this an attractive method for naproxen adsorption in aquatic environments.

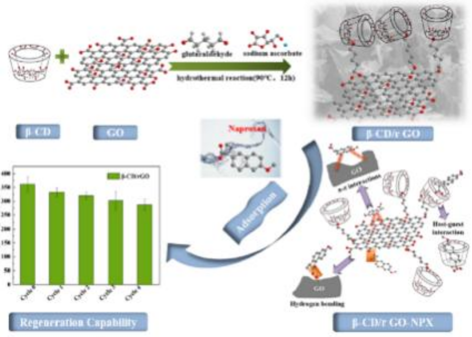

Figure 1: Graph abstract

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MSNs SYNTHESIZED FROM LIPIDIC CILASTATIN DERIVATIVES TEMPLATES AS DRUG DELIVERY SYSTEMS FOR KIDNEY PROTECTION

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Nanocarriers have become a promising tool in modern drug delivery because they allow the release of the desired pharmaceutical in a controlled and selective manner to the corresponding biological target, avoiding, moreover, its interaction with other biomolecules. Among all the nanocargos investigated over the last decades, mesoporous silica nanoparticles (MSNs) are of particular interest. Their specific textural properties such as their high surface area and extensive and uniform network of pores allow the easy loading of a vast array of drugs into their structure. Importantly, their excellent *in vivo* biocompatibility ensures low toxicity. A recurring issue in the employment of MSNs as drug delivery systems is their tedious fabrication. It requires numerous steps that include the removal of the surfactant and the subsequent loading of the drug. For that reason, our group has reported the concept of drug structure-directing-agents (DSDA), based on the use of molecules with pharmacological activity as surfactants in the synthesis [1].

Nephrotoxicity is a major complication of cancer-based chemotherapies, leading to acute kidney damage in patients. Cilastatin is an inhibitor of dehydropeptidase DHP-I that has been proved to reduce the damage in the kidney caused by antitumoral drugs *in vitro* and *in vivo* [2]. Herein, we describe a synthetic method of a drug delivery system of cilastatin in a single-step and fast process. In this work, lipidic cilastatin derivatives have been successfully synthesized and employed as templates for the obtention of MSNs *via* the concept of DSDAs [3].

The synthesized cilastatin@MSNs have been extensively characterized and showed good spherical morphology and excellent textural properties. The release of the drug from the materials have been studied in a simulated biological media. The results confirmed that the release is slow and constant over several days, illustrating the potential utility of these materials as drug delivery systems for cilastatin.

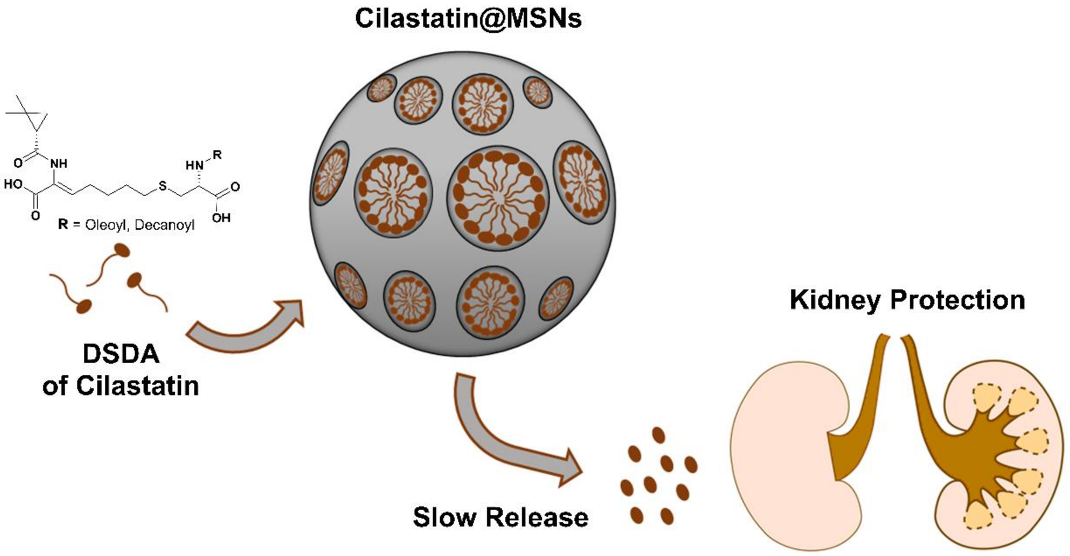

Figure 1: MSNs synthesized using DSDAs of cilastatin for kidney protection.

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INKJET PRINTING OF POLYSTYRENE SPHERES MONOLAYER FOR NANOLITHOGRAPHY APPLICATION

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ABSTRACT:

Nanolithography is a promising fast-growing field of techniques aimed at the creation of small structures. Mainly it is applied for semiconductor fabrication, where nanolithography provides the opportunity to build more compact devices with higher performance. In microsphere nanolithography, each sphere acts as a ball lens. It focuses UV-light in a photoresist layer, coated on the silicon substrate, further, to provide nanowells by an etching technique. These wells are used for the epitaxial growth of nanowires.

One of the key points for successful nanolithography is microspheres monolayer[1]. Therefore, the present study shows that it can be obtained by the inkjet printing method, which is prospective, precise, and cheap[2]. Polystyrene spheres (PSS) are chosen as microlenses due to their self-assembling property. Ink composition based on PSS has proper rheological parameters for printing and are chemically inactive to photoresist. Thus, this work demonstrates the technology of printing the monolayer of PSS for nanolithography application: fabrication of personalized optoelectronic devices with high efficiency and low price.

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The growth mechanism of platinum nanoparticles

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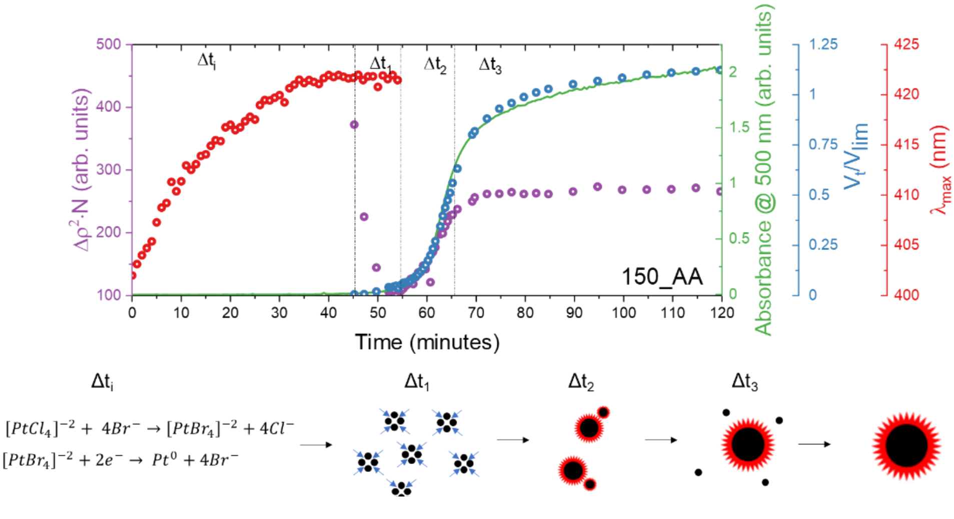
ABSTRACT:

Platinum nanocrystals play an important role in several applications, such as catalyst on CO and NO_x oxidation reactions and hydrogenation reactions[1]. It is well established that size and shape can play important role in the nanoparticle (NP) materials properties, so that, unravelling the growth mechanism of such materials could enlighten the path for controlling such quality attributes. The synthesis of platinum NP reduced with ascorbic acid (AA)[2,3] and stabilized with tetradecyltrimethylammonium bromide (TTAB) was studied. The role of TTAB concentration ($TTAB/Pt^{2+}$ molar ratio of 50, 100 and 150) in the particle size, kinetics and growth mechanisms was focused on. The growth kinetics was evaluated using *in situ* SAXS and UV-Vis spectroscopy data, from which we could follow how NP number (N) and size evolved over time. The overall mechanism is displayed in Figure 1 and follows 4 steps: Δt_i, Δt_1, Δt_2 and Δt_3. Δt_i is the incubation period, where $[PtCl_4]^{-2}$ is transformed into $[PtBr_4]^{-2}$, which is quickly reduced in Pt^0 nuclei; these nuclei readily aggregate into bigger Pt particle during Δt_1 period. The following growth period, Δt_2, is characterized by concomitant size and number of particles growth (aggregative nucleation step), while in Δt_3 Pt NP grows as their number stabilize (Ostwald ripening (OR) mechanism). As conclusion, $TTAB/Pt^{2+}$ plays an important role in the growth mechanism steps: the higher the content of TTAB the higher the influence of OR in the overall mechanism. Furthermore, TTAB has also influenced the aggregative nucleation steps, directly altering the rate and the time interval of aggregative nucleation, i.e., the higher the content the bigger the time and the lower the rate. These factors directly impacted both size and polydispersity of platinum nanoparticles.



$[PtCl_4]^{-2} + 4Br^- \rightarrow [PtBr_4]^{-2} + 4Cl^-$

$[PtBr_4]^{-2} + 2e^- \rightarrow Pt^0 + 4Br^-$

Figure 1: Integrated representation of particle number (N), absorbance at 500 nm, normalized particle volume and wavelength. Each step of the growth mechanism (Δt_i, Δt_1, Δt_2 and Δt_3) is shown below.

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Acknowledgments

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P122

Elucidating the Low-Temperature Intermixing between Ceria and Zirconia Nanoparticles

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ABSTRACT:

Ceria-zirconia systems are promising materials for various heterogeneously catalyzed oxidation reactions, such as the automotive three-way catalysis, the steam reforming, and the HCl oxidation.[1] While CeO_2 provides the active part resulting from the beneficial Ce(III)/Ce(IV) redox properties, ZrO_2 acts as supporting additive increasing both activity and stability. Especially, a sharp CeO_2/ZrO_2 interface recently showed a superior behavior in catalyzing the HCl oxidation.[2] In this regard, a particle-on-particle system of pure CeO_2 and ZrO_2 nanoparticles, respectively, would be desired in order to maximize the amount of this interface. However, neither its nature nor its stability is sufficiently understood.
To fill this gap, nanoparticles of both metal oxides were prepared by a sol-gel route leading to particle sizes between 3 – 4 nm. A physical mixture obtained from drying a mixed nanoparticle sol was converted into a mixed crystal, *i.e.*, a solid solution, after a thermal treatment at 500 °C albeit being thermodynamically unfavored for the bulk phase.[3] *In-situ* X-ray diffraction and *ex-situ* Raman spectroscopy enable a tracking of the intermixing process and reveal that the latter starts at already 300 °C and is completed at 350 °C. In literature, calcination temperatures of about 800 °C are typically chosen to guarantee a solid solution formation,[4] which evokes the questions why the intermixing occurs at such low temperatures, and how mixed oxides are formed in general. Since diffusion of the involved cations is estimated to be slow, the pronounced reduction in melting point by around 2000 °C as a consequence of the nanoscale is regarded as the major origin of intermixing: a high homologous temperature beyond 0.5 tremendously enhances diffusion whilst preserving crystallinity and the small particle size as shown by *in-situ* XRD. This study presents a pathway for a low-temperature synthesis of mixed oxides and highlights the influence of curvature on both thermodynamics and diffusion.

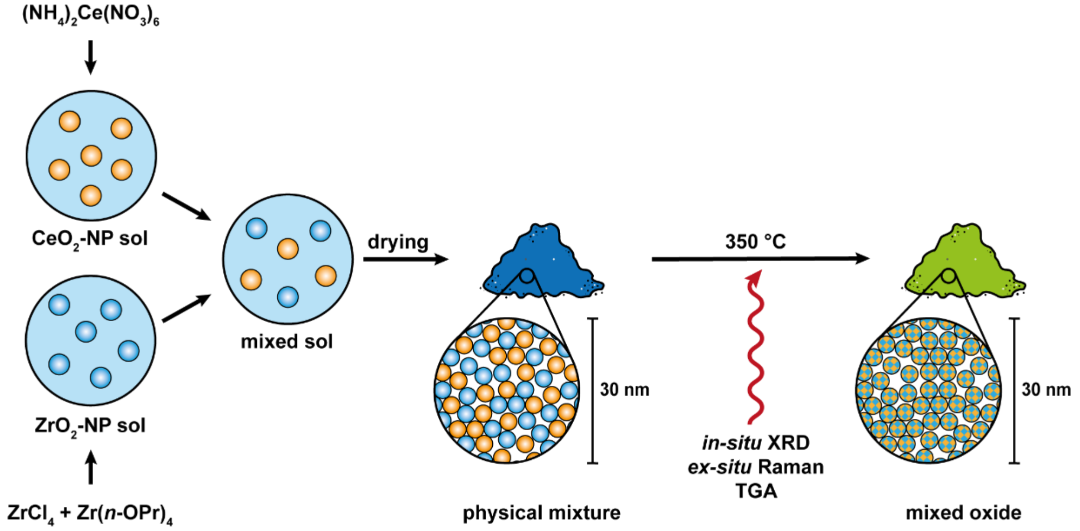

Figure 1 : Sol-gel preparation and low-temperature intermixing of CeO_2 and ZrO_2 nanoparticles.

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Self-assembled $Mg(OH)_2$ Gels driving to MgO nanoribbons

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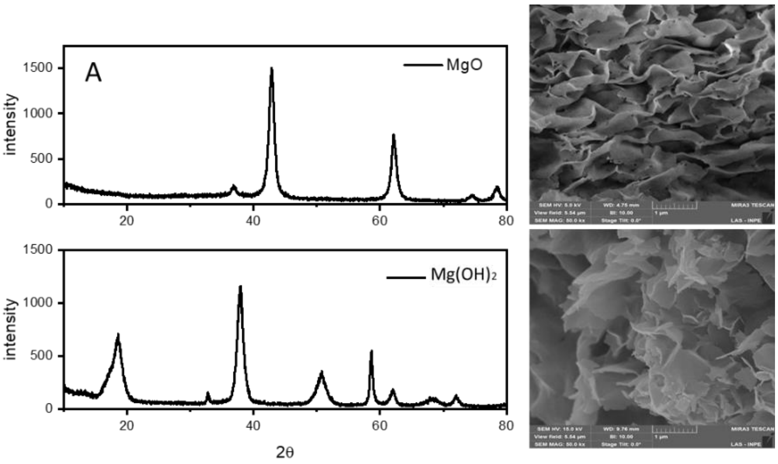
ABSTRACT:

Sol-gel process is a recognized way to synthesize metal oxides leading to well-defined textures, narrow size-distribution, and porous inorganic and/or hybrid materials [1,2]. Herein, a glycerol-solvent route to prepare MgO nanoribbons without structure-directing agents is reported. It consists on preparing gels wherein the $Mg(OH)_2$ were formed as an ordered solid structure. Thereafter, calcination of these Mg(OH)2 gels lead to long nanoribbons of MgO, Fig. 1. As an default procedure: 0.05 mol of $Mg(NO_3)_2$ is dissolved in glycerol-isopropanol 3:1 mol ratio (30 mL) at room temperature, further addition of 0.1 mol NaOH solution (5 mL) forms a gel that can be washed up with water aiming to remove residual salt and organic solvent, in fact, turning an organogel into hydrogel. Further characterization by DRX, SEM and TEM showed the peculiar MgO structure that is tailored based on the previous $Mg(OH)_2$ particles arrangements. Overall, we have developed an unprecedent sol-gel route of great value for further preparations involving nanostructures and to afford metal oxide inorganic gels, as well as underpinning applications in which metal oxide gels may be used.

Figure 1: DRX and SEM of the $Mg(OH)_2$ and MgO



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MODIFICATION OF $FE_3O_4@SIO_2$ CORE-SHELL MATERIAL BY VARIOUS SILANES

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Thus, so far, magnetic nanoparticles especially Fe_3O_4 become the study focus of material scientists due to their unique physicochemical and high application potentials. Silica has more stable properties towards acidic conditions, has hydroxyl groups that enable the functionalization of Fe_3O_4 to bind diverse biological ligands. Another excellence related to the properties of SiO_2 is having a nanometre particle size with interface energy and adequate bounds to connect with the core. Besides, SiO_2 particles in nontoxic, biocompatible, also have hydrophilic properties due to the existence of a silanol group on the surface. The combination of Fe_3O_4 and SiO_2 in the nanocomposite system has more advantages such as having biocompatibility, high biostability, and excellent response in drug delivery [1-3]. In recent work, we present Bio-On-Magnetic-Beads (BOMB) [4] synthetic route. We successfully prepare nano-Fe_3O_4 cores using precipitation reaction. In the next step of the work, we covered cores with a non-porous silica shell. the resulting core-shell material will be modified with several selected ligands with amine or mercapto groups (Figure 1). Modified core-shell materials were fully characterized using elemental analysis, Fourier-transform infrared (FTIR) spectroscopy, thermogravimetric analysis and adsorption techniques. The elemental analysis confirmed containing functional ligand on the surface of core-shell material. The thermal analysis was characterised in the range of 50 to 900 °C and confirmed the presence of different ligands on the surface of the core-shell materials. The infrared spectrum of $Fe_3O_4@SiO_2$ nanocomposites was characterized using FTIR spectroscopy which was run at the wavenumbers ranging between 4000-400 cm^{-1}. This analysis was used to study the organic and inorganic bonds formed in $Fe_3O_4@SiO_2$ nanocomposites.
Detailed results will be presented in the form of a poster.

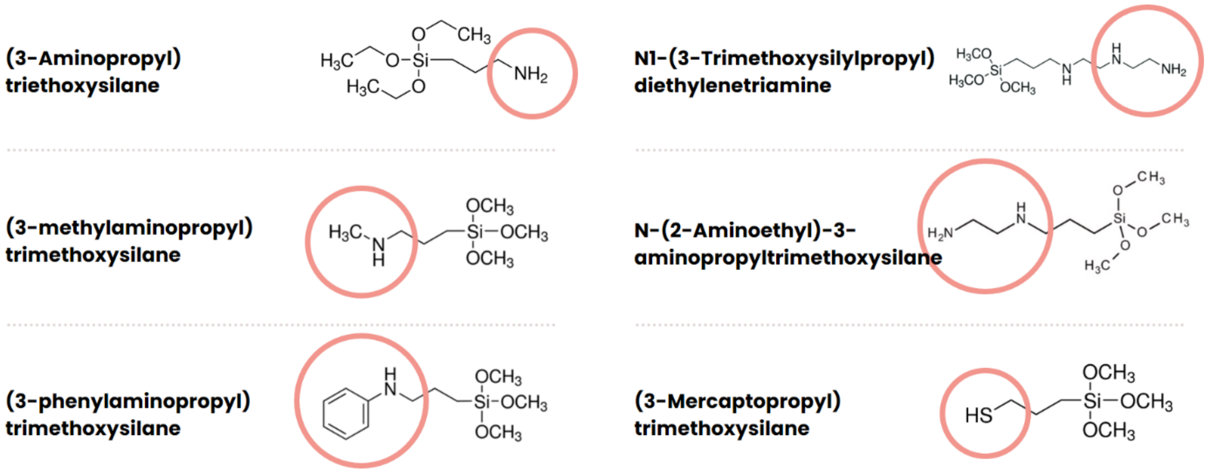

Figure 1 List of used ligand for modification

ACKNOWLEDGEMENT:

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P125

USING SOLVENT PROPERTIES TO CREATE PATTERNED NANOPARTICLE MONOLAYERS IN CONVECTIVELY ASSEMBLED FILMS

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ABSTRACT:

Dip-coating in the evaporative regime offers a straightforward method for the self-assembly of nanomaterials into two-dimensional close-packed monolayers. However, certain conditions, such as small nanoparticles at low concentration require a set of dip-coating parameters that result in meniscus pinning, leading to the accumulation of a multilayer in a band followed by a band of sparsely deposited nanoparticles. These inhomogeneous films have semi-regular patterns, featuring stripes of controllable spacing and width.[1] Pinning can be used to create other non-linear patterns,[2] but controlling their formation is less well studied. In parallel, creating 2D substrates with correlated disorder is of high interest to obtaining engineered optical properties.[3]

We present recent experimental results showing that solvent viscosity is an effective tool to control surface coverage. Silica spheres were suspended in a series of alcoholic solvents having similar surface tension, boiling point and density, but different viscosities. By isolating the impact of viscosity on film formation, stick-slip behavior was most pronounced at low viscosity and low withdrawal speeds. Increased viscosity resulted in lower distances between stick-slip bands and more homogeneous deposition. Surface tension was modified by adding glycerol to the solution. Surface tension plays a role in both particle pinning and in convective currents within the meniscus.

The different patterns were measured using goniospectroscopy to quantify the diffuse halo produced by the different types of correlated systems. The colors are homogeneous across large areas, and from batch to batch, demonstrating the reproducibility of this technique. The optical results for these silica particles decorating silicon substrates emphasize how simple variations in solvent properties can lead to dramatic differences in assembly behavior and thus material appearance.

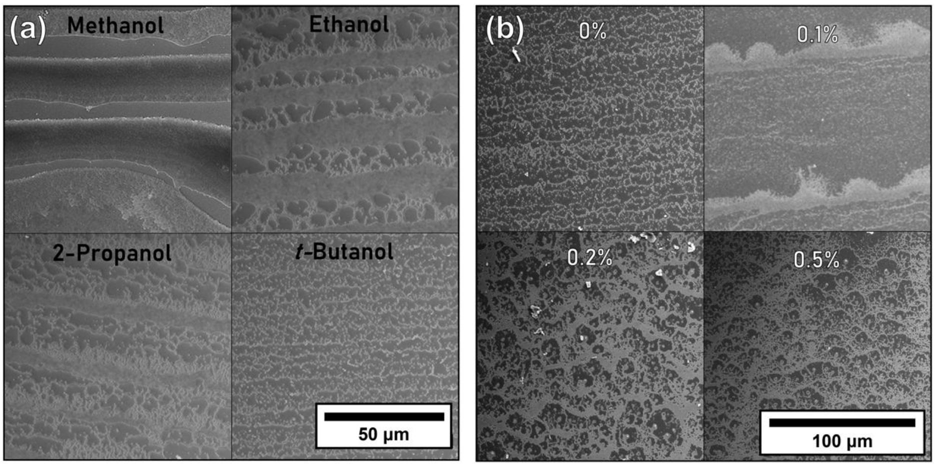

Figure: (a) Monolayers of silica particles prepared using different viscosity solvents. (b) Monolayers of silica particles prepared using solvents containing different % v/v glycerol.

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WIRELESS ELECTROCHEMICAL BIOSENSOR USING POLYMER DOT ELECTRODE TO SELECTIVELY DETECT GRAM BACTERIA

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ABSTRACT:

Until now, the method to distinguish between Gram-negative and Gram-positive bacteria has been dependent on Gram staining, which takes a lot of time and causes misuse of antibiotics. Accordingly, the wireless electrochemical biosensor developed by us is designed to selectively detect pathogens as Gram-negative and Gram-positive bacteria in actual clinical samples, going beyond Gram bacteria. Polymer dot-coated electrodes(PD-Colis and PD-Vanco) conjugated with colistin and vancomycin bind to the cell walls of gram-negative and gram-positive bacteria, respectively, causing an increase in electrode resistance. In the case of Gram-negative bacteria, the PD-Colis electrode causes a resistance change of 12-15kΩ depending on the concentration of the bacteria, and in the case of Gram-positive bacteria, the PD-Vanco electrode causes a resistance change of 13-17kΩ. In addition, PD-Colis electrode (3.0 CFU/mL, R^2=0.995) and PD-Vanco electrode (3.1 CFU/mL, R^2=0.994) have good limit of detection (LOD), enabling detection even at low concentrations. Our electrodes can also detect resistant bacteria that are resistant to antibiotics, and selectively detect other heterogeneous conditions such as serum. In addition, it can show excellent performance of selective detection of pathogens even in real clinical samples. All these processes can be monitored in real time using a smartphone by mixing the electrode and wireless sensing system developed by us. Finally, we expect that our wireless electrochemical biosensor has great potential for rapid and accurate diagnosis in hospitals.

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VISIBLE LIGHT-RESPONSIVE MECHANICALLY AND ELECTRONICALLY TUNABLE HYDROGEL FOR WIRELESS ANTIFOULING SENSOR

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ABSTRACT:

In this work, a wireless pressure and strain sensor has been developed from the visible light tuneable mobility of a conductive hydrogel with carbon dots (CD) for mechanically force-regulated antifouling operation. The conductivity, in addition to strain and pressure sensing ability of the hydrogel, had been controlled through the alteration of hydrophobic to hydrophilic nature of the CD additives that managed the impact of the antifouling thru slight mechanical forces, permitting the cells to be squeezed out from the hydrogel. The photocatalytic activity of CD changes the swelling property, improving mobility, quadrupling conductivity, increasing mechanical strength by 158%, boosting stretchability by 231%, and improving pressure and strain sensor response. Furthermore, the consequence of the exerted mechanical force on the antifouling behaviour for the successful removal of cells from the hydrogel was demonstrated by the antifouling phenomenon. The physical deformation associated with changes in the electrochemical behaviour of the hydrogel was observed by wireless detection. Real-time monitoring of the wireless response was also used to assess the efficacy of the antifouling action as a function of pressure or strain. The hydrogel's antifouling feature, in conjunction with visible-light tuneable hydrophobic–hydrophilic transition, may pave the way for the development of hydrogel-based electronics and biosensing applications.

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NIR/pH-CONTROLLED CONDUCTIVE, SELF-HEALABLE HYDROGEL FOR SELF-POWERED AMPLIFIED HUMAN MOTION SENSING PERFORMANCE

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ABSTRACT:

Here, we have developed a reusable electronic skin sensor from NIR/pH-responsive polymer dot (PD) embedded hydrogel that shows enhanced mechanical, electrochemical, and amplified sensing performance with prolonged lifetimes of the sensor after NIR/pH-driven self-healing. The tunability is achieved by controlling the hydrogen bond formation with regulating mobility from the PD units. Hydrogel produced at pH 7.4, after treatment with pH 10 and healed with NIR, mechanical expansion (585%), electrical conductivity (6.8 mS cm^{-1}), and capacitance (184.2 mF cm^{-2}), increased by 125 %, 4.9 times, and 37% respectively. Thus, it can be explored as a reproducible physiological strain sensor and multipurpose supercapacitor electrolyte. The fabricated strain sensor has shown excellent sensitivity of 0.36 kPa^{-1} with remarkable stability over 12000 stretching-bending cycles. Furthermore, the hydrogel supercapacitor was attached with a solar cell device and a self-power body sensor was achieved with an overall efficiency of 2.32%. The NIR/pH-driven durability, the reproducible amplified mechanical and electrical performance of the self-powered electronic skin can be efficiently used for detecting movements ranging from a subtle human wrist pulse to rough finger motions.

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Main Menu

Composite materials and polymers

DEVELOPMENT OF IRON SUBSTITUTED HYDROXYAPATITE FOR MEDICAL APPLICATIONS

Silviu-Adrian Predoi[1,2], Alina-Mihaela Prodan[3,4], Nicoleta Vineticu[5], Mircea Beuran[3,4,*]

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ABSTRACT:

Iron substituted hydroxyapatite (FeHAp) magnetic nanoparticles have been little studied. Magnetic nanoparticles of FeHAp could be a new alternative for numerous biomedical applications. This study presents both the method of synthesis and the physico-chemical and biological properties of FeHAp. FeHAp magnetic nanoparticles were obtained by an adapted co-precipitation method in an aqueous solution by adding different concentrations of Fe^{2+}.The stability of FeHAp magnetic nanoparticles suspension was evaluated by dynamic light scattering (DLS), ultrasonic measurements (US) and zeta potential (ZP). Physico-chemical properties were assessed by X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS) were conducted. The purity of the FeHAp magnetic nanoparticles was appraised by Energy-dispersive X-ray spectroscopy (EDS) and the presence of the constituent elements such as Calcium, Phosphorous and Iron in the analyzed sample were confirmed. The positions of the peaks correspond to the structure of the pure hydroxyapatite. XRD studies have shown that there is no individual peak that matches the γ-Fe_2O_3 peak which shows that Fe^{2+}/Fe^{3+} were substituted in HAp. On the other hand, the crystallinity decreased with increasing iron ion concentration. Our results are in agreement with previous studies presented by Zuo et al. [1] which proved that the presence of Fe^{2+} ions with a lower ionic radius (0.0835 nm) than that of Ca^{2+} affects the network parameters. The *in vitro* cytotoxicity of the FeHAp magnetic nanoparticles suspensions was evidenced using osteoblast cells. The MTT assay showed that the FeHAp magnetic nanoparticles suspensions exquisite excellent biocompatible properties.

Acknowledgments: This work was supported by the Romanian Ministry of Research and Innovation through the project PN-III-P2-2.1-PED-2019-0868 contract no. 467PED ⁄ 2020 and project PN-III-P2-2.1-PED-2019-1375 contract no. 331/PED/2020.

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REMOVAL OF Pb (II) IONS FROM CONTAMINATED WATER USING NEW HYDROXYAPATITE-CTAB COMPOSITE AS ADSORBENT

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ABSTRACT:

Hydroxyapatite (HAp) nanoparticles coated with cetyltrimethylammonium bromide (CTAB) are very promising biocompsite for wastewater treatment. The first goal of this study was to prepare HAp-CTAB composite by an adapted method [1] keeping constant the stoichiometric ratio Ca / P stoichiometric ratio at 1.67. The second objective was to examine the performance of HAp-CTAB biocomposites as an adsorbent for lead removal from aqueous solutions. The morphological and structural properties were evaluated by various analysis such as X-ray diffraction (XRD), transmission electron microscopy (TEM), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX). The ultrasonic measurements conducted in order to evaluate the efficacy of HAp-CTAB biocomposites as an adsorbent for lead removal from aqueous solutions. On the other hand, the Langmuir and Freundlich models underlined that HAp-CTAB biocomposite were favorable for the adsorption of lead ions from aqueous solutions. Moreover, the toxic effect of lead ions adsorbed by HAp-CTAB biocomposites from contaminated water on fibroblast cells was assessed. The ultrasound measurements as a non-destructive method used in decontamination proces of wastewater will lead to essential advances in the complex analysis of the effectiveness of various materials used in different environmental applications. Furthermore, the present study clearly shows the efficacy of HAp-CTAB biocomposite in removing lead ions from contaminated solutions.

Acknowledgments: This work was supported by the Romanian Ministry of Research and Innovation through the project PN-III-P2-2.1-PED-2019-0868 contract no. 467PED ⁄ 2020 and project PN-III-P2-2.1-PED-2019-1375 contract no. 331/PED/2020.

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FUNCTIONAL BLOCK COPOLYMERS FOR *IN-SITU* FUNCTIONALIZATION OF MESOPOROUS SILICA FILMS

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Nature provides the ultimate inspiration – able to direct, gate and selectively transport through pores and channels with technologically unreached performance. To approach this performance, the precision in nanoporous material design has to be significantly improved. For example, material architecture and structural as well as functional hierarchy have to be precisely designed. To do so nanoscale layer-wise material build up, e.g. using printing techniques for nanoporous structure formation in combination with *in-situ* functionalization approaches, is envisioned to allow precise structural and functional hierarchy design at the nanoscale.

Specifically, stimuli-responsive mesoporous silica films were prepared by evaporation-induced self-assembly through physical entrapment of functional block copolymers as structure directing agent, which simultaneously serve as functionalization of the mesopores. By this way highly filled pores with e.g. PS-*b*-PAA that exhibit remarkable gating ionic permselectivity with changes in pH[1], enabling the switching between cation- and anion-selectivity under basic and acid conditions, were achieved. Stimuli-responsive transport characteristic can also be observed in partly filled pores. Different examples of functional templates for *in-situ* functionalization and the resulting ionic permselectivity will be presented. Mesoporous films are characterized regarding their porosity and film thickness using ellipsometry, TEM and SEM. Ionic permselectivity is determined using cyclic voltammetry and correlated to porous structure and *in-situ* functionalization. Using functional templates for *in-situ* functionalization of mesoporous layers bears the potential for localized stimuli-responsive polymer functionalization within a precisely designed architecture[2] and fabrication of *in-situ* functionalized porous silica films by high throughput printing methods[3]. This direct and simple approach of *in-situ* functionalization of mesoporous silica using functional block copolymers is expected to be highly relevant for a variety of technologies based on molecular transport in nanoscale pores, such as sensing, separation, catalysis and energy conversion.

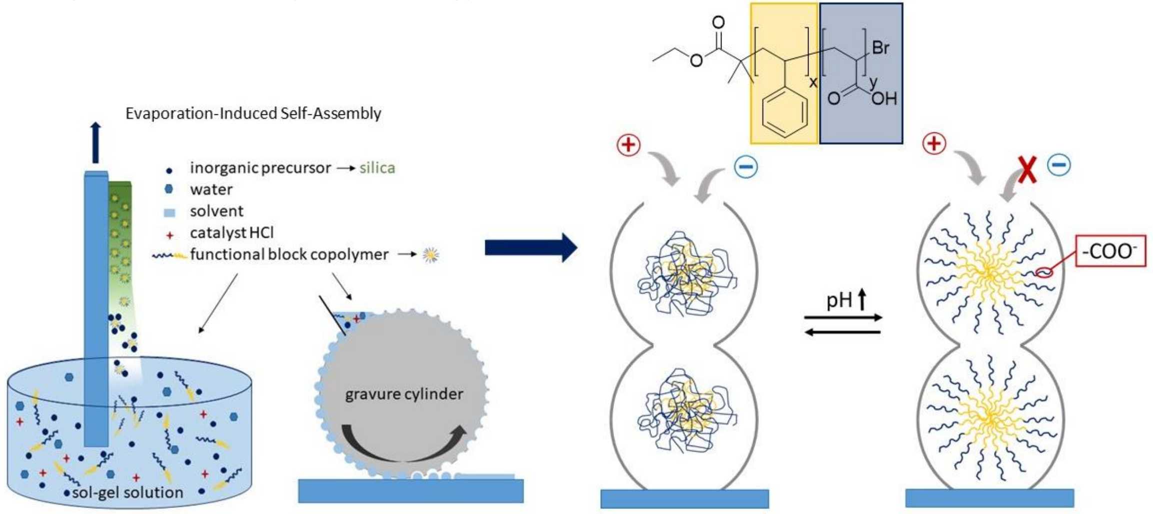

Figure 1 : Stimuli-responsive mesoporous silica thin films prepared in an one step procedure by Evaporation-Induced Self-Assembly (EISA) have achieved tunable ionic permselectivity, thereby demonstrating their high potential for developing multifunctional, complex architectures with to date unreached transport performances.

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P132

INFLUENCE OF SILICA OXIDE MATRIX ON FEATURES OF SILVER IODIDE IN THE COMPOSITION OF A HYBRID POWDERS

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Hybrid powders (hereinafter HPMs) based on mesoporous silica dioxide and crystalline silver iodide can become an alternative reagent for precipitation of atmospheric moisture (fog) in areas of increased technological activity at the temperature range from minus 10 to plus 15 ° C. Due to the multifunctionality of hybrid powder particles, new composite materials can be much more effective than existing solid-phase reagents [1], because the condensation processes are occurring due to the silica matrix-base, and phase transitions “liquid water - ice” is due to silver iodide crystals.

HPMs are obtained as a result of hydrothermal synthesis [2], and silver iodide particles are formed before the start of the physicochemical process of the formation of the silica oxide structure. The formation of silver iodide occurs as a result of an exchange reaction. The basis for the silica matrix is mesoporous silica of the MCM-48, MCM-41 and SBA-15 types.

In this study, it was noted that the type of mesoporous silica matrix significantly affects the possibility of the formation of the crystal lattice of silver iodide. It was found that the formation of the β-phase of silver iodide in the HPM for the MCM-48 matrix occurs at the ratio [Ag] / [Si] = 0.02. The formation of the crystalline form for MCM-41 and SBA-15 types of matrix occurs only when at the ratio [Ag] / [Si] = 0.08.

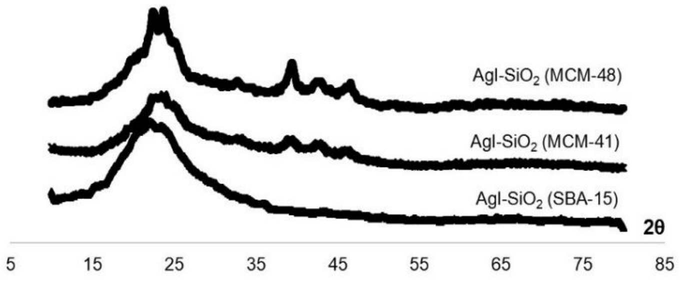

Figure 1: X-ray diffraction pattern of HPM samples with the ratio [Ag] / [Si] = 0.02

This phenomenon can be explained by the types of mesoporous silica dioxide MCM-48, MCM-41 and SBA-15 differ in the specific surface area and size of pores [3]. It is assumed that the 3D structure of MCM-48 is most favorable for the formation of a hexagonal crystalline phase of silver iodide in comparison with the 2D structure of MCM-41 and SBA-15.

The possibility of joint control of the properties of the silica matrix and silver iodide can promisingly create unique materials.

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P133

Electrical treeing properties of epoxy nanocomposites with *in situ* synthesized SiO_2, TiO_2, and Al_2O_3

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ABSTRACT:

Epoxy nanocomposites containing inorganic oxide nanoparticles exhibit novel properties such as reduced complex permittivity, higher breakdown strengths, and increased resistance to electrical treeing making them attractive nanodielectrics for high voltage power applications [1]. These improvements in properties are contingent upon a homogeneous dispersion of the filler particles with no agglomeration [2]. In this work, an *in situ* sol-gel based synthesis procedure was used to form surface functionalized SiO_2, TiO_2 and Al_2O_3 nanoparticles (5 wt% filler content) directly in the epoxy monomer (DGEBA) prior to polymerization and curing. The SiO_2 and Al_2O_3 formed hierarchical clusters (10-60 nm and 100-200 nm respectively) while the TiO_2 formed discrete particles (20-50 nm), and the amount and type of surface functionalization affected the state of dispersion significantly. Electrical treeing is a pre-breakdown phenomenon in nanodielectrics, and an increased resistance to electrical tree propagation is required in high voltage insulation materials [3]. The tree initiation voltage was unchanged from that of pure epoxy in the epoxy-Al_2O_3 nanocomposites, whereas in epoxy-TiO_2 and epoxy-SiO_2 nanocomposites initiation voltage decreased. All the nanocomposites showed increased resistance to electrical tree growth at 10 kV, with the epoxy-Al_2O_3 nanocomposites exhibiting the slowest tree growth. However, at 15 kV only the epoxy-TiO_2 nanocomposites had a slower growth rate than pure epoxy. Partial discharge measurements showed the formation of conducting tree channels from initially non-conducting channels. The electrical tree propagation in the epoxy-SiO_2 nanocomposites was also observed to be dependent on the synthesis conditions and the resulting dispersion of the SiO_2. The results highlight the importance of particle dispersion, morphology, and composition in the electrical treeing properties of the nanocomposites.

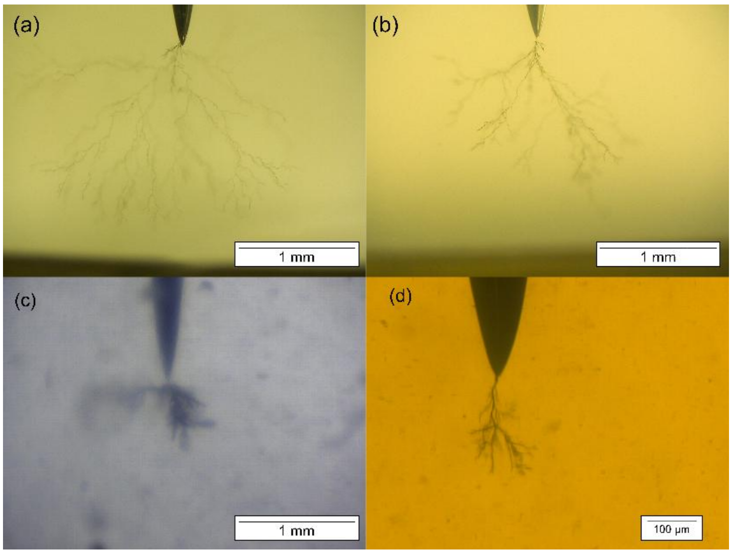

Figure 1: Electrical tree growth in (a) pure epoxy, (b) epoxy-SiO_2, (c) epoxy-TiO_2, and epoxy-Al_2O_3 nanocomposites (all with 5 wt% filler content).

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POLYUREA GEL PREPARED BY SOL-GEL CHEMISTRY FOR DUAL RELEASE OF ANTIINFLAMATORY AND ANTICANCER DRUGS

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ABSTRACT

A synergistic effect when combining drugs and administered together using a reservoir/carrier system has been widely observed.[1,2] In general, these drug combinations (dual-delivery) are applied for cancer therapy purposes.[3] Considering the relevance of combining therapy and polymer systems for drug release purposes, this work presents an elegant strategy for simultaneous incorporation of two drugs with distinct actions in a unique polymeric material. A simple reaction between an amino-terminated-polyether PEO (Jeffamine ED-2003) and a tridentate ligand hexamethylene diisocyanate trimer (HDI) at room temperature (sol-gel chemistry) led to the formation of a transparent, rubber, and scalable polyurea (PUr) device for medical purposes. The final material was charaterized by Fourier Transform Infrared Spectroscopy (FTIR) and Differential Scanning Calorimetry (DSC). The isocyanate-free and the formation of urea groups after PEO-HDI reaction was evidenced by the band absence at 2266 cm^{-1}, characteristic of N=C=O asymmetric streching, and the presence of amide I - amide II vibrational modes in the region between 1500 and 1800 cm^{-1}. The incorporation of Naproxen (Nap) and 5-fluorouracil (5FU) drugs (individually or simultaneously) into the PUr affected the rigidity of the polyether and the crystallinity degree of PEO (DSC studies). The presence of the two drugs in the gel network did impact the amount released compared with the individual profiles. The dual-drug release showed an initial burst exhibiting 67 % (Nap) and 43% (5FU) release from PUr. This work demonstrates the PUr gel´s suitability as a dual-drug release delivery system and opens positive perspectives to prepare multifunctional materials for health, optical, and environmental applications.

Acknowledgements: Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – (CAPES) – Finance Code 001, Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) – n° 306271/2017-6, and Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP grant n° 2013/20455-2, n° 2019/17860-9 and n° 2020/06531-1).

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SYNTHESIS AND CHARACTERIZATION OF MAGNETIC HALLOYSITE/Fe_3O_4 COMPOSITE FOR ADSORPTION OF DYES

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In recent years, considerable attention has been paid to studies of the properties of magnetic nanomaterials in connection with the prospects for their use in biotechnology, medicine, and for solving environmental problems. Among magnetic materials, iron oxides, such as magnetite Fe_3O_4, which are widely used for targeted drug delivery, as sorbents, biosensors, etc. have the greatest practical application.

Another important direction in the use of magnetite is associated with the preparation of composite materials of Fe_3O_4 with clay minerals. One of the common clay minerals is halloysite, which is widely applied in ceramics, tissue engineering, antimicrobial coatings, cosmetology, etc. It can be expected that the modification of halloysite with magnetite will synthesize new composite materials with physicochemical properties that depend on the properties of the components.

In the present study, a halloysite/magnetite composite material was obtained, its surface morphology, porosity, crystal structure, and adsorption properties with respect to various dyes were investigated.

Magnetite powder was obtained by a two-stage method using the sol-gel technology. The halloysite/magnetite composite (magnetized clay) was synthesized by the method of chemical coprecipitation of iron salts in the pores of halloysite.

In accordance with the data of nitrogen low-temperature adsorption-desorption, the investigated halloysite and magnetized halloysite can be classified as mesoporous materials. The X-ray diffraction patterns of the composite exhibit peaks characteristic of its individual components, such as the (001) reflex corresponding to an interplanar distance of 0.734 nm in halloysite, and the (311) reflex corresponding to magnetite.

It was found that the adsorption kinetics of methylene blue (MB) and malachite green (MG) on halloysite and composite was described by a pseudo-first order reaction equation. It was found that the process of dye adsorption on both adsorbents occurs at a high rate. The adsorption activity of the halloysite/magnetite composite with respect to MB and MG is 20% higher than the analogous characteristic for unmodified halloysite.

SIMULTANEOUS REMOVAL OF CATIONIC AND ANIONIC METALS USING A DUAL-FUNCTION HYDROGEL: BATCH AND COLUMN STUDY

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ABSTRACT:

Water pollution has been seriously threatening global biospheres and affecting the lives of millions of people. Of that global water pollution, heavy metals account for around 31%, a major share of which comes from electroplating effluents (Bolisetty et al., 2019). Thus, we developed a dual-function hydrogel composite via a facile method to remove heavy metals from electroplating effluents. The performance of the dual-function composite was tested in batch and in a fluidized-bed column. For the batch treatment, both adsorption and desorption reached equilibrium within 30 minutes, showing the dual-function composite's fast adsorption capacity. Its removal efficiency was also found to be pH-independent, and insignificant effect was found in the co-presence of monovalent ions. Further, the reusability of composite material was studied for six cycles in which the treated effluent quality was found to be excellent, satisfying the discharge standards of China and Hong Kong SAR (Fig. 1). The reused adsorbent was confirmed by FTIR and XPS to be highly stable. The fast settling by gravity of the dual-function composite in batch motivated us for studying the material further in a fluidized-bed column. Process variables such as feed flow, airflow, and adsorbent's bed depth, which significantly control the metal removal efficiency of a fluidized-bed column, were optimized using response surface methodology (RSM), a statistical tool for process optimization. Under RSM optimized operation conditions, a maximum bed volume of 2.39 BV (597.5 mL) was treated and the discharge met China's national standards. In terms of practicality (fast removal, pH-independence, high stability, and gravity-driven separation), the application of the dual-function composite in a fluidized-bed reactor has shown much promise for the treatment of electroplating wastewater.

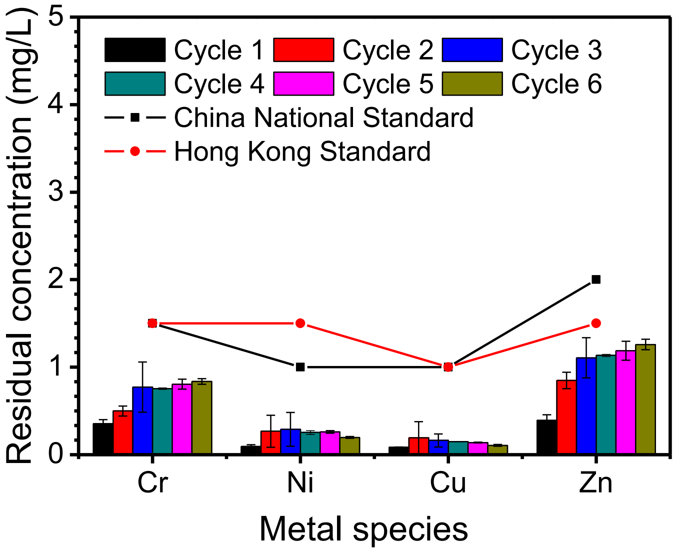

Figure 1: Reusability study of the dual-function hydrogel composite for simultaneous removal of cationic and anionic metals from a simulated electroplating wastewater.

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Flexible Conductive Blend based on PEDOT:PSS with Natural Rubber Latex

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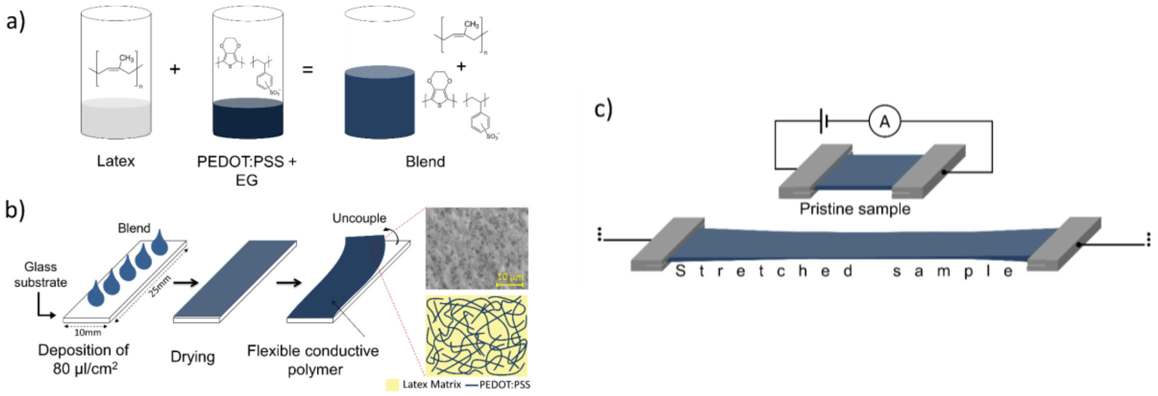
ABSTRACT:

We introduce a blend of Natural Rubber Latex (NRL) with Poly (3,4-ethylene dioxythiophene) - poly(styrene sulfonate), PEDOT:PSS. NRL is obtained from the *Hevea brasiliensis* tree and is a biocompatible electrically insulating material with exceptional mechanical properties. On the other hand, PEDOT:PSS is a biocompatible highly conductive organic material. The study involved different NRL/PEDOT:PSS volume ratios and temperatures of curing aiming at an optimal combination of flexibility and conductivity. Low-temperature annealing, at 60°C, dries and cures the blend in a few minutes and improves its tensile strength and conductivity. The blends present elongation at break higher than 700% of its initial length, elastic deformation and small Gauge Factor up to 100% elongation. Among the different concentrations studied the membranes with ratio 1/4 and thermally cured present the most promising conductive flexible properties for bioelectronic applications.

Figure 1 : Schematic steps to produce the flexible conductive blend of NRL/PEDOT:PSS: **a)** preparation of the blend, and **b)** deposition of the blend on a glass substrate. The flexible blend is detached from the glass for **c)** electrical characterization under stretching.



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CARBON DOTS IMMOBILIZATION ON LAYERED HYDROXIDE SALTS AND CONVERSION INTO METAL OXIDE – NANOCARBON COMPOSITES

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ABSTRACT:

The immobilization of fluorescent nanomaterials in host–guest systems is one of the important factors for the further development of light-emitting properties in nanocomposite materials. In general, it is difficult to immobilize the different type of nanomaterials, such as metal nanoparticles and nanocarbon, into inorganic materials such as oxides by just mixing them due to poor interaction. This study solves the incorporation and immobilization problems by focusing on the structural characteristics of fluorescent carbon dots (C-dots) and layered hydroxide salts, because the present synthetic strategy inducing active chemical bonding between them using the solution reaction is a useful approach for immobilizing the C-dots with the inorganic matrix (**Figure 1**). In this study, one-pot hydrothermal synthesis was performed to generate an advanced fluorescent nanocomposite by immobilizing C-dots in a layered hydroxide salt matrix while synthesizing them in a zincite reaction systems. The one-pot reaction was performed by hydrothermal treatment starting from zinc acetate, urea, and diammonium hydrogen citrate in solution as precursor. The reaction condition that C-dots and hydrozincite could be simultaneously synthesized in a one-pot hydrothermal reaction at 200°C was investigated by adjusting the pH of the precursor, and the formation criteria of the hydrozincite and C-dots composite depending on the pH were clarified. Based on the changes in crystal structure and in the surface state of the resulting composite powder compared with the single hydrozincite powder, the interaction that contributed to the immobilization of carbon dots was discussed. The fluorescence properties of the C-dots immobilized zinc compounds were characterized. Further sintering under an appropriate condition for the C-dots–hydrozincite composite allowed conversion into the C-dots–zinc oxide composite exhibiting quite different fluorescent characteristics.[1]

Figure 1: Synthetic strategy for the immobilization of carbon dots on layered hydrozincite by one-pot hydrothermal treatment.

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Zinc single sites curing activator to drive the cross-links local distribution in elastomeric nanocomposites

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ABSTRACT:

ZnO is the worldwide most employed activator in the sulphur vulcanization process, as it promotes both the process efficiency and rate, as well as the shortening of sulphur cross-links, leading to highly cross-linked elastomeric nanocomposites (NCs). Its reactivity and distribution are strongly influenced by its morphology and strongly affect the resulting chemical cross-link networks and mechanical properties. In fact, Zn(II) must be both highly available to promote the formation of highly reactive zinc-based intermediate complexes with the other curing agents, and well distributed into the elastomeric matrix, to favour the homogeneous cross-linking process into the NCs.

In this perspective, the aim of this work is the investigation of the relation between the morphology of Zn-based activators and the resulting cross-link networks of vulcanized isoprene (IR) NCs. Thus, an innovative activator where zinc single sites were anchored onto the surface of SiO_2 filler nanoparticles (Zn@SiO_2 NPs) was used in an IR NC for its potential interesting way to localize the curing process close to the filler and compared with conventionally SiO_2 filled NC vulcanized by using microcrystalline ZnO (m-ZnO).

First, Zn@SiO_2 was synthesized through a two-step procedure, by coordinating Zn(II) to the surface amino groups available on SiO_2 surface [1]. Then, IR NCs were prepared by blending and compression molding, later vulcanized in a hydraulic press (170°C). Zn(II) centres, behaving as heterogeneous catalytic sites onto SiO_2 surface, localized their activity in proximity of SiO_2 providing higher cross-linking density close to the filler particles and different microscopic structures of vulcanized NCs compared to NCs with m-ZnO, as demonstrated by TEM and NMR. Besides, different mechanical behaviours were evidenced through tensile tests at both high and low deformations, along with different fracture phenomenology induced by the modified microstructural properties, paving the way to the deeper understanding of the relationship between micro- to macro-properties.

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LPSQ-g-PEO AS FILLER IN POLYMERIC MATRICES OF PEO AND PMMA

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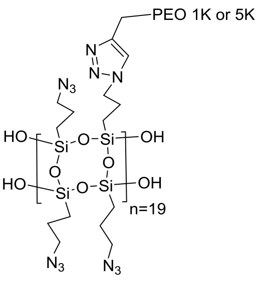
ABSTRACT:

Among the various nano-fillers (NFs) for preparing composite materials, polysilsesquioxanes (PSQs) have been the subject of a particular attention. They can be prepared as random, ladder, lamellar[1], cage or partial cage structure[2].The characteristics of the final nanocomposite materials depend particularly on the form of the dispersed phase[3]. The addition of PSQs to polymers can enhance the performance of the latter. However, the irreversible aggregation of bare PSQs within the polymer matrix due to their immiscibility often impairs properties enhancement of the final composites. Achieving good NF dispersion is thus vital to fully exploit the potential properties of polymer nano-composites (PNCs).

Our study deals with ladder form (LPSQ) fillers, which are currently under-explored compared to other structures. A range of LPSQ properly substituted were synthetized via sol-gel process and used as NF in PEO and PMMA to study their impact on thermal and mechanical properties of these polymers. In order to improve the dispersion of NF in polymer matrix, LPSQ were functionalized with PEO chains of 1000 or 5000 g/mol through a click reaction (Fig. 1). Controlled ratios of PEO (1K or 5K) and backbone $(SiO_{1,5})_n$ were obtained. The chemical structure of these nano-objects and their morphology were fully characterized (NMR, IR, TGA and TEM). LPSQ filler provides a reinforcement effect when dispersed in PEO 100 kg/mol matrix, and conversely softening effect in the case of PMMA 89 kg/mol matrix.



LPSQ filler

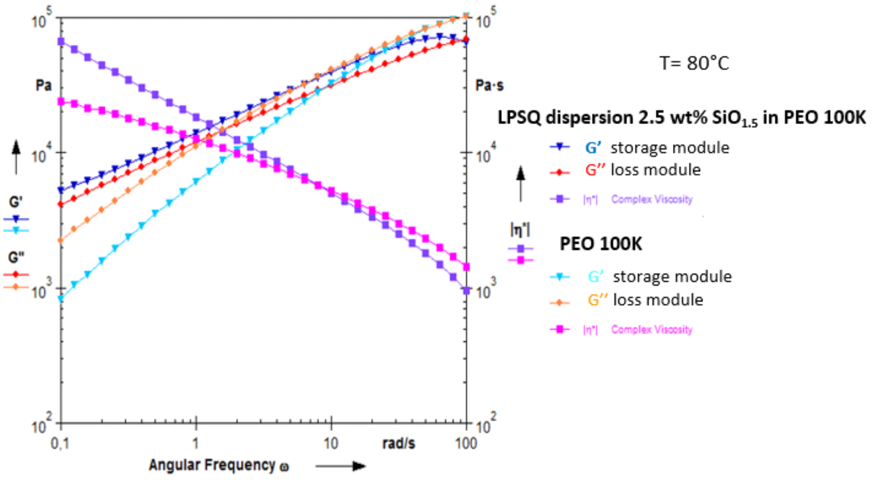


Figure 1: Viscoelastic properties of PEO/LPSQ functionalized PEO of 1K. The amount of LPSQ filler was fixed at 2.5 wt% of $SiO_{1.5}$ in PEO100K

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Enhanced thermal properties of functionalized epoxy-$ZnO/Zn(OH)_2$ nanocomposites fabricated via sol-gel method

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ABSTRACT:

Epoxy resins form highly crosslinked network polymers through ring-opening polymerization with a wide range of chemical hardeners [1]. Their thermal properties including glass transition temperature and structural stability over a wide range of temperatures are generally improved by inorganic reinforcements [2]. The choice of resin, hardener, and typical inorganic reinforcement determine their overall properties and applications in industry and aerospace. This work presents the synthesis of functional $ZnO/Zn(OH)_2$ nanoparticles via a sol-gel method, and their subsequent inclusion into a bisphenol A diglycidylether (epoxy resin). The amount of $ZnO/Zn(OH)_2$ nanoparticles is varied between 0-2 wt% to prepare several mixtures of functional epoxy-$ZnO/Zn(OH)_2$ pre-polymers, which are later thermally cured with 2,2'-dimethyl-4,4'-diaminodicyclohexylmethane (a diamine hardener) for several hours. The resultant epoxy-$ZnO/Zn(OH)_2$ nanocomposites are characterized by different advanced analytical techniques. The structure and functionality of $ZnO/Zn(OH)_2$ nanoparticles and epoxy-$ZnO/Zn(OH)_2$ nanocomposites are confirmed by X-ray diffraction and Fourier-transform infrared spectroscopy. Scanning electron micrographs of epoxy-$ZnO/Zn(OH)_2$ nanocomposites exhibit uniform distribution of functional $ZnO/Zn(OH)_2$ nanoparticles into the polymeric matrix, which translates into a significant increase in the glass transition temperature of the resulting epoxy-$ZnO/Zn(OH)_2$ nanocomposites as measured by differential scanning calorimetry. Also, thermogravimetric analyses of the nanocomposites demonstrate an increase in the initial decomposition temperatures thereby delaying thermal degradation to above 355°C. The superior thermal properties of epoxy-$ZnO/Zn(OH)_2$ nanocomposites are attributed to improved interfacial adhesion and compatibility of functional $ZnO/Zn(OH)_2$ nanoparticles with epoxy matrix.

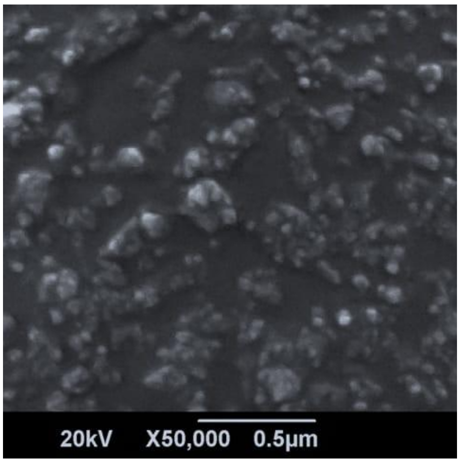

Figure 1: A scanning electron micrograph of epoxy-$ZnO/Zn(OH)_2$ nanocomposite.

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DEVELOPMENT OF RARE EARTH-FREE ALUMINIUM BORATE-BASED PHOSPHORS AND COMPOSITE FILMS

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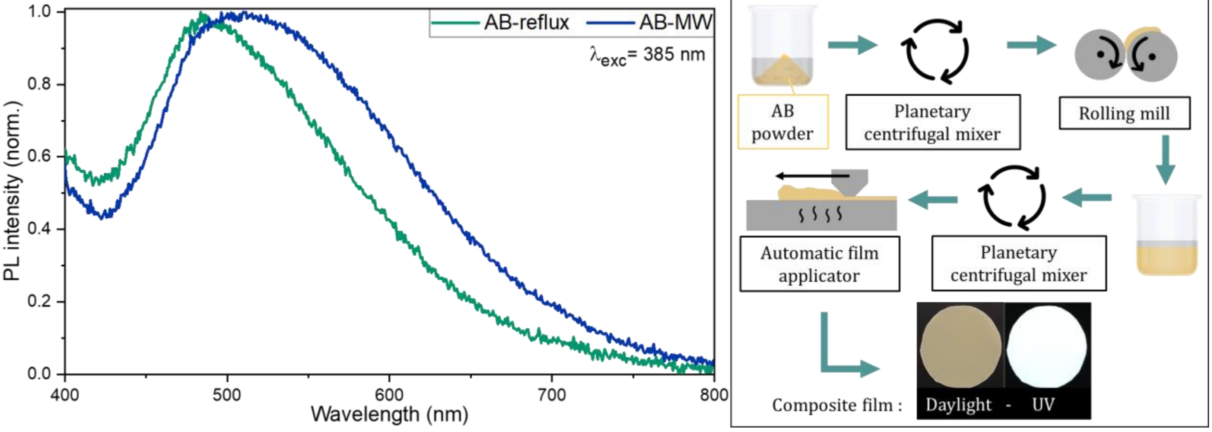
ABSTRACT:

Solid-state white light sources using light-emitting diodes (LEDs) are a breakthrough technology in the lighting and display markets allowing a significant reduction of the energy consumption. Major part of current LED devices converting near-UV or blue excitation in white or colored light contain rare earths elements (REE). The latter are associated to environmental and economic issues. This context has led to the search for alternative LED phosphors materials. Here, based on previous works carried out at Néel Institute, REE-free aluminium borate matrices have been developed.[1] These innovative luminescent compounds generate a broad and adjustable luminescence emission band on the entire visible spectrum under commercial UV LED excitation (365 nm; 385 nm; 405 nm) (Fig. 1) linked to organic emitting centres.[2] The aluminium borate (AB) micronic powders are originally prepared by modified Pechini synthesis. This method allows to get a very homogeneous metal oxides matrix. The optimisation of this synthesis protocol by replacing the reflux heating step with microwave (MW) heating will be presented. In addition to the fact this process allows to save two days on the whole synthesis, the optical performances of the resulting powders are clearly improved. Besides, the AB powders were dispersed in a polymer matrix to elaborate luminescent coatings. The stability of the powders and coatings under thermal and photonic stresses was also studied and the results will be presented and discussed.

Figure 1 : Emission spectra of aluminium borates (AB) synthesized by Pechini method (reflux) and microwave assisted hydrothermal process (MW) and composite film preparation process



Acknowledgement
The authors thank Region Auvergne Rhône Alpes for its financial support (Pack Ambition Recherche LUMINOLED project).

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Shear melting and recovery of cellulose nanocrystal-polymer gels

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ABSTRACT:

Cellulose nanocrystals (CNC) are naturally-derived nanostructures of growing importance for the production of composites having attractive mechanical properties and offering improved sustainability over purely petroleum-based alternatives. Fabrication of CNC composites typically involves extrusion of CNC suspensions and gels in various solvents in the presence of additives such as polymers and curing agents. Most studies so far have focused on aqueous CNC gels, yet the behavior of CNC–polymer gels in organic solvents is essential to their wider processability. Here, we study the rheological behavior of composite polymer-CNC gels in dimethylformamide, including additives for UV and thermal crosslinking[1]. Using rheometry coupled with in situ infrared spectroscopy, we show that under external shear, CNC-polymer gels display progressive and irreversible failure of the hydrogen bond network that is responsible for their pronounced elastic properties. In the absence of crosslinking additives, the polymer-CNC gels show an instantaneous but partial recovery of their viscoelasticity upon cessation of flow, whereas the presence of additives allows the gels to recover over a much longer timescale via van der Waals interactions. By exploring a broad range of shear history and CNC concentrations, we construct master curves for the temporal evolution of the viscoelastic properties of the polymer-CNC gels, illustrating the universality of the observed dynamics with respect to gel composition and flow conditions. We find that polymer–CNC composite gels display a number of the distinctive features of colloidal glasses and, strikingly, that their response to the flow conditions encountered during processing can be tuned by chemical additives. These findings have implications for processing dense CNC-polymer composites in solvent casting, 3D printing, and other manufacturing techniques.

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PVP-BASED COMPOSITES CONTAINING SOL-GEL NANOSIZED SiO_2 AND HYBRID TiO_2 MICROPARTICLES FOR WATER PURIFICATION

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Non-woven composite fiber mats are used in several applications including catalysis, tissue engineering, filtration, etc [1]. The electrospinning process is a sustainable approach, because benign solvents and biocompatible polymers can be exploited [2]. Poly(vinylpyrrolidone) (PVP) has been extensively studied, as its pyrroles can interact with several organic and inorganic compounds, leading to membranes with tailored interface [3]. The Sol-Gel methodology can be coupled with electrospinning to prepare organic-inorganic composite with novel properties, working with controlled stoichiometry and mild process conditions [4]. Through a particular Sol-Gel route, it is possible to obtain hybrid TiO_2-acetylacetonate (TiO_2acac, hybrid titania) amorphous xerogels with intrinsic oxidative ability, which are able to degrade different aqueous organic pollutants without need for light irradiation [5]. Besides, the incorporation of silica nanoparticles (SiO_2NP) into thermally treated electrospun PVP fibers results in the manufacturing of sustainable water- and fire-resistant (i.e. self-extinguishing) ternary composite mats (TCMs) [6]. Herein, SiO_2NP and TiO_2acac microparticles (~90 μm) were synthetized via Sol-Gel to be used in the fabrication of electrospun TCMs based on PVP. The spinning solution was prepared with different amount of TiO_2acac to study the effect of hybrid titania on the electrospinning performance. The chemical composition of TCMs and the incorporation of the fillers into the nanofiber matrix was confirmed through spectroscopic (FTIR, EPR) and microscopy (SEM, TEM) analysis (Figure 1). The Zeta potential and EPR measurements were exploited to assess the surface charge value and the presence of superoxide radicals on the TCMs, respectively. TiO_2acac microparticles generated stable superoxide radicals on the TCMs, which oxidatively degraded methylene blue in absence of light, with an initial rate ~70 % higher with respect to a binary composite mat containing only SiO_2NP. These results highlight the possible application of PVP/SiO_2NP/TiO_2acac mats as functional membranes in water purification process [7].

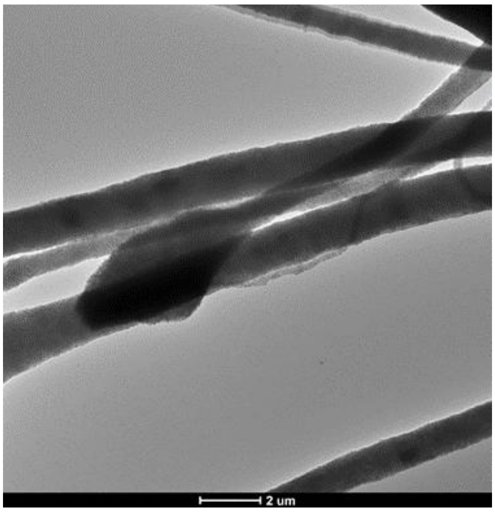

Figure 1: TEM image of PVP/SiO_2NP/TiO_2acac electrospun mat at different magnification: TiO_2acac microparticle covered by a thin layer of PVP and SiO_2NPs.

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PREPARATION OF MXENE/RGO COMPOSITES VIA HYDROTHERMAL TREATMENT: EFFECT OF THE SOLVENT

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ABSTRACT:

The natural hydrophylicity of MXenes is an important advantage for their processing and incorporation in different matrices [1]. The decrease of their conductivity though, due to formation of TiO_2, is a serious drawback. Coupling with graphene has been reported to protect MXenes against oxidation and to enhance their conductivity [2].

In this work, $Ti_3C_2T_x$ MXene and graphite oxide (GtO) were prepared by etching of Ti_3AlC_2 MAX phase and oxidation of graphite, respectively. Water and isopropanol dispersions of MXene/GtO were treated in autoclaves at 180 °C for 16 h. It was found that hydrophilic MXene/rGO was produced after treatment in water (w-MG), while treatment in isopropanol resulted in MXene/GtO composite (i-MG) with strong hydrophobic behaviour. The XRD patterns (Fig.1a) of the composites demonstrated the characteristic peaks of the MXene and the parent MAX phase. The peak of GtO was absent due to delamination and reduction to rGO. Formation of TiO_2 was found for w-MG, whereas titania peaks were not observed for i-MG. The SEM analysis confirmed the presence of TiO_2 nanoparticles on the MXene surface (Fig.1b). The hydrophilicity of w-MG was ascribed to intense oxidation of the MXene in water, while the hydrophobic behavior of i-MG was related to the influence of the solvent facilitating the reduction of GtO and the removal of -OH functional groups from the MXene surface. This outcome can be utilized in preparation of MXene/rGO with tuned hydrophylicity / hydrophobicity.

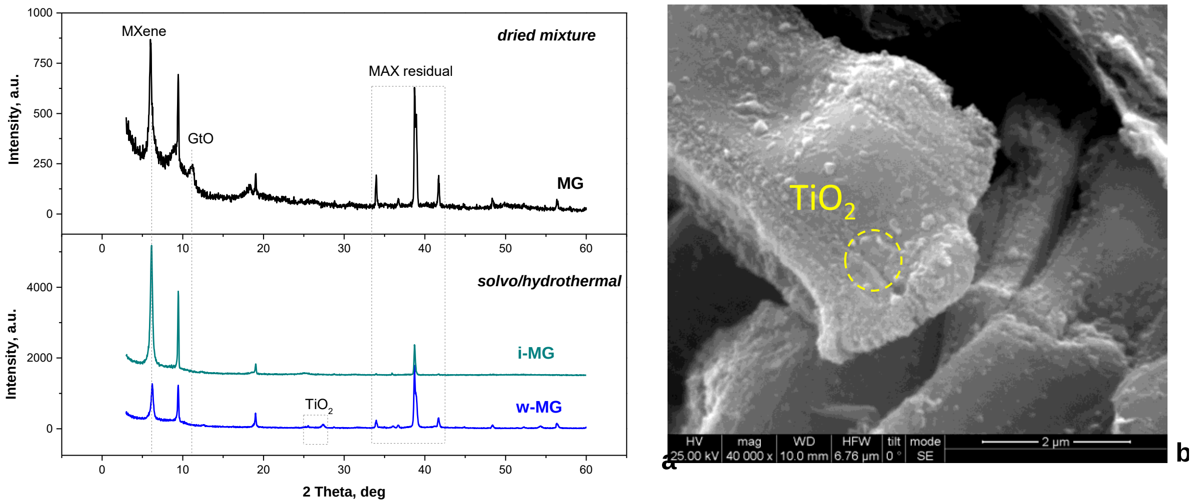

Figure 1: (a) XRD patterns of composites obtained in water (w-MG) and isopropanol (i-MG); (b) SEM image w-MG.

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OPTICAL RESPONSE OF Cd-BASED EMITTORS AND Au NANOPARTICLES - COMBINED IN SOL-GEL GLASSES

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ABSTRACT:

Development of the efficient methods for the formation of new nanostructures systems leads to a fundamental change in the physical properties of the new material [1]. Interactions between nanoparticles (NPs), especially when they have different properties (e.g. photoluminescence or localised surface plasmon resonance), are complex and can lead to enhancement or quenching of the excited state [2].

In our study we had prepared sol–gel silica composites incorporating gold and cadmium-based nanoparticles (Figure 1). Their photophysical properties are investigated and compared with the properties of similarly structured nanoparticle systems in solutions.

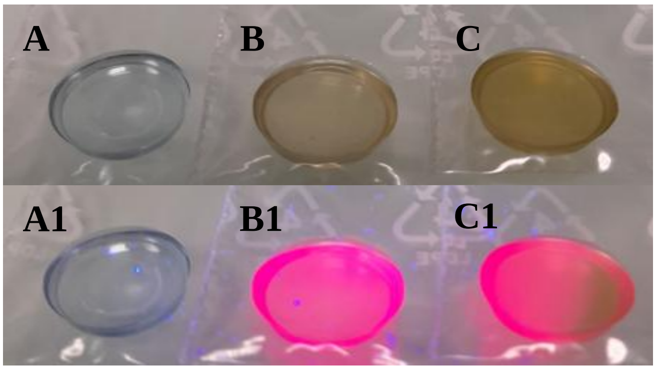

Figure 1. Digital image of materials prepared with (A) gold and (B, C) gold/cadmium-based nanoparticles with increasing concentration of emitters; (A1,B1,C1) materials excited by a laser.

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Porous materials

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MANUFACTURE OF IRON OXIDE AEROGELS FOR HIGH ENERGY DENSITY PLASMA PHYSICS EXPERIMENTS

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ABSTRACT:

The AWE Target Fabrication group produces iron oxide aerogels that are used as target components in plasma physics experiments undertaken on the National Ignition Facility (NIF) high power laser system. Target Fabrication have previously produced iron oxide aerogels to a density of 50-60 mg/cc using an epoxide-assisted sol-gel synthesis[1].

A new campaign required the material at a density of 135 ± 15 mg/cc[2], with the goal to measure radiation transport through an Fe_2O_3 sample and thus determine the opacity of iron. Aerogels of this density were achieved[3] but this work has focussed on further understanding and improving the formulation to present a more reproducible and robust manufacture process.

In addition, a new capability for critical point drying was embedded in the process. Target Fabrication have previously used a Polaron critical point dryer for manufacture of certain aerogels. However, this manual and time-consuming process has been dramatically improved by the use of the automated Leica EM CPD300. Experimentation was carried out to determine optimal parameters to yield high quality, supercritically dried iron oxide aerogels from the Leica critical point dryer.

This poster will highlight the conclusions regarding optimal formulation and critical point drying variables for iron oxide aerogels at a density of ~135 mg/cc.

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TRANSPARENT ZRO_2–SIO_2 AEROGELS, DEPENDENCE OF THE REFRACTIVE INDEX ON DENSITY

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ABSTRACT: SiO_2 aerogels occupy an intermediate position in the refractive index scale (1.13–1.007) laying between liquids (water - 1.33) and gases (freon 114–1.0014, CO_2 at 10 at m. - 1.0043). This feature of aerogels gives several advantages over liquids and gases to use in Cherenkov detectors: there is no need for high pressures; the blocks are compact, convenient and easy to operate. The advanced particle identification is essential for the successful realization of the broad physics program especially for search of “new physics” and study of rare processes. For this, aerogel blocks must have a refractive index >1.05 [1]. It is known that ZrO_2 and zircon ($ZrSiO_4$) have high refractive indices of 2.23 and 1.9, respectively, which is noticeably higher than that for SiO_2 (1.46).

ZrO_2–SiO_2 aerogels with ZrO_2 content of 3, 6 and 10 mol. % in the form of transparent blocks were synthesized using the sol-gel method (Figure 1). The possibility of introducing ZrO_2 into a SiO_2 aerogel without considerable decline of the optical characteristics of the material was shown for the first time. Aerogel samples were studied by several techniques including UV–Vis, ATR-FTIR spectroscopy and nitrogen adsorption, the refractive index was determined using beam tests [2]. It was shown that the addition of ZrO_2 to SiO_2 aerogel increases the refractive index without increasing of the aerogel density (Figure 2). For the first time, the possibility of obtaining highly transparent ZrO_2–SiO_2 aerogel blocks with acceptable optical characteristics for radiator in Cherenkov detectors has been demonstrated. This result makes it possible to achieve high refractive indices in the production of aerogel blocks for Cherenkov detectors to increase their performance.

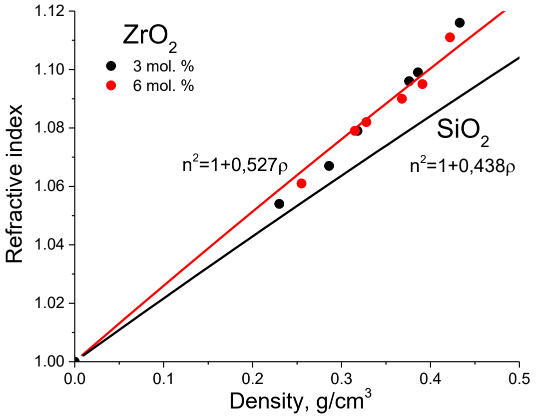

Figure 1. Photographs of aerogel samples (from left to right): only SiO_2, 3, 6 and 10 mol. % ZrO_2, after calcination at 500 °C (top) and 600 °C (bottom).

Figure 2. Dependence of the refractive index on the density for ZrO_2-SiO_2 aerogels with ZrO_2 content of 3 and 6 mol. % (black and red points). The black line is the empirical dependence of the refractive index on density for SiO_2 aerogel blocks [2, 3].

This work was supported by the Russian Science Foundation.

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Monolithic Tannin Gels as Metal and Dye Adsorbent for Environmental Applications

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ABSTRACT:

Adsorption is defined by concentrating the adsorbate from a fluid phase onto the adsorbents' surface or adsorbents' pores. In regard to environmental applications, particularly the wastewater treatment, the adsorption process depicts a powerful tool in the recovery of critical metals and textile dyes. Most commonly, activated carbons or activated alumina are employed.[1] However, their generation requires high process temperatures. Therefore, natural biopolymers adsorbent materials have gained increased interest in wastewater treatment due to their low costs and low temperature processing as well as environmental and economic sustainability. Among others, tannins show great potential as biosorbents based on their ease of conversion into insoluble matrices, as well as their natural affinity to dyes and metals in wastewaters.[2] Tannin-based gel adsorbent materials are produced in a gelation process, whereby tannin is polymerized in a reaction with an aldehyde (mostly formaldehyde), yielding a crosslinked tannin network. However, in accordance to the biosorbents' sustainability, the usage of toxic formaldehyde should be avoided. Hence, alternative bio-friendly crosslinking agents have to be found in order to obtain a fully sustainable class of tannin-based biosorbents.

Within this work, we present the synthesis of different classes of monolithic tannin-based gels, synthesised using different crosslinkers as well as templating approaches, in order to evaluate their usage as biosorbent in wastewater treatment. Their ability to adsorb heavy and critical metal ions, such as cooper, zinc and silver as well as different textile dyes, like methylene blue or congo red, is carefully investigated. Precisely, the adsorption capacity is determined as a function of the used tannin material, its surface modification (e.g. amino- or carboxyl modified tannin gels), the adsorbate as well as the pH value. Furthermore, the applicability in a flow-through adsorption process and the recyclability and thus its circular economic sustainability is evaluated.

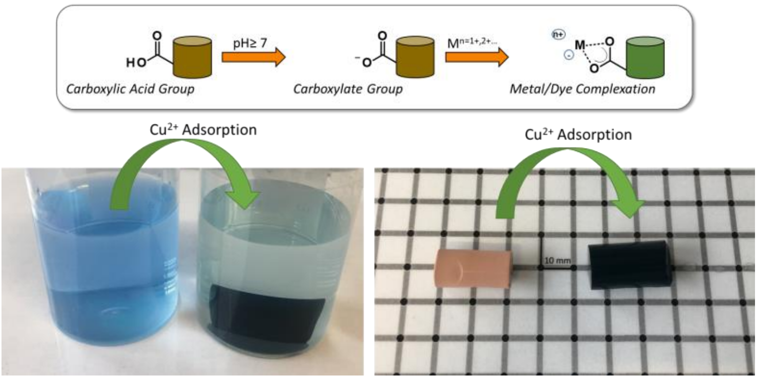

Figure 1: Carboxyl-modified tannin gel as adsorbent material for copper ions.

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Green synthesis route of Al_2O_3-SiO_2 aerogels

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ABSTRACT:

Silica-alumina aerogels exhibit tremendous potential in high-temperature applications because of their excellent temperature stability at temperatures up to 1200°C. The synthesis of these aerogels is well-studied using propylene oxide as a gelation initiator which is unfortunately toxic and carcinogenic. [1]

Within this presentation we report on a new synthesis route which is developed to replace propylene oxide by non-toxic urea receiving silica-alumina gels. The gel bodies are dried under supercritical CO_2 conditions to receive the aerogel. The route provides a significant advantage given their easy scalability.

A systematic and conscious approach is followed to develop a green synthesis route for developing Al_2O_3-SiO_2 aerogels. With the aim of improving the temperature stability of the Al_2O_3-SiO_2 matrix, the molar ratios of urea, the type of solvent and the admixture of added metal oxides, such as ZrO_2, are optimized. All aerogel variants are analyzed with respect to gelation, their density, porosity, internal surface area and thermal conductivity. Furthermore, the influence of heat treatment (25–1100°C) on the granular aerogels is investigated and additionally supported by X-ray powder diffraction, scanning electron microscopy and thermal analysis coupled with Fourier-Transform-Infrared (FT-IR) spectroscopy. In the contribution, all aspects concerning the importance of the careful examination on material parameters to ensure long term thermal stability will be presented. The results will be discussed and an outlook on potential applications will be demonstrated.

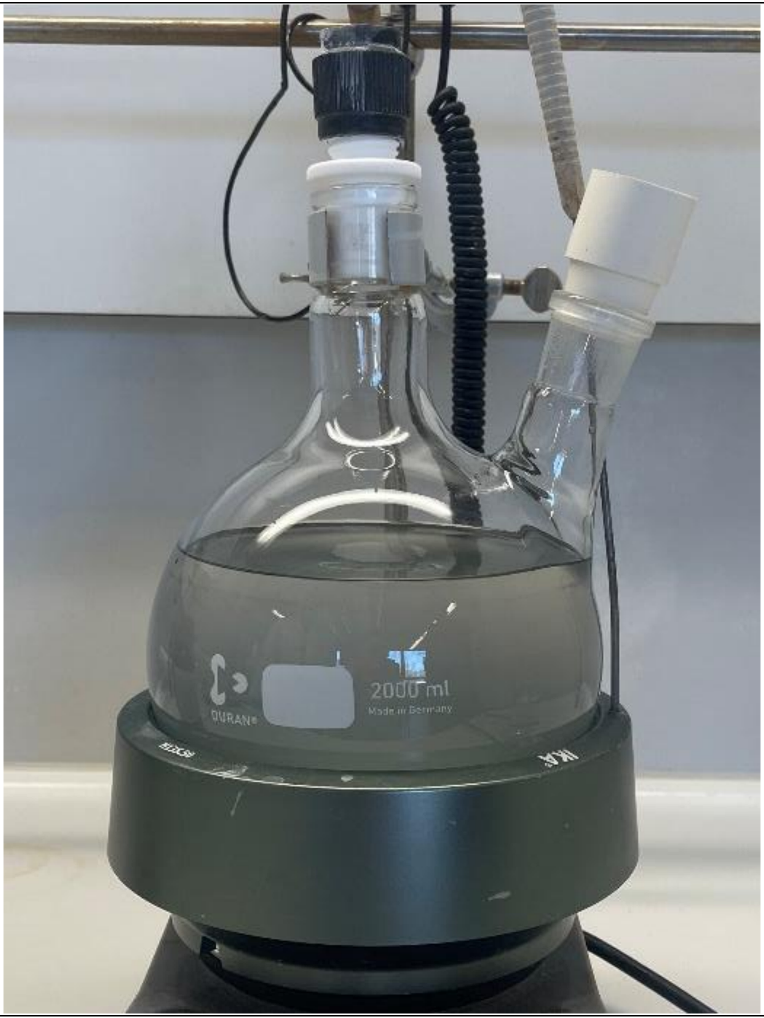

Figure 1: Sol of $AlCl_3$/TEOS

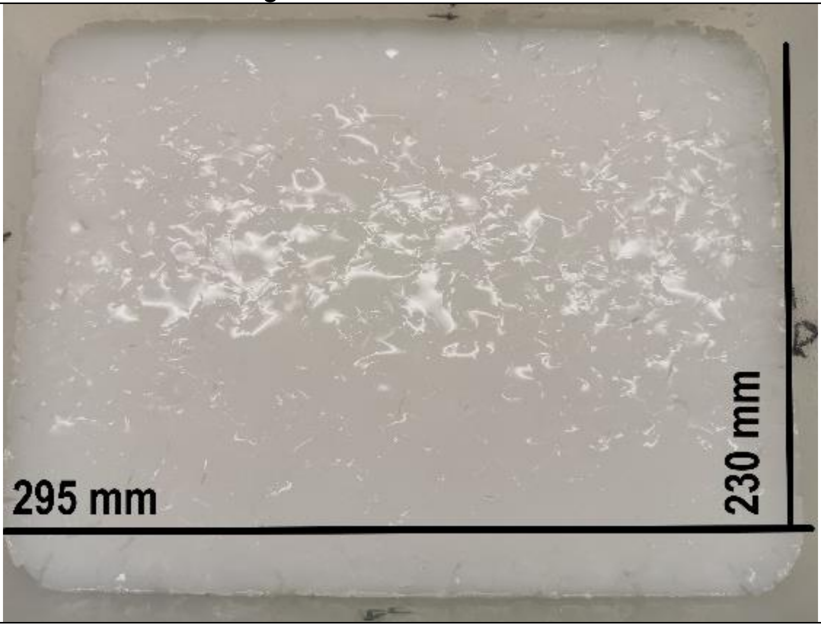

Figure 2: Gelled body

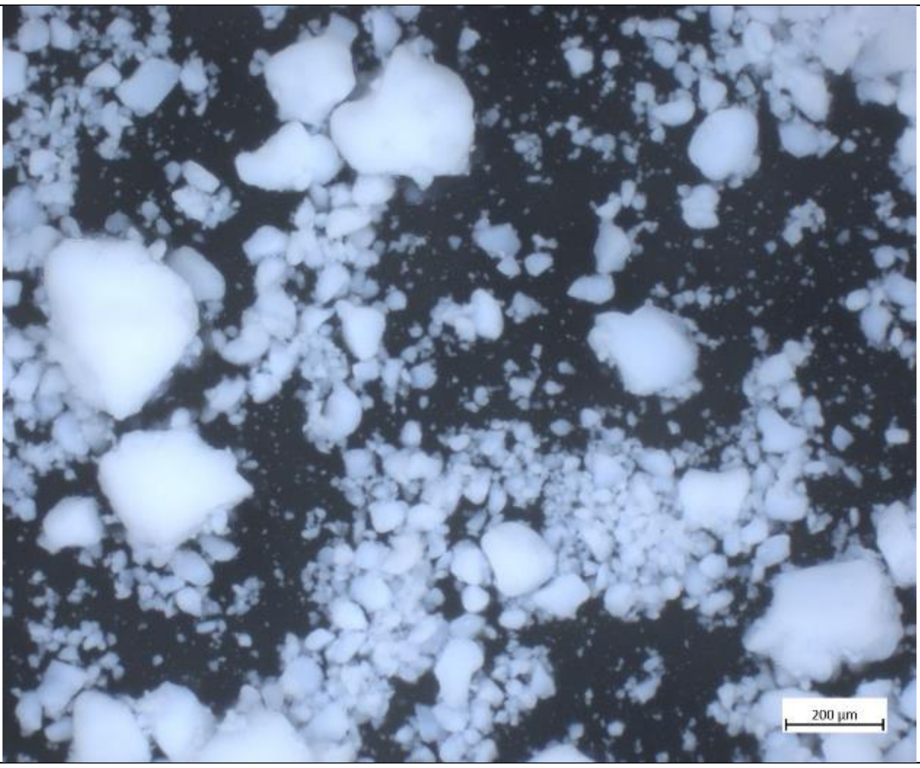

Figure 3: Hybrid alumina-silica-based aerogel after supercritical drying.

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EFFECT OF INCREASING TEMPERATURE ON HIGH FREQUENCY DIELECTRC of NANO-COMPOSITES ZnO DOPED WITH IRON

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Pure and Iron with different concentrations (0.02, 1, 5, 10, 15,20 and 25 mol. %) doped zinc oxide, symbolic as Zn: (0.02, 1, 5, 10, 15,20 and 25 mol. %) were synthesized using the self-modified sol–gel technique in powder form. Structural and morphological properties of the samples were studied comparatively by X-ray diffraction (XRD), fielde mission scanning electron microscopy (FESEM) and High Resolution transmission electron microscopy (HRTEM), which revealed that the samples adapted the hexagonal wurtzite structure. Some structural parameters such as strain, crystallite size, dislocation density, were calculated to have accurate investigation giving rise to nano-structure phase. The Laser-based Raman micro-spectroscopy presents the homogenous distribution of the iron oxide. The sensing performance of the samples toward the effect of increasing the temperature on the dielectric high frequency range between 1 MHz upto 1 GHz were investigated by the help of a network impedance analyzer (KEYSIGHT-E4991B). The obtained data revealed an increase in both A.C. conductivity (σ_{ac}) and real part of the permittivity (ε') by increasing the temmperature up to 130°C at constant 0.2 mol. % of Fe_2O_3. This makes the prepared samples promissing candidate for spintronic and energy storage applications.

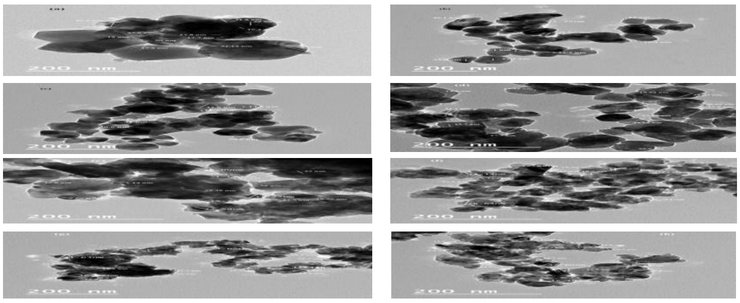

Figure 1

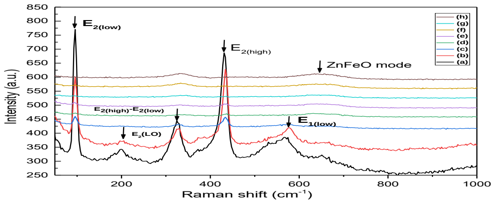

Figure 2

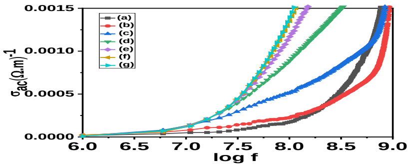

Figure3

Figure 1& 2: TheHRTEM micrographs Fig (1)and Raman spectra Fig (2) of (a) Z, (b) Z02F, (c) Z1F, (d) Z5F, (e) Z10F, (f) Z15F, (g) Z20F and (h) Z25F, respectively sintered at 600°C for 6 hours.

Figure 3: The Ac conductivityσ_{ac}as a function of frequency for Z02F sintered at 600°C for 6 hours measured at diff. Temp. (a) 25°C ,(b) 50 °C ,(c) 80 °C , (d) 97 °C , (e) 115 °C, (f) 130 °C and (g) 150 °C, respectively .

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P152

Attapulgite-reinforced polyimide hybrid aerogels with high dimensional stability and excellent thermal insulation property

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ABSTRACT:

Strong low-density polymer aerogels have received intensive attention as thermal or sound insulator, filtration media and sensors, etc. However, dimensional instability has been regarded as one of issues that limits the wide application of polymer aerogels in a harsh temperature. In present work, polyimide aerogels were reinforced with attapulgite (AT) nanorods, one of natural fibrillar minerals, through the strong hydrogen-bonding interaction. In hybrid aerogels, AT nanorods act as the rigid skeleton that supporting the framework of aerogels. The resultant hybrid aerogels exhibit improved mechanical properties. At the 80% strain, the compressive stresses for the aerogels containing 10 wt% AT are 100% as high as those of the pure polyimide aerogels. Interestingly, modulus of hybrid aerogels increases as the density decreases. For example, the compression Young's and specific modulus increase by 100% and 105% for the hybrid ODA-based aerogel compared to the pristine sample, meanwhile, the density decreases by 10%. Furthermore, the AT nanorods show strong supporting effects in maintaining the structural integrity of aerogels, which produce a significant effect on reducing the shrinkage of hybrid aerogels at high temperatures and retaining their excellent thermal insulation performance. The detailed investigation reveals that the AT is an effective and low-cost additive for preparing high performance polymer nanocomposites aerogels with improved mechanical property and thermal dimensional stability.

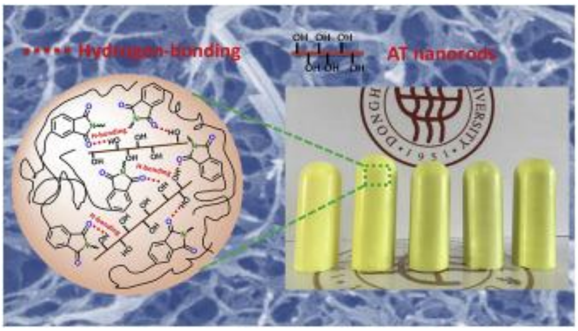

Figure 1 : Schematic diagram for the interaction between AT and polyimide aerogels.

P153

SYNTHESIS AND CHARACTERISATION OF HYBRID XEROGELS DOPED WITH Eu(III) or Tb(III) AND A WATER SOLUBLE ANTENNA LIGAND

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ABSTRACT: Hybrid organic-inorganic materials are a key focus within the nanoscience area as they combine advantages of inorganic materials (high thermal, mechanical, and structural stability) without losing characteristics intrinsic to organic molecules (flexibility and functionality). The combinations that can be established between different organic fragments bearing one or more functionalities are nearly infinite, and therefore, structured materials with tailored properties for specific applications can a priori be designed. In the past years, our research group has designed and synthesized hybrid siliceous xerogels (HSXG) with porosities and surface chemistries on demand for a range of applications, such as membranes for fiber optic sensors [1]. Although HSXG are mainly amorphous materials, recent studies by our group have demonstrated that introducing specific organic fragments on the precursors can induce self-organization during the sol-gel process to obtain a series of transparent nanostructured HSXG [2].

In the present work the applicability of this type of HSXG takes a step forward by using them as host matrices for optically active coordination complexes based on lanthanide cations (HSXG-Ln). For this reason, as shown in Figure 1, a series of HSXG-Ln doped with Eu(III) or Tb(III) cations and a water soluble pybox-type ligand have been prepared and characterised by means of FTIR, ^{29}Si NMR, N_2 and CO_2 adsorption, FE-SEM, X-Ray diffraction and photoluminescence spectroscopy. Inclusion of photoluminescent guests in nanostructured siliceous xerogels will allow the design of new materials that benefit from the synergy between complex/matrix properties to achieve promising perspectives as sensors or materials with applications in solar cells devices.

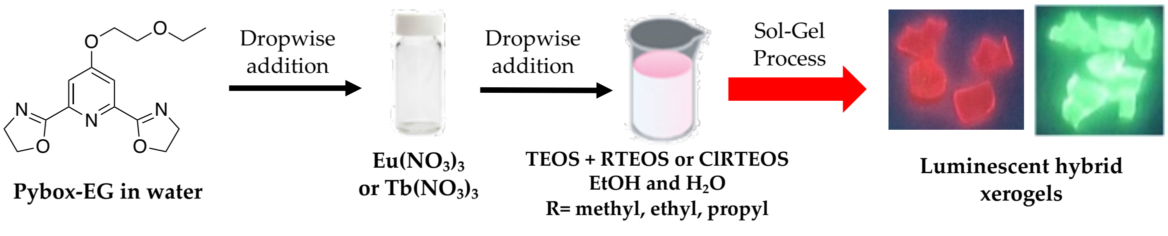

Figure 1. Schematic synthesis of luminescent hybrid xerogels

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DENSITY MANAGEMENT OF MONOLITHIC AEROGELS DRIED IN SUPERCRITICAL FLUID CONDITION

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ABSTRACT:

Plasma physics is a multidisciplinary research domain which relates astrophysics, matter sciences or even the energetic challenging issue of thermonuclear fusion. Inertial confinement fusion is a major French research program devoted to this latter topic. CEA/DAM contributes to it through its simulation program in the framework of the nation defense strategy and with the large facility MegaJoule Laser (LMJ). Fusion plasmas modelling requires to reach fundamental thermophysical properties of matter. They are obtained from experiments of laser-matter interaction with methods for the fast diagnostics of high-energy matter over a broad domain of the phase diagram, up to very high pressure and temperature. Aerogels are materials considered in laser targets and the knowledge of their density is essential for experiments. The present work addresses inorganic monolithic aerogels and the development of the synthesis and drying process implemented to master aerogels density.

P155

Development of Silica Aerogels with Exceptional Transmission and Zero Shrinkage

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ABSTRACT:

Silica aerogels were originally produced in the 1930s and since then were implemented in a variety of applications and research fields (thermal and acoustic insulation, Cherenkov detectors, inertial confinement fusion experiment, space research and more). Yet common drawbacks of aerogels such as shrinkage, light scattering and sensitivity to humidity, hinder their wider implementation.

Using TMOS (tetra methyl ortho-silicate) as the silica source, in a single step basic catalysis (NH_4OH solution), with Ethanol as solvent (instead of methanol which is the common solvent for TMOS single step recipes[1,2]), we were able to increase the aerogels' transmission significantly. Additionally, by partial substitution of Ethanol with Iso-propyl alcohol, the shrinkage of the aerogels was eliminated, while their transparency remained almost unaffected.

The modified recipe is fully compatible with "Hot" super-critical drying in alcoholic solvents, which is beneficial for achieving hydrophobic aerogels. Since it does not include NH_4F catalyst, this recipe eliminates the requirement for pre-washing of the gels, in contrast to many TEOS (tetra ethyl ortho-silicate) based recipes, as even traces of fluorine, could cause the gels to dissolve during the drying process.

This modified recipe is also compatible with other pre-developed methodologies, such as, production of aerogels in a wide range of densities from 10 mg/cm³ up-to 200 mg/cm³ through changing precursors' molar ratios[3] (as seen in figure 1); and production of doped aerogels through introduction of nanoparticles' suspension in either ethanol, H_2O or mixture of the two[4].

To conclude, by implementing the modified recipe as stated above, one can obtain silica aerogels with exceptional transmittance, zero shrinkage which are resistant to humidity, these aerogels can be produced in a wide range of densities and also in doped form. This flexibility is crucial in applications like optics, for achieving refractive index matching, filtering, fluorescence and even lasing.

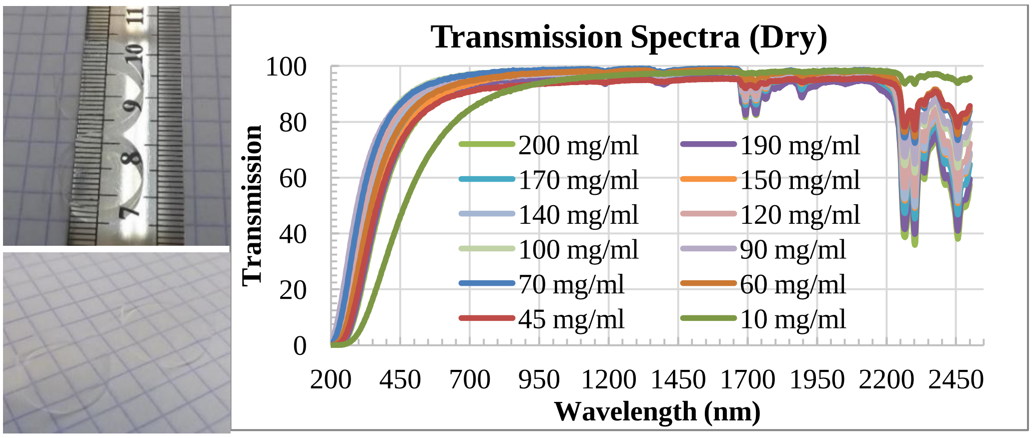

Figure 1: (Left) High transparency silica aerogels, (Right) transmission vs. bulk density.

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CARBON MONOLITHS WITH TUNABLE MESOPOROSITY BY SOL-GEL POLYCONDENSATION OF RESORCINOL AND FORMALDEHYDE

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ABSTRACT:

Porous carbon materials especially with monolithic shape and tunable porosity are considered as highly promising for a whole range of applications like energy storage, catalysis and adsorption. Thus, hierarchically porous carbon monoliths were developed in our previous work [1] via sol-gel polycondensation of resorcinol and formaldehyde with Na_2CO_3 as catalyst combined with soft-templating using Pluronic F127. This procedure enabled synthesis of carbon monoliths with mesoporosity in the range 5 – 10 nm and of the volume about 0,28 $cm^3\ g^{-1}$.

Herein, the tunability of mesoporosity of the previously prepared hierarchically porous carbon monoliths was investigated by varying parameters of sol-gel synthesis. The effects of different ratios of starting compounds, addition of non-polar solvents, change of ionic strength and altering of pore structuring agent were examined. The porosity of the prepared materials was characterized by DSC thermoporometry.

Based on the results, the mesopore diameters of the carbon monoliths can be tailored from 5 up to 15 nm, the volume of mesopores can be retained or increased up to almost twice (to 0,47 $cm^3\ g^{-1}$).

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LIPASE IMMOBILIZED ON SILICA-BASED MAGNETIC XEROGEL APPLIED AS BIOCATALYST

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ABSTRACT:

Biocatalysts based on enzymes immobilized on solid supports have received increasing interest in the last decade. The main advantages of this approach are the production of materials with great catalytic efficiency and the reactions can be conducted under mild conditions. In this work, new magnetic support for the immobilization of the lipase enzyme from *Thermomyces lanuginosus* (TLL) was proposed. A mesoporous and magnetic material was obtained by the sol-gel method in the presence of natural magnetite particles. The magnetic xerogel (MNX) was modified with gold nanoparticles stabilized by chitosan (MNXAuNP) and subsequently, TLL enzyme was immobilized on the surface of both materials, to produce MNX/TLL and MNXAuNP/TLL, respectively. The materials were characterized by X-ray diffraction, N2 adsorption-desorption isotherms, thermogravimetric analysis and magnetism measurements. The gold nanoparticles dispersion was characterized by UV-Vis spectroscopy and Transmission Electron Microscopy. The results indicate that the materials are mesoporous, magnetic and the enzyme was immobilized inside of the pores. The enzymatic activity was evaluated by using a colorimetric method that involves the *p*-nitrophenillpalmitate hydrolysis. The immobilization parameters were optimized applying a two-level factorial design which led to the immobilization time of 15 h and pH of 5. In these conditions, about 97% of immobilization efficiency is obtained. Also the biocatalyst can be reutilized, since after 12 cycles the MNX/TLL and MNXAuNp/TLL biocatalysts preserved 30 and 45% of the initial activity, respectively. Moreover, the MNXAuNp/TLL biocatalyst can be stored for four months without activity loss. Therefore, the magnetic materials with a planned porous structure developed in this work have potential application as easy-recoverable and recyclable lipase support.

P158

Synthesis of polyvinylidene fluoride aerogels with controlled crystal phases

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ABSTRACT:

Aerogels are an advanced class of highly porous solids combining extraordinary properties in a single material[1]. Apart from their well-known fields of application, crossover with systems of a completely different nature is of high interest to broaden the variety of applications[2,3]. In this study, polyvinylidene fluoride (PVDF) aerogels with special electroactive properties were prepared starting from the dissolution of PVDF pellets in dimethylformamide (DMF) at 80 °C, followed by the stepwise addition of ethanol and water. Upon cooling at room temperature, a wet gel was formed. Finally, the aerogel was dried using supercritical extraction with CO_2. The gelation behaviour has been systematically investigated by dissolving the polymer in various mixtures of dimethylformamide and ethanol as solvent and non-solvent, respectively. The results show that the nucleating agent role of ethanol not only allows to produce low-density aerogels, but also influences the particle's crystal polymorphs. The gelation-induced crystallization of PVDF results in different crystalline phases including the polar β and γ phases, but also the non-polar α phase. Interestingly, the application of a second non-solvent, such as water, allows the fine-tuning of the aerogels phase composition, resulting in aerogels composed of purely polar β and γ phases. Thus, in this simple three-step approach, ethanol and water play important roles as nucleation and phase stabilizer agents, respectively. These PVDF aerogels with controlled physicochemical properties exhibit surface areas ranging between 113 – 160 m^2 g^{-1}, porosities between 92 – 95%, pore sizes of 19 – 22 nm and densities of 0.12 – 0.07 g cm^3.

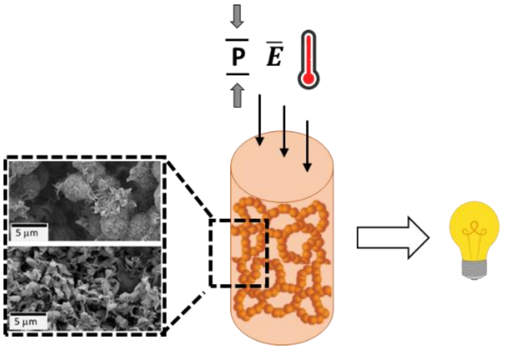

Figure 1: PVDF aerogels with adjustable microstructural and crystalline composition showing electroactive response.

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P159

MORPHOLOGICAL CONTROL AND ALIOVALENT DOPING OF POROUS SnO_2 MONOLITHS

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ABSTRACT:

Tin oxide (SnO_2) is widely applied to electrically conductive materials because it exhibits good oxidation resistance[1] and the conductivity can be controlled by incorporating various dopants[2]. Conductive SnO_2 particles[3] and thin films[2] with porosity have already been fabricated with the purpose of applying to gas sensors, electrodes and catalysts. However, there are no reports on porous SnO_2 monolith incorporated with various dopants. Porous monolithic materials with appreciable conductivity can be applied as free-standing electrode in energy storage devices and electrochemical cells.

Hierarchically porous SnO_2 monoliths have been prepared from the metal salt precursor by the sol–gel method accompanied by phase separation[4]. In this study, Nb(V) chloride was added in the starting composition for the purpose of aliovalent doping into the porous SnO_2 to increase the electrical conductivity. By optimizing the synthetic conditions and the starting composition, the monolithic gels with well-defined macroporous structures were successfully obtained.

Macroporous structure was controllable by changing the starting composition to adjust the tendency of phase separation and gelation time. The elemental analysis of the gel sample with the nominal atomic ratio of Nb/(Nb + Sn) = 5 % revealed that Nb ions were homogeneously distributed in the gel networks, and the actual Nb/(Nb + Sn) was about 4.2 %. The XRD analysis of heat-treated samples indicated the development of rutile-type crystalline structure, suggesting the substitutional doping of Nb into macroporous SnO_2.

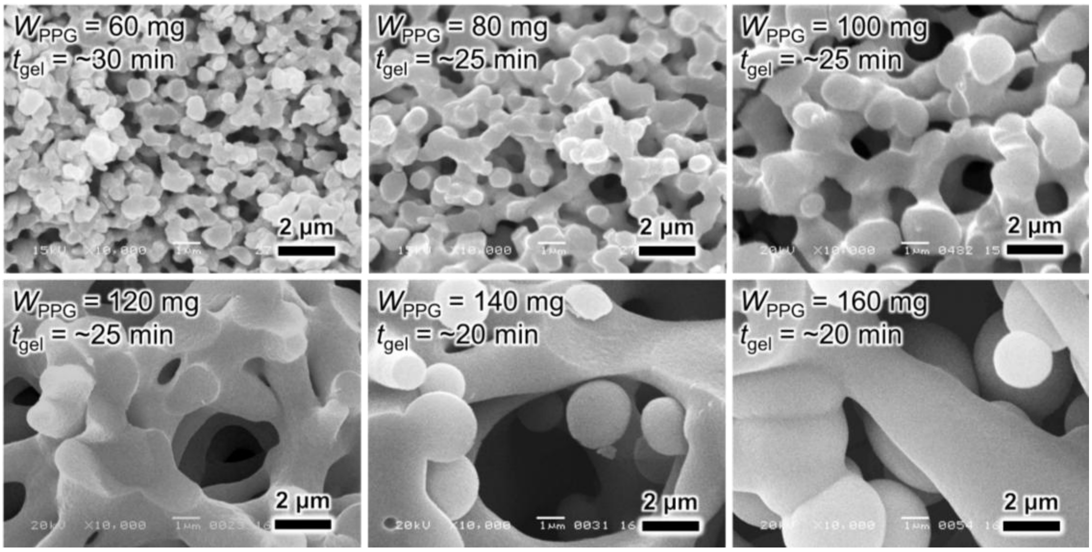

Figure 1 : SEM images of porous Nb-doped SnO_2 prepared with different amounts of PPG.

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Optimizing Drying of Hierarchically Organized Porous Silica Monoliths – Comparison of Ambient Pressure and Supercritical Drying

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ABSTRACT:

Hierarchically organized monolithic materials exhibit unique physical and chemical properties making them very attractive for a wide range of applications in areas such as chemical separation, thermal insulation or heterogeneous catalysis.[1] The structural characteristics like pore widths, pore structures, surface areas, as well as the mechanical properties of these materials prepared by *e.g.*, sol–gel processing, are highly influenced by post synthetic treatments and drying conditions. In particular, the drying procedure constitutes a crucial step in the preparation of mechanically stable porous monoliths. Drying of porous oxides can be realized by various techniques, ranging from drying in air under ambient conditions to supercritical drying with *e.g.* CO_2. Usually, ambient drying procedures require post- treatments of the material surfaces to minimize shrinkage, whereas supercritical drying is more costly and needs complex equipment for its operation.[2]

Herein, we present an innovative idea for a new technique to dry hierarchically organized porous monoliths, adapting and adjusting the approach from previous studies to challenge the specific characteristics of silica, whereas this method is especially characterized by its uncomplicated setup and feasibility.[3] Based on the model system of hierarchically organized, anisotropic ethylene glycol-based silica gels we discuss the effect of drying on the pore properties. To evaluate this procedure, a comparison to supercritical drying is provided, considering changes in important parameters such as pore size, pore volume, specific surface area, and shrinkage. Through comprehensive characterization of the materials, it will be demonstrated that drying under "ambient" conditions can certainly compete with supercritical drying or even outperform it in terms of favored parameters such as surface area or pore volume. Additionally, these parameters as well as the pore widths can be influenced and controlled by adjusting the drying conditions.

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3- Kohns R, Anders N, Enke D, Tallarek U (2020) Adv. Mater. Interfaces, 8: 2000163

Springback effect in silica aerogels: *In-situ* X-ray scattering investigations during drying

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ABSTRACT:

Silica aerogels are materials that exhibit exceptional properties, such as low densities, thermal conductivities, and dielectric constants, as well as high specific surface areas [1]. They are typically produced by supercritical drying (SCD) or ambient pressure drying (APD) through diligent solvent exchange and surface modification [2]. During APD, the structure might shrink to almost 50 % of its size, followed by an almost complete re-expansion [3]. This phenomenon is called springback effect and is particularly interesting because of its surprisingly large volume change in a ceramic material. Although APD aerogels are produced on an industrial scale, the production of crack-free monolithic samples is still challenging. It is key to understand the springback effect to control the re-expansion of the material, and therefore the APD of aerogels.
However, the impact of synthesis parameters and structural fundamentals on the springback effect are still unknown. Here we present a novel *in-situ* X-ray scattering characterization during drying, giving insights into the structural evolution of the APD aerogels. From X-ray scattering profiles, the kinetics of the solvent evaporation and various parameters characterizing the nanostructure were evaluated. It was possible to correlate these distinct features with the macroscopic sample characteristics, i.e., the shrinkage and re-expansion of the material. According to our knowledge, the springback effect and its structural characteristics have not been investigated *in-situ*. Our findings may contribute to optimize the production of monolithic APD aerogels.

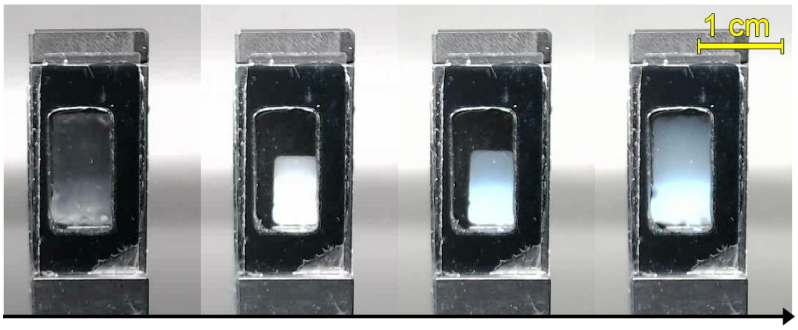

Figure 1: Series of photographs of a silica aerogel (inside a measurement cell) during solvent evaporation and the related shape change. The surface modification of silica gels leads to shrinkage and re-expansion during drying, referred to as springback effect.

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LOW DENSITY MATERIALS FABRICATION

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ABSTRACT:

In the french Simulation program, CEA Valduc is in charge of, among other missions, conceiving and fabricating the targets experimented on the Megajoule Laser. It requires many different skills, among them synthesis, shaping and assembly of low density material target elements.

A wide range of compositions, densities and geometries are required for those elements.

Various materials such as polyHIPE foams, organic aerogels or silica and tantalum oxide aerogels are thus elaborated through different processes. Sol-gel synthesis followed by supercritical drying is used for some of those materials in order to obtain the expected properties. These different materials are then transformed into target elements through machining (classic, high precision or laser) and assembly. Direct moulding of target elements is also investigated to avoid some machining and assembly steps.

Target elements are characterised in density, homogeneity, elementary composition and structure. Studies are carried out to warranty the material characteristics until the laser shot.
The presentation will show an overview of recent realisations regarding these low density materials.

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HYBRID ACID CATALYSTS PREPARED VIA TRIMETHYLSILYLATION OF ALUMINOSILICATES SYNTHESIZED BY NON-HYDROLYTIC SOL-GEL

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ABSTRACT:

Hybrid materials based on aluminosilicates are extensively studied for their enhanced catalytic performance. Organic groups can change acidity, hydrothermal stability, and porosity. First, we have shown, that non-hydrolytic sol-gel (NHSG) provides highly homogeneous and porous aluminosilicate materials exhibiting superior activity and long-term stability in ethanol dehydration [1]. Second, the ethylene selectivity was improved by one-pot incorporation of organic groups [2]. Interestingly, this approach did not display the direct influence of hydrophobicity on alcohol dehydration in contrary to other reports [3].

In this study, the NHSG-prepared aluminosilicate catalysts (fully inorganic) were post-synthetically modified by grafting trimethylsilyl groups onto their surfaces. Trimethylsilyl groups were attached to the surface using trimethylchlorosilane or trimethyl(methoxy)silane. The number of reacted ≡Si−OH moieties and thus the trimethylsilyl groups loading was controlled via a temperature-vacuum pretreatment of aluminosilicate samples. Trimethylsilyl groups loading was evaluated by ^{29}Si MAS NMR measurements (Figure 1). Structure, porosity, acidity, and hydrophobicity of NHSG-prepared catalysts were closely followed by MAS NMR studies, N_2 physisorption, IR-pyridine analyses, and water adsorption. Moreover, aluminosilicates were tested in a gas-phase fixed-bed catalytic reactor in ethanol dehydration and in a batch reactor in aminolysis of styrene oxide (liquid phase). These tailored NHSG-prepared aluminosilicate catalysts exhibited varying catalytic activity and selectivity in both catalytic reactions depending on trimethylsilyl groups loading in the samples.

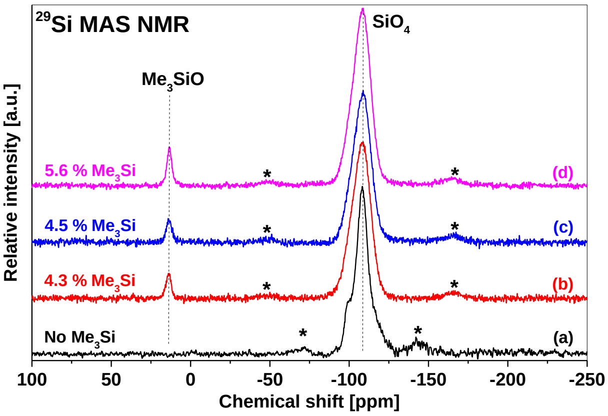

Figure 1: Comparison of pristine aluminosilicate with post-modified aluminosilicate samples. Trimethylsilyl groups loading was controlled by different conditions during temperature-vacuum pretreatment of pristine aluminosilicate. (a) Pristine aluminosilicate without Me_3Si groups; (b) Pretreatment at 500 °C under vacuum, then silylated; (c) Pretreatment at 150 °C under vacuum, then silylated; (d) Pretreatment at room temperature under vacuum, then silylated. Asterisks denote spinning sidebands.

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Resuspensible titanium xerogel for optical application

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ABSTRACT:

Titanium dioxide possesses the high photocatalytic and optical activity (high refractive index) which could change the properties in regard of the particles size and crystal face.

Hereby we obtain the new synthesis of titanium nanoparticles based on aqueous and aqua-alcohol solutions which approved sol-gel transition in the presents of peptizing agent. This technology provides the low-temperature sol-gel synthesis of titanium nanoparticles near room temperature (60°C). In contrast with other methods described in the literature[1,2]. We synthesized the titanium xerogel by drying under vacuum in low temperature with control drying rate. The final compound was approved the following characteristics: Z-potential (30 mV), average particle size (64 nm), X-ray phase analysis and others.

The functionality of the xerogel was estimated by holographic application the resuspension properties of titanium xerogel was achieved in the aqua-alcohol solution (80 g/l) and then coated their surface of rainbow (microembossed) holograms with the high reflective index properties. At the end we achieved the high holographical effect in the masked and patterned zones and high adhesion properties of titanium nanoparticles.

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MESOPOROUS MAGNETIC SILICA/NIOBIA XEROGEL AS ELECTROCHEMICAL SENSOR FOR *p*-NITROPHENOL DETERMINATION

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A mesoporous magnetic silica/niobia xerogel containing embedded spherical magnetite particles was successfully obtained. In order to achieve this purpose, the material synthesis was planned and the sol-gel method was employed as strategy. The heterocondensation of niobium and silicon alkoxide precursors was applied in the presence of spherical magnetite particles, which present approximately 330 nm of diameter. The magnetite particles were previously synthesized by using the solvothermal method and they were coated with a shell of silica. The resulting material is composed of magnetite (Fe_3O_4, *ca*. 25% m/m), silica (SiO_2, *ca*. 42% m/m) and niobia (Nb_2O_5, *ca*. 33% m/m). The xerogel presents interesting characteristics such as magnetism, large mesopores, in the range from 20 to 50 nm, and 68 $m^2 g^{-1}$ of surface area. These features allowed its use as a modifier of carbon paste electrode for *p*-nitrophenol determination, since niobia has never been used in electrochemical sensors for the determination of nitrophenol compounds. By using differential pulse voltammetry technique, the electrode was applied in a wide range of *p*-nitrophenol concentration, from 10 to 490 μmol L^{-1}, with a limit of detection of 1.2 μmol L^{-1} and sensitivity up to 0.60 μA L μmol^{-1}. The proposed electrode presented good reproducibility, repeatability, as well as sensitivity and selectivity and it was applied in real water samples.

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ENLIGHTENMENT OF MULTICOMPONENT OXIDE POROUS MICROSPHERES GENERATION

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ABSTRACT:

Sol-gel derived silica-titania (SiO2-TiO2), and silica-titania-hafnia (SiO2-TiO2-HfO2) microspheres with tailored interconnected macroporosity (MICROSCAFS) have been developed by microemulsion techniques combined with polymerization induced phase separation, without the employment of a phase separation additive. The inherent gelation capability of the silanes involved, together with the action of the Ti and Hf precursors and the control of pH, water content and temperature, allow to well-master this technique, enabling a fine-tuning of the pore size morphology and reproducibility of the MICROSCAFS´ characteristics. These new products are being evaluated for solar-driven photocatalysis and are attractive for other applications in biomedical, energy, chromatography, etc.

However, the core phenomena occurring inside the water droplets of the microemulsion, critical for the interconnected macroporosity generation, such as the way macromolecules assemble in the sol and the phase separation evolves, are still not completely understood.

This work targets a mechanistic study of the sol-gel reaction in its first stages. For such purpose, cryo-scanning electron microscopy (cryo-SEM) was employed, i.e. aliquots of the reaction batch at specific times during the synthesis of the MICROSCAFS were taken, cryogenized and analyzed by cryo-SEM. This procedure was simultaneously combined with energy dispersive spectroscopy (EDS) to provide answers through the visualization of the phase separation and study of the chemical elemental composition at specific locations and reaction times. The oligomers form within the aqueous phase of the emulsion homogeneously and exhibit the theoretical elemental composition since the first stages of the MICROSCAFS´ synthesis. Next, they are shown to accumulate at the water/oil interfaces (Figure 1a), possibly to reduce the surface energy, which explains the presence of the thin layer that wraps the microspheres (Figure 1b). This is followed by the formation of the skeleton domains, which grow by gelation/phase separation until the MICROSCAFS achieve their final morphology (Figure 1b).

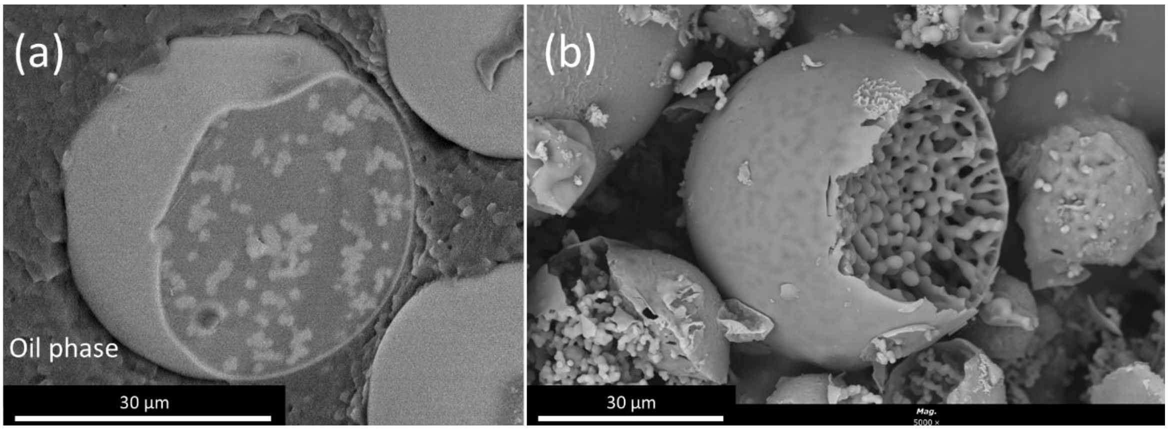

Figure 1: (a) Cryo-SEM image of a SiO_2-TiO_2-HfO_2 MICROSCAF during its synthesis; (b) SEM image of solid, dried SiO_2-TiO_2-HfO_2 MICROSCAFs after the synthesis.

SPIROPYRAN-BASED POROUS POLYSILSESQUIOXANES WITH ION SENSING PROPERTIES FOR COLORIMETRIC ANALYSIS

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ABSTRACT:

Dynamic materials comprising spiropyrans have emerged as one of the most interesting and promising class of stimulus-responsive materials. A prerequisite for the design of stimuli-responsive devices, often also referred to as “smart materials”, is the incorporation of responsive entities into a matrix that does not restrict the conformational freedom. In our previous work, we demonstrated that a silylated spiropyran derivative can be covalently incorporated into ultralight silsesquioxane-based bulk materials by a two-step co-condensation sol–gel approach.[1] The special feature of these organic molecules is their ability to undergo isomerization reactions at external stimuli, e.g. light, heat or pH changes. Spiropyrans can exist in two states. The ring-closed (SP) 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 coloured open merocyanine (MC) form has a fully conjugated π-system throughout the molecule (Figure 1). The reversible switchability can effectively alter the surface polarity of the material. Additionally the MC form is able for form unique colored complexes with different metal ions. For this purpose, we prepared monoliths based on two spiropyran derivatives with different chelating groups.[2] The colorimetric response of merocyanine-metal ion (MC-M^{2+}) interactions are investigated, as well as the photoluminescence properties and characteristics of the bulk material.

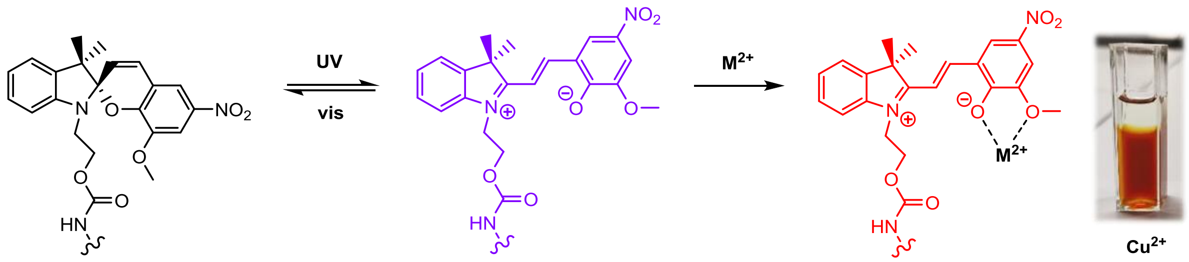

Figure 1: Isomerization reaction of the colorless, ring-closed (SP) isomer into the fully conjugated merocyanine (MC) and the merocyanine-metal ion (MC-M^{2+}) complex

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EFFECTS OF SONICATION ON SOL-GEL SYNTHESIS AND CATALITYC ACTIVITY OF VANADIUM AND TUNGSTEN OXIDE CATALYSTS

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ABSTRACT:

Sonication can modify the properties and activity of catalysts synthesized by the sol-gel method since it influences the molecular interactions between the active centers and the support. In the present work we show a comparative study of vanadium, tungsten and vanadium-tungsten catalysts prepared by sol-gel method. These catalysts have been prepared by two different methods in order to identify the sonication influence in physical and chemical properties, and their activity in xylose dehydration into furfural. Catalytic materials were synthesized by the sol-gel method with a metal loading of 5.0 wt % (5V/Si, 5W/Si and 5VW/Si (2.5 wt % of vanadium and 2.5 wt % of tungsten) calcined at 750 °C. The synthesis procedure requires the preparation of a solution of the metal salt and the structuring agent in absolute ethanol. Then, these two solutions were added to a defined mass of tetraethyl orthosilicate (TEOS). Gelation process was carried out at 60 °C with constant stirring at 120 rpm. Samples were dried at 105 °C for 12 hours and calcined for 6 hours. The same procedure was realized changed stirring for sonication (5V/Si-Son, 5W/Si-Son and 5VW/Si-Son (2.5 wt % of vanadium and 2.5 wt % of tungsten). Materials were characterized by FT-IR, XRD, Raman, UV-Vis, N_2 adsorption, H_2-TPR, and tested in xylose dehydration into furfural. Catalysts without sonication show less surface area, pore volume and size pore, but the co-presence of vanadium and tungsten lead to an increase these properties, figure. 1. The catalytic results indicate the binary materials presents the highest levels of activity and selectivity.

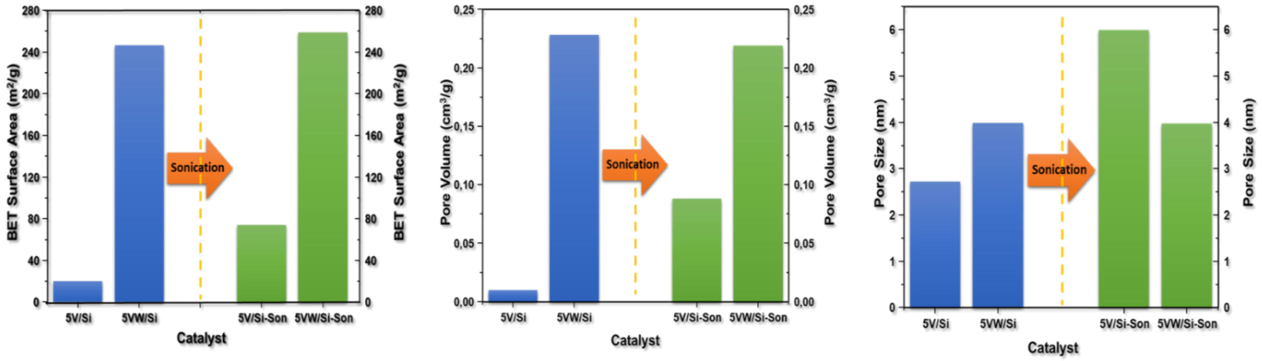

Figure 1: Effects of sonication on sol-gel synthesis of vanadium and tungsten catalysts: 5V/Si, 5W/Si, 5VW/Si, 5V/Si-Son, 5W/Si-Son and 5VW/Si-Son.

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Calcium(II)-containing borosilicate aerogels as promising materials for application in regenerative medicine

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ABSTRACT:

Nowadays, in the field of the regenerative medicine of bone defects, the main focus is on the design and development of materials that can be promising replacements of conventional autographs, allographs, metallic or ceramic scaffolds. The new synthetic bone scaffolds have to mimic both the hybrid composition and the microscale structure of human bone [1]. Therefore, the control of the structure of porous inorganic and organic hybrid materials at the nano- and micro levels plays a crucial role in the design of biocompatible and bioactive scaffolds [2].

Hybrid aerogels in general are promising scaffolds for bone regeneration owing to the high porosity, nanostructured surface and versatile functionalization of this family of sol-gel materials [3]. Our study focuses on the design, synthesis, in-depth structural characterization and *in vitro* biological testing of calcium(II)-containing hybrid borosilicate aerogels. Little is known about the behavior of nanostructured porous borosilicate materials in biological media (changing micro- and nanostructure, altered physical and chemical properties, reaction to environmental influences, etc.). Understanding the structure-property-function relationships in relation to biological systems is the most important objective of the present research.

Hybrid borosilicate aerogels (Figure 1) were made by sol-gel synthesis using polyvinyl alcohols (MW: 23000, 49000, 90000) as network modifiers, and different calcium sources ($CaCl_2$, $Ca_3(PO_4)_2$, hydroxyapatite) as bioactive ingredients. The structural characterizations were done employing various techniques in terms of composition (FTIR, solid-state NMR), texture and morphological properties (N_2–sorption porosimetry, small angle neutron scattering, electron microscopy). These studies reveal the interconnected mesoporous structure of the scaffolds with pore diameters of 20-45 nm and apparent surface areas of 540-1038 m^2/g. The suspensions of the aerogels were studied by dynamic light scattering and Zeta potentials were measured. Selected materials were submitted to *in vitro* experiments to determine their biocompatibility and bioactivity. Viability assays and time lapse video microscopy imaging of cell proliferation and scratch closure were performed using human mesenchymal stem cells. These experiments revealed the high affinity of the cells towards the hybrid borosilicate aerogels.

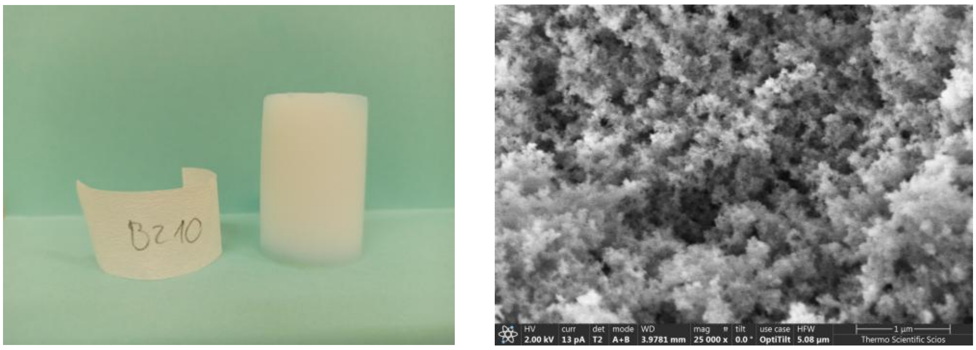

Figure 1: Calcium(II)-containing hybrid borosilicate aerogel

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MESOPORES FORMATION IN THE MACROPOROUS MONOLITHIC SILICA GEL

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ABSTRACT:

Monoliths with hierarchical porosity containing interconnected macropores and mesopores have a wide range of applications [1]. The macrostructure of these monoliths is formed in the phase separation process simultaneously with the sol-gel transition. Further hydrothermal treatment in the basic conditions is carried out to hardening of the skeleton and forms the mesopores system. The mesopores formation occurs without changing the macrostructure parameters [2].

It is assumed that mesopores are formed by spherical particles that form upon dissolution and reprecipitation of the amorphous silica. According to the assumptions put forward earlier, the low-density gel is fragmented into small clusters in the basic conditions. The each cluster grows to be a particle-like structure [3]. In further processes, the dissolution of small particles leads the growth of large particles. According to this model, the intermediate stage in the mesopores formation is the transformation of the solid silica gel into the colloidal gel [4]. However, it is not clear why the transformation of the continuous gel network into many particles without maintaining connection does not lead to the loss of initial shape and macrostructure of wet gel. Elimination of contradictions and understanding of the mechanism formation of mesoporous structure will allow more accurately control of its parameters.

In this work, using the high-resolution scanning microscopy, the phenomena occurring at the stage of hydrothermal treatment during the synthesis of hierarchically porous silica monoliths are described. The change in the structural characteristics of macroporous monolithic materials during the mesopores formation was studied in detail. Based on the information obtained, a model of mesopores formation is presented, that to allow explain of the keeping of the porous monolith macrostructure.

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METAL-DOPED MONOLITHIC CELLULOSE BASED CARBON ELECTRODES FOR SUPERCAPACITORS

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ABSTRACT:

Metal-doped carbons are promising materials for catalysis and energy storage applications. In particular, carbons derived from bio-based sources that constitute the bioeconomy as well as a viable alternative to fossil carbon are highly desirable. This contribution addresses carbon electrodes derived from intrinsically metal-doped monolithic cellulose gel for use in supercapacitor applications. Three metal precursors (Cu, Mn, and Fe) with different weight percentages were used to mix with cellulose to make monolithic xerogels, followed by carbonization to obtain carbons with intrinsic metal doping. Such carbons were slurry coated on carbon paper for testing in the electrochemical cell.
The results show that Fe-doped carbon electrodes deliver higher electrochemical performance compared to Cu- and Mn-doped carbon electrodes (Figure 1). The primary reason is that the higher mesopore volume arising in Fe-doped carbon electrodes provides easier access for electrolyte ions to introduce faradic storage. In addition, the stable phase formed in the Fe-doped carbon electrode during the electrochemical cyclic voltammetry experiment provided additional faradic storage. Furthermore, the Fe-doped carbon electrode tested in an asymmetric set-up against a resorcinol-formaldehyde-derived carbon xerogel electrode shows promise of energy and power density for practical applicability.

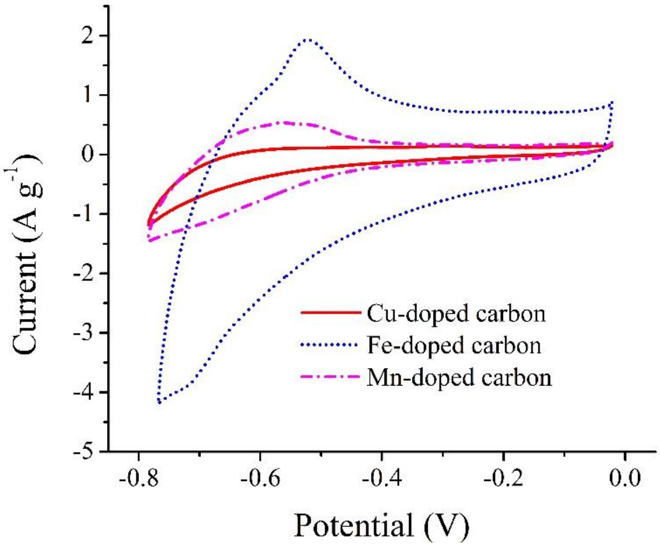

Figure 1: Electrochemical performance using cyclic voltammetry at 10 mV s^{-1} for metal-doped carbon electrodes obtained from 10 % weight doping of metal precursors in cellulose

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HIGH STABILITY SOL-GEL ENTRAPPED ENZYMES FOR BIOCATALYSIS

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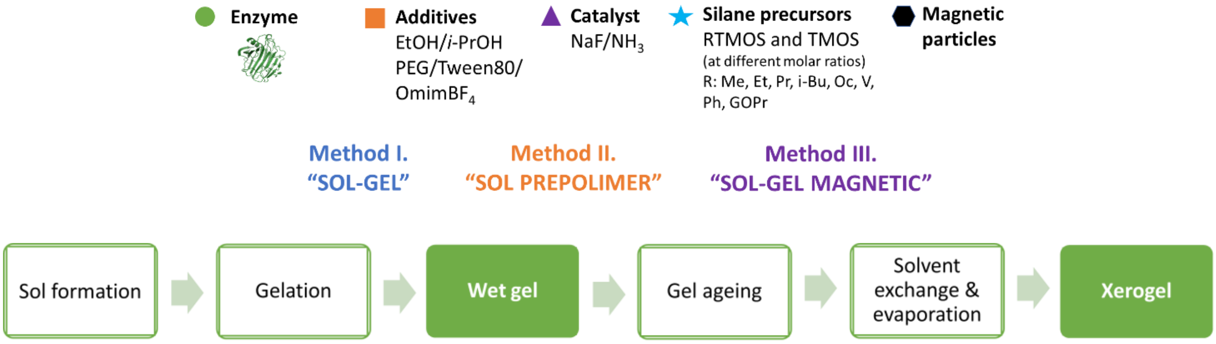
In recent decades, enzymes have gained immense attention as industrial biocatalysts with a wide range of applications. Due to high costs owing to the instability of native enzymes and impossibility of reuse, enzyme immobilization becomes almost compulsory [1].

Immobilized enzymes are excellent biocatalysts however, their catalytic activity greatly depends on the selected immobilization method. To date, there are no straightforward protocols concerning the optimal immobilization procedure, thus customizing the method for each enzyme is necessary. Sol-gel entrapment of enzymes in silica matrices has important advantages such as facile immobilization method with no modifications of the enzyme structure, flexibility in the pore's dimension and geometry, possibility to immobilize a high quantity of protein and recycle the enzyme, biocompatibility, as well as high thermal and chemical stability [2-4].

In this study, two different types of enzymes (cellulase and lipase) were immobilized by entrapment in tailored sol-gel matrices (figure 1) using binary and ternary silane systems of functionalized methoxy-silanes at different molar ratios, and epoxy functionalized silane precursors.



● **Enzyme**

■ **Additives**
EtOH/*i*-PrOH
PEG/Tween80/
OmimBF$_4$

▲ **Catalyst**
NaF/NH$_3$

★ **Silane precursors**
RTMOS and TMOS
(at different molar ratios)
R: Me, Et, Pr, i-Bu, Oc, V,
Ph, GOPr

⬢ **Magnetic particles**

Method I.
"SOL-GEL"

Method II.
"SOL PREPOLIMER"

Method III.
"SOL-GEL MAGNETIC"

Sol formation → Gelation → **Wet gel** → Gel ageing → Solvent exchange & evaporation → **Xerogel**

Figure 1 : Sol-gel entrapment protocols for tailored enzyme preparations.

The influence of key immobilization parameters in the sol-gel entrapment of enzymes (immobilization protocol, nature of the silane precursors, additives) on the catalytic efficiency of the immobilized enzymes was investigated. The catalytic efficiency of the immobilized enzymes was tested in model reactions: hydrolysis of carboxymethyl-cellulose and microcrystalline cellulose, and synthesis of flavour ester n-amyl hexanoate in batch and continuous (in organic solvents as well as solvent-free media).

The characterization of the immobilized biocatalysts and the correlation of their catalytic efficiency with the morphological and physicochemical properties of the sol-gel matrix were accomplished. The presence and distribution of the enzyme in the sol-gel matrix, as well as the temperature loss profile as a function of temperature, were highlighted. The operational and thermal stability of the enzymes were increased as a result of the immobilization.

Acknowledgments

This work was supported by a grant of the Romanian Ministry of Education and Research, CNCS - UEFISCDI, project number PN-III-P1-1.1-TE-2019-1179, within PNCDI III, contract number TE 94.

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Main Menu

Hierarchically structured materials

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HIERARCHICALLY ORGANIZED MAGNETIC NANOPARTICLES OF IRON OXIDES AND TEOS-DERIVED SILICA SOLS FOR USE IN AGRICULTURE

Olga Shilova[1,2], **Tamara Khamova**[1], **Gayane Panova**[3], **Anastasiya Kovalenko**[1], **Anton Nikolaev**[1], **Anna Zhuravleva**[3], **Olga Udalova**[3], **Gennady Kopitsa**[1,5]

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(corresponding author: olgashilova@bk.ru)

ABSTRACT:

SiO_2 and FeO_x nanoparticles (NPs) have a positive effect on the development and productivity of agricultural crops [1, 2]. For the first time, the seeds treatment of a number of cabbage crops with the synthesized TEOS-derived sols, including with the additives of NPs of maghemite-magnetite series γ-Fe_2O_3-Fe_3O_4 (0.0001-100 mg/L) was carried out [2, 3]. The researches with a variety of methods (XRD, FT-IR, SEM, TEM, low-temperature N_2 adsorption, SAXS) allowed us to characterize their structure and properties and to determine the dependences on the synthesis conditions [4]. The NPs magnetic structure was determined with the method of small-angle scattering polarized neutrons. All these materials had a hierarchical structure at the nanolevel. These data will be presented. It was important for pre-sowing seed treatment of plants to use the NP_S friendly low concentration and to eliminate organic solvents. So, TEOS was hydrolyzed in an acidic aqueous medium. Thus, silica sol based on 1 vol. % TEOS was synthesized. It was important to check, whether SiO_2 NPs are formed under these conditions. It was found, the silica sols were characterized by a three-modal particle size distribution DV (R), with the largest volume fraction falling on small particles (<1 nm) (Fig. 1a). The iron oxide NPs additives led to a shift in the DV (R) distribution to a larger region, and to an increase in the volume fraction of larger particles up to 10 nm (Fig. 1b). These silica sols with NPs have a positive effect on the germination energy and germination capacity of cabbage varieties seeds.

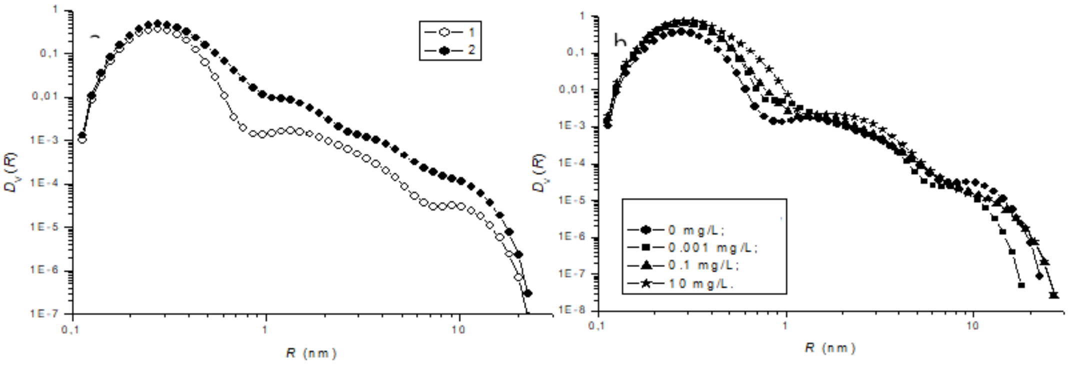

Figure 1: Size distribution functions of NPs – DV (R) for: (a) silica sols with TEOS concentration: 1 – 1 vol.% and 2 – 10 vol.%, respectively; and (b) silica sol (0.1 vol.% TEOS) containing varying amounts of iron oxides NPs

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HIERARCHICALLY POROUS ZEOLITE-GEOPOLYMER COMPOSITES FOR Sr REMOVAL FROM NUCLEAR WASTEWATER

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ABSTRACT:

The treatment of Sr-contaminated wastewater is still a challenge for the nuclear industry, particularly in case of highly saline effluents. For this purpose, contaminant extraction on solid supports in fixed bed processes is a promising technology but the development of materials highly selective for Sr with an appropriate porosity is needed. Furthermore, a hierarchical porosity should increase the sorption kinetic and improve the hydrodynamic properties of the material when used in dynamic processes.

We introduce here the synthesis of meso-macroporous geopolymer containing Linde Type A (LTA) zeolite nanoparticles, which are highly selective for Sr [1]. The macroporosity of the material is obtained through the stabilization of an emulsion in a solution containing geopolymer precursors. After geopolymerization, a solid and monolithic material is obtained and the macroporous network is created by eliminating the internal phase of the emulsion. Zeolite nanoparticles are introduced as soon as the emulsification step, allowing their homogeneous dispersion in the structure [2]. The mesoporosity is directly induced by the geopolymerization mechanism, which allow a better accessibility of the zeolite for the wastewater to be treated. The selective removal efficiency of these materials is demonstrated both in static mode (batch) and dynamic mode using column (breakthrough curves) experiments. The sorption mechanisms are highlighted as well as the beneficial interest of the hierarchically porous network on the global performances of the process.

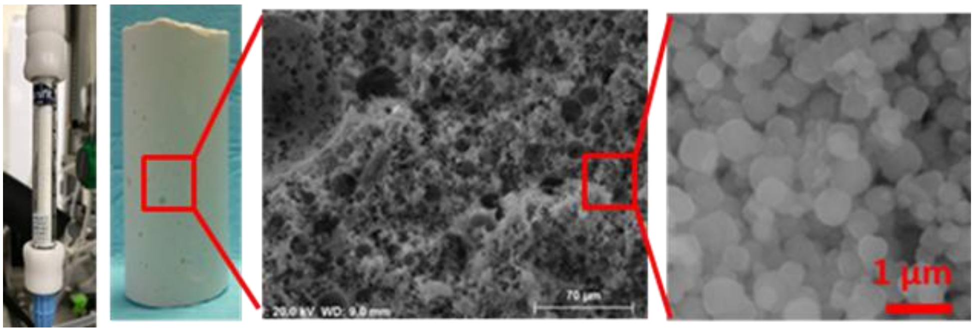

Figure 1: Realization of a breakthrough curve using a hierarchically porous zeolite-geopolymer composite.

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FUNCTIONAL BLOCK COPOLYMERS FOR *IN-SITU* FUNCTIONALIZATION OF MESOPOROUS SILICA FILMS

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Nature provides the ultimate inspiration – able to direct, gate and selectively transport through pores and channels with technologically unreached performance. To approach this performance, the precision in nanoporous material design has to be significantly improved. For example, material architecture and structural as well as functional hierarchy have to be precisely designed. To do so nanoscale layer-wise material build up, e.g. using printing techniques for nanoporous structure formation in combination with *in-situ* functionalization approaches, is envisioned to allow precise structural and functional hierarchy design at the nanoscale.

Specifically, stimuli-responsive mesoporous silica films were prepared by evaporation-induced self-assembly through physical entrapment of functional block copolymers as structure directing agent, which simultaneously serve as functionalization of the mesopores. By this way highly filled pores with e.g. PS-*b*-PAA that exhibit remarkable gating ionic permselectivity with changes in pH[1], enabling the switching between cation- and anion-selectivity under basic and acid conditions, were achieved. Stimuli-responsive transport characteristic can also be observed in partly filled pores. Different examples of functional templates for *in-situ* functionalization and the resulting ionic permselectivity will be presented. Mesoporous films are characterized regarding their porosity and film thickness using ellipsometry, TEM and SEM. Ionic permselectivity is determined using cyclic voltammetry and correlated to porous structure and *in-situ* functionalization. Using functional templates for *in-situ* functionalization of mesoporous layers bears the potential for localized stimuli-responsive polymer functionalization within a precisely designed architecture[2] and fabrication of *in-situ* functionalized porous silica films by high throughput printing methods[3]. This direct and simple approach of *in-situ* functionalization of mesoporous silica using functional block copolymers is expected to be highly relevant for a variety of technologies based on molecular transport in nanoscale pores, such as sensing, separation, catalysis and energy conversion.

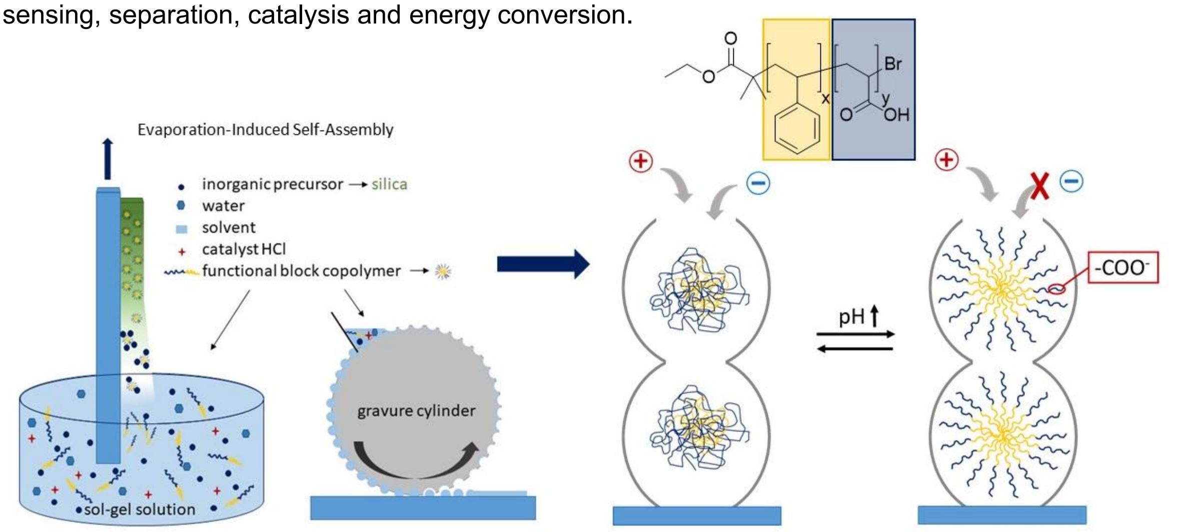

Figure 1 : Stimuli-responsive mesoporous silica thin films prepared in an one step procedure by Evaporation-Induced Self-Assembly (EISA) have achieved tunable ionic permselectivity, thereby demonstrating their high potential for developing multifunctional, complex architectures with to date unreached transport performances.

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Dual-porous cellulose nanofibril aerogels via modular drying and cross-linking

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Nanofibrillar foams and aerogels are traditionally either macroporous with low surface area and high mechanical strength, or mesoporous with high surface area and low mechanical strength. In this work, an anionic cellulose nanofibril (CNF)-based dual-porous aerogel with BET specific surface area up to 430 m^2/g was prepared via a modular process combining directional freeze-thawing (creating macro-pores, ca. 50-200 µm) and supercritical drying (creating meso-pores, ca. 2-50 nm). Furthermore, by optionally utilizing both physical and chemical cross-linking strategies, aerogels with a Young's modulus of up to 711 kPa and good stability in aqueous conditions were demonstrated. By altering cross-linking strategies, the properties of resulting aerogels can be precisely controlled for different applications, such as hydrophilicity, mechanical strength and stability in water. As a result, cationic methylene blue (MB) and metal ions (Ag^+) were chosen as model species to investigate the absorption properties of the physically cross-linked aerogels in water. The aerogels showed a maximum adsorption of MB up to 234 mg/g and of Ag^+ up to 116 mg/g as a result of the high specific surface area of the aerogels and their strong electrostatic interaction with the model species. Importantly, the hierarchical dual porosity of the aerogels enabled fast adsorption kinetics combined with a considerable adsorption capacity overall. Finally, it was shown that the adsorbed Ag^+ could be converted to metallic Ag, demonstrating the additional functionality of these dual porous hybrid aerogels for antibacterial or catalytic applications.

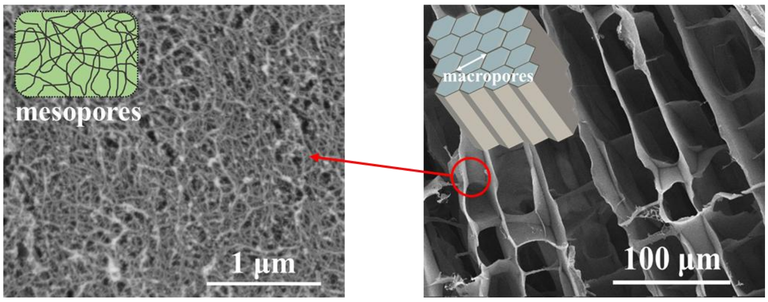

Figure 1 : Schematic diagram for the hierarchical dual-pore structure of CNF aerogels.

Hierarchically Structured Tannin-Based Carbons

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ABSTRACT:

Due to their enormous potential, nanoporous carbons have attracted considerable interest in the field of energy- and environment-related technologies. Especially as key component in electrical double layer capacitors (EDLCs), also called supercapacitors, such materials demonstrate superior performances. In this respect, the design of specific surface areas and pore structures of the carbon-based electrodes is highly relevant, as it is known that the capacitance of EDLCs directly correlates.[1] In particular, accurate tailoring of the carbons' pore structure can beneficially influence the electrochemical performance of the material: macro- and mesoporosity provide fast and efficient ion transport, while micro- and ultramicropores enable high specific surface areas yielding in high energy densities.[1,2] Such hierarchically organized carbon materials can be synthesized for example via nanocasting (NC), resulting in hexagonally, packed nanofibers, or via a soft-templating approach, yielding cylindrical nanopores arranged on a hexagonal lattice. However, these materials are often based on organic precursors, such as resorcinol-formaldehyde (R/F), compounds that are considered environmentally harmful and toxic, which is not in line with the concept of sustainability.[1,2]
Thus within this work, the synthesis as well as characterization of hierarchically structured nanoporous carbons from biomass, is presented. These highly porous, nanocasted carbons have been prepared via sol–gel processing using the tree extract mimosa tannin and the biobased crosslinker 5-(hydroxy)methylfurfural (5-HMF) in combination with a hierarchically and anisotropic glycol based silica hard template. The resulting materials are thoroughly investigated regarding their chemical and physical properties and the synthesis-structure relationships will be discussed in detail. In addition, the usage of these biobased, nanostructured carbon material will be investigated regarding its electrochemical properties and evaluated for its usage as EDLCs electrode material.

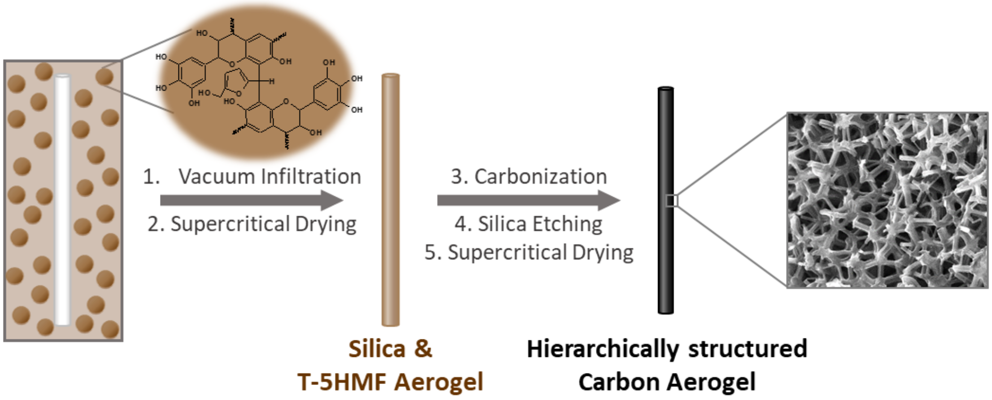

Figure 1: Synthesis of tannin-based hierarchically structured carbon aerogels.

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RELEVANCE OF SOL-GEL TRANSITION AND SPINODAL DECOMPOSITION FOR HIERARCHICALLY STRUCTURED POROUS ALUMINA MONOLITHIC

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ABSTRACT:

Real time monitoring of nanostructure were used to investigate the hierarchical porous structure of alumina monoliths formed by the combination of concurrent processes involved in the sol-gel transition and spinodal phase separation.[1] The addition of low molecular weight poly(ethylene oxide) (PEO) in the sol-gel reaction of aluminum chloride induced phase separation between aluminate gel and PEO-solvent. *In situ* time-resolved small-angle X-ray scattering (SAXS) measurements revealed that structural evolution during gelation of a sample without PEO was dominated by Ostwald ripening. With PEO addition, this coarsening mechanism, occurring during a short intermediate stage (6 min), was followed by the aggregative coalescence of phase separating domains during the late stage of spinodal decomposition. The effect of PEO in the gelation mechanism also influenced the porous structure formed by calcination of the alumina monoliths. During calcination for PEO removal and conversion from xerogel to ceramic, *in situ* SAXS monitoring evidenced that the formation of mesopores followed the spinodal decomposition mechanism proposed by Cahn's theory.[2] Alumina with well-defined mesopore and macropore families, high specific pore volume (2.0 cm^3 g^{-1}), and high surface area (252 m^2 g^{-1}) was obtained as a result of spinodal decomposition during the sol-gel transition followed by heat treatment.

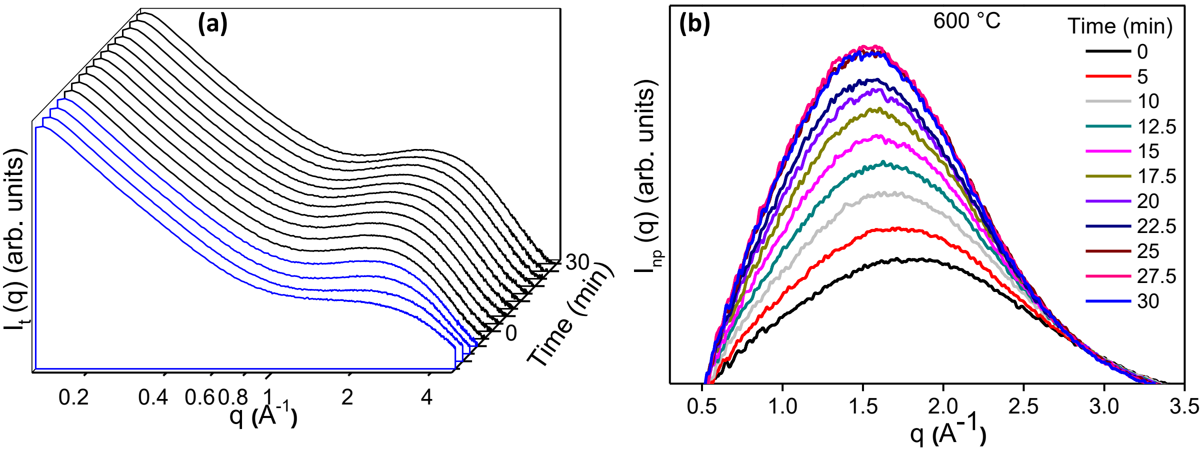

Figure 1: (a) Time-resolved SAXS patterns measured during the heating ramp from 500 to 600 °C and the isothermal regime at 600 °C. (b) Time dependence of the nanopores scattering component during isothermal treatment.

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Acknowledgements: This work was undertaken in collaboration with the National Institute on Advanced Eco-Efficient Cement-Based Technologies and was supported by Brazilian funding agencies CNPq, FAPESP, CAPES and Synchrotron Brazilian Light Laboratory (LNLS).

NbO5/SILICA NANOCOMPOSITES WITH HIERACHICAL PORE STRUCTURE AS METHYLENE BLUE AND DOXYCYCLINE ADSORBENT

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ABSTRACT:

Monolith nanocomposites formed by niobium pentoxide dispersed in a silica matrix were prepared by sol-gel process, with pores modulated by the addition of a soluble polymer (polyethylene glycol 10000) in the precursor solution prepared with TEOS and ethanol. After drying at 80°C, the porous monoliths were calcined at different temperatures between 300 and 900 °C and applied to remove methylene blue (MB) and doxycycline (DOX) from water. The temperature of calcination changed the morphology of the niobium pentoxide nanoparticles inserted in the silica matrix and the textural characteristics of the nanocomposites, influencing their adsorption properties. The adsorption of the two contaminants used was sensitive to the pH variation of the solution, being optimal at pH 11 and 9 for the removal of MB and DOX, respectively. The effect of ionic strength corroborated by the zeta potential and FTIR analyzes of the nanocomposite, before and after adsorption, showed that the adsorption of MB (exothermic process) is due only to electrostatic interaction, while the adsorption of DOX (endothermic process) is due to electrostatic and n-π interactions. Both removal processes were spontaneous. The use of the nanocomposites for the adsorption of the two contaminants is efficient and economical since they can be regenerated and reused.

ENLIGHTENMENT OF MULTICOMPONENT OXIDE POROUS MICROSPHERES GENERATION

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ABSTRACT:

Sol-gel derived silica-titania (SiO2-TiO2), and silica-titania-hafnia (SiO2-TiO2-HfO2) microspheres with tailored interconnected macroporosity (MICROSCAFS) have been developed by microemulsion techniques combined with polymerization induced phase separation, without the employment of a phase separation additive. The inherent gelation capability of the silanes involved, together with the action of the Ti and Hf precursors and the control of pH, water content and temperature, allow to well-master this technique, enabling a fine-tuning of the pore size morphology and reproducibility of the MICROSCAFS´ characteristics. These new products are being evaluated for solar-driven photocatalysis and are attractive for other applications in biomedical, energy, chromatography, etc.

However, the core phenomena occurring inside the water droplets of the microemulsion, critical for the interconnected macroporosity generation, such as the way macromolecules assemble in the sol and the phase separation evolves, are still not completely understood.

This work targets a mechanistic study of the sol-gel reaction in its first stages. For such purpose, cryo-scanning electron microscopy (cryo-SEM) was employed, i.e. aliquots of the reaction batch at specific times during the synthesis of the MICROSCAFS were taken, cryogenized and analyzed by cryo-SEM. This procedure was simultaneously combined with energy dispersive spectroscopy (EDS) to provide answers through the visualization of the phase separation and study of the chemical elemental composition at specific locations and reaction times. The oligomers form within the aqueous phase of the emulsion homogeneously and exhibit the theoretical elemental composition since the first stages of the MICROSCAFS´ synthesis. Next, they are shown to accumulate at the water/oil interfaces (Figure 1a), possibly to reduce the surface energy, which explains the presence of the thin layer that wraps the microspheres (Figure 1b). This is followed by the formation of the skeleton domains, which grow by gelation/phase separation until the MICROSCAFS achieve their final morphology (Figure 1b).

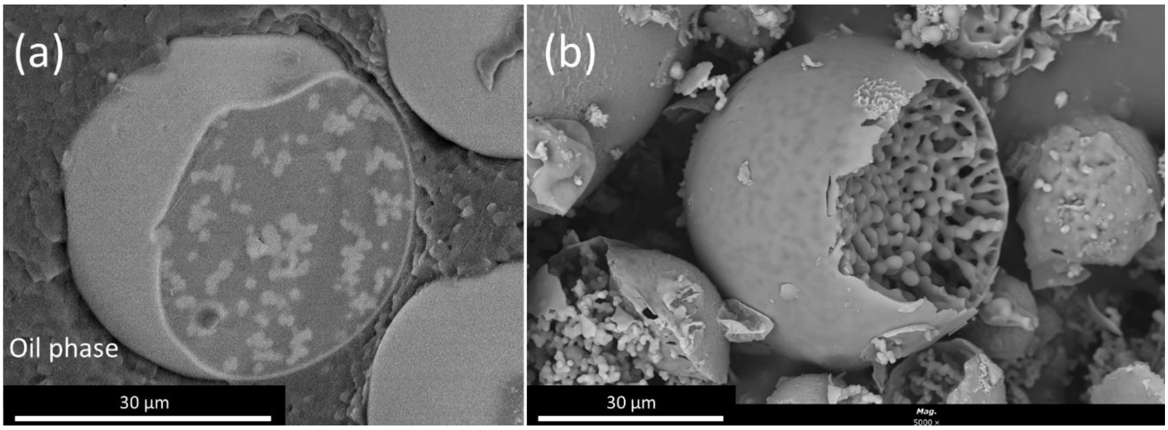

Figure 1: (a) Cryo-SEM image of a SiO_2-TiO_2-HfO_2 MICROSCAF during its synthesis; (b) SEM image of solid, dried SiO_2-TiO_2-HfO_2 MICROSCAFs after the synthesis.

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Development of a uniquely engineered mixed metal-oxide-zeolite material for the purification of exhaust waste streams

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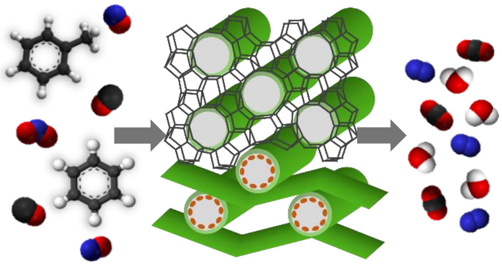
ABSTRACT:

Fossil fuel combustion is still today the major energy source in industrial processes. However, the generated energy is accompanied by the release of high amounts of particulate and gaseous pollutants such as CO, VOC, PAH and NO_x. Using catalysts having a structured porous texture and a carefully constructed structure stands out as a highly efficient strategy in eliminating the full spectrum of pollutants present in exhaust streams. Classic oxide-based materials such as alumina, aluminosilicates, zeolites, ceria and ceria-zirconia have long been studied as catalyst supports for the removal of pollutants.[1–3] These systems have nonetheless reached a deadlock as they are usually selective towards one part of the pollutant mixture. Moreover, the use of adsorbents as catalytic supports has proved being both favourable and unfavourable: adsorption of pollutant molecules enhances their degradation but is commonly accompanied by a rapid deactivation of the catalyst due to an enhanced coke deposition.[4] Our work focused on combining adsorption and catalytic oxidation in one uniquely engineered material that addresses these disadvantages while being capable of eliminating gaseous and particulate pollutants. We put in place a synthesis strategy that allowed us to combine two efficient supporting materials into one unique high performing oxide support for the elimination of particulate and gaseous pollutants. First, hierarchically structured zeolites have been prepared using an optimized synthesis strategy. These materials show high surface area values and a coexistence of micro and mesopores constitutes their robust surface structure. Narrow pore size distributions have been achieved where pores having 0.5 and 4 nm in diameter were obtained. We then induced an *in situ* growth of already tuned mesoporous metal oxide crystals at the surface of these zeolite thus increasing the oxygen storage capacity of the resulting material while favouring oxygen mobility at their surface. The final material was then transferred at the surface of a ceramic substrate where it endured testing in and industrial pilot platform. Results show a high elimination rate of VOC and PM and a near total elimination of PAH and CO molecules.

Figure 1 : schematic representation of the mixed metal-oxde-zeolite material



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SURFACE MODIFIED SBA-15 AS DRUG DELIVERY SYSTEM: EFFECT OF SURFACE POLARITY, PH AND DRUG FORM

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The ability to functionalize the surface of nanocarriers based on mesoporous silica with stimuli-responsive functional groups [1, 2], supramolecular systems (cyclodextrins–amine) [3, 4], photoactive ligands [5-7] and polymers [8] that work as caps and gatekeepers for controlled release of various cargos is an intensively studied area in drug delivery today. In the present study, mesoporous material SBA-15 was functionalized with different polar and nonpolar groups: 3-aminopropyl, (SBA-15-NH_2), 3-isocyanatopropyl (SBA-15-NCO), 3-mercaptopropyl (SBA-15-SH), methyl (SBA-15-CH_3) and phenyl (SBA-15-Ph). The resulting surface grafted materials were investigated as matrices for controlled drug delivery. Anti-inflammatory drug, naproxen (as acid or sodium salt) was selected as a model drug and loaded in the unmodified and functionalized SBA-15 materials. Materials were characterized by EA, IR, TEM, nitrogen adsorption, SAXS, PXRD, solid-state NMR spectroscopy and TG. It was shown that surface modification has an impact on both encapsulated drug amount and release properties. Release experiments were performed into two media with different pH: simulated body fluid (pH = 7.4) and simulated gastric fluid (pH = 2). In general, the effect of pH was reflected by the lower release of naproxen under acidic conditions (pH = 2) compared to slightly alkaline saline environment (pH = 7.4). The release rate of drug from propylamine– and phenyl–modified SBA-15 was found to be effectively controlled by intermolecular interactions as compared to that from pure SBA-15, SBA-15-SH, SBA-15-NCO and SBA-15-CH_3, which evidenced a steady and similar release. The highest release was observed for methyl–functionalized material whose hydrophobic surface accelerates the naproxen release. In the case of effect on the form of used drug, a faster release of the sodium salt was observed compared to the acid due to the higher solubility.

Acknowledgement: This work was supported by APVV 20-0512, ITMS 2014+:313011AUW7 and MESRSSR Triangel - Top Research Teams in Slovakia.

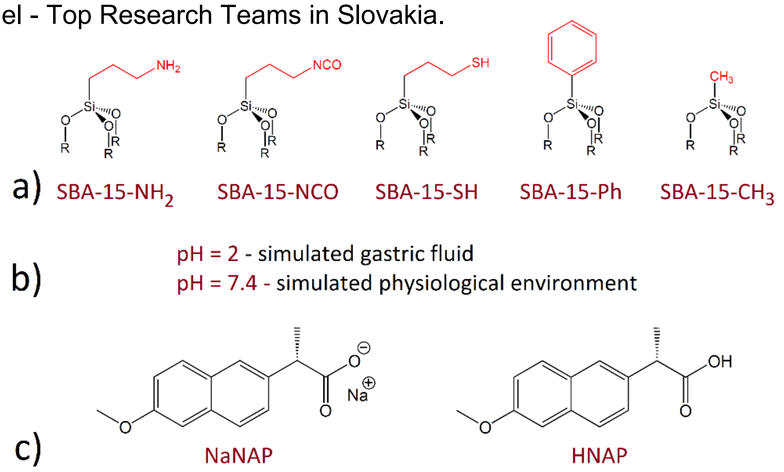

Figure 1 : Studied factors on adsorption/release behaviour of drug from SBA-15: a) surface polarity, b) pH of solution and c) naproxen in the form of sodium salt and acid.

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SOL-GEL SYNTHESIS OF ZIRCONIA NEEDLES AND THEIR ORGANISATION VIA ICE-TEMPLATING

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ABSTRACT:

Technical ceramics such as zirconia are employed in a range of advanced technological applications due to their functional and mechanical properties **[1]**. It is classified as a high performance ceramic due to its remarkable mechanical properties. The toughness of zirconia is strikingly improved when doped with 3 mol% yttrium. This improvement is credited to its phase transformation toughening abilities (tetragonal to monoclinic phase transformation) at the site of mechanical fracture. The increase in volume due to phase transformation induces compressive stress that slow down crack propagation **[2]**. The mechanical properties can also be enhanced by designing textured material with an organised microstructure. Multiple examples exist in nature. Nacre, for example, is an organic-inorganic hybrid material arranged in a “brick-and-mortar” architecture. This microstructure displays a remarkable damage resistance by inducing several processes such as crack bridging and deflection at the origin of fracture **[3]**. Inspired by such designs, this work focuses on the development of zirconia-based ceramics with high strength and toughness by fabricating yittrium doped zirconia anisotropic particles and organising them to have microstructure with highly oriented texture. The chemical composition, shape and uniformity of the particles were investigated to assess their impact on the materials microstructure and properties.

Thus, this project describes the enhancement in functional properties achieved by exploiting the synergy of materials composition and micro-structural arrangement via (i) the synthesis of anisotropic zirconia-based particles using a bottom-up approach technique, and (ii) the alignment of these particles to create novel textured materials. Here, zirconia needles were produced using a sol-gel technique, and the methodology was optimised to produce monodisperse needles with controlled aspect ratio devoid of using surfactants **[Fig 1]**. The needles were then organised by ice templating technique to achieve the desired microstructure. This technique involves in freezing suspensions to induce self-assembly of particles via the growth of ice crystals. The freezing parameters were also studied to facilitate the organisation of the particles and reached the desired microstructure **[4]**. Finally, the properties of the materials were studied and correlated to the needle orientation.

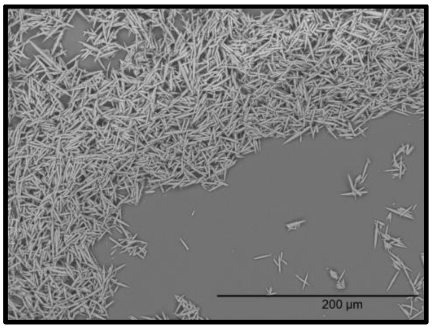

Fig 1: SEM micrograph of zirconia needles produced using a sol-gel approach

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Main Menu

Surfaces and interfaces

SURFACE MICROSTRUCTURE OF THE ALKYL SILOXANE-DERIVED COATINGS: SELF-ASSEMBLY AT DIFFERENT SCALES

Andrei Novikov[1], **Tatiana Alekhina**[1], **Viktoria Segliuk**[1], **Ekaterina Ivanchina**[2], **Alexandra Kuchierskaya**[1], **Marina Shcherban'** [2], **Vladimir Vinokurov**[1]

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ABSTRACT:

Hydrophobic and superhydrophobic coatings provide unique functional properties but have to be developed considering the feasibility of large-scale production [1]. Nevertheless, they are promising for many technical applications, e.g., oil-water [2] and gas-liquid separation [3]. The degree of wetting is characterized by the contact angle, which depends on the surface microstructure. We studied the self-assembly of alkyl siloxanes with various carbon chain lengths on the glass substrates in the different regimes: monolayer self-assembly, nucleation of nanoparticles, and gel formation.

Coverslips (18×18 mm) were cleaned in argon plasma and silanized in the different regimes. Smooth coatings were produced in toluene with the addition of hydrochloric acid and an alkyltrialkoxysilane (C3, C8, and C16). The conventional Stober process was employed to produce rough coatings (with nucleated particles). Gel layers were produced from alkyltrialkoxysilane/alcohol mixtures with an addition of concentrated nitric acid [4]. We characterized the obtained coatings by contact angle measurements and laser confocal scanning microscopy.

As expected, the carbon chain length affects the hydrophobicity of the coatings. The longer it is, the greater the contact angle. The microstructure of the resulting surface also influences hydrophobicity. The smallest water contact angle was measured on the smooth surfaces, while gel surfaces have slightly larger contact angles, and rough surfaces with nucleated particles are the most hydrophobic. The systematic studies of the surface microstructure would lead to the development of scalable hydrophobic coatings for oil and gas applications.

This work in Gubkin University is funded by the Ministry of Science and Higher Education of the Russian Federation within the State Assignment (project 0768-2020-0007).

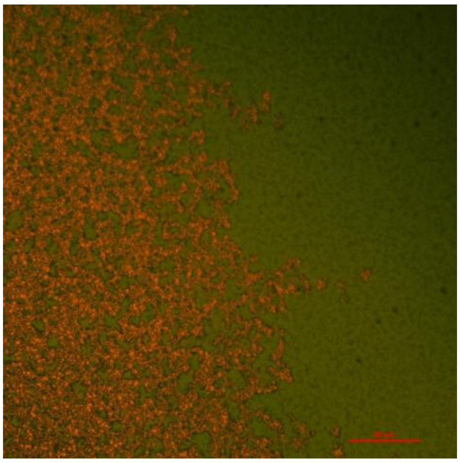

Figure 1 : Methyltrimetoxysilane-derived gel microstructure studied with a confocal microscopy (polar phase is green, oil phase is red)

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Effect of experimental conditions and electrokinetic models on the determination of the zeta potential and colloidal stability prediction for inorganic nanoparticles

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ABSTRACT:

A set of experimental electrophoretic mobility (μ_e) data and finite element simulations was used to show how inappropriate selection of the electrokinetic model used to calculate the zeta potential (ζ-potential) can compromise the interpretation of the results for inorganic nanoparticles (NPs). The main consequences of using ζ-potential values as a criterion for colloidal aggregation growth and the consequent sol-gel transition are discussed based on DLVO interaction energy predictions. For this, magnetite (Fe_3O_4) NPs were synthesized and characterized as a model system for performing the experiments. The results showed that the Fe_3O_4 NPs formed mass fractal aggregates in solution, so the ζ-potential could not be determined under ideal conditions as (μ_e) depends on the NP radius. The asymmetric ion distribution around the aggregate and the concentration gradients present within the pores can give rise to several effects, such as increased local conductivity and non-uniform ζ-potential distribution, which decrease the μ_e. The Dukhin number (*Du*) estimated from potentiometric titration results indicated that stagnant layer conduction (SLC) could not be neglected for this system. The electrokinetic models that do not consider SLC underestimated the ζ-potential values by a factor of 2 or more. The DLVO interaction energy predictions for the colloidal stability of the Fe_3O_4 NP dispersions also depended on the electrokinetic model used to calculate the ζ-potential. The results obtained in this work also suggested that, contrary to many reports in the literature, high ζ-potential values do not necessarily reflect high colloidal stability for charge-stabilized NP dispersions.

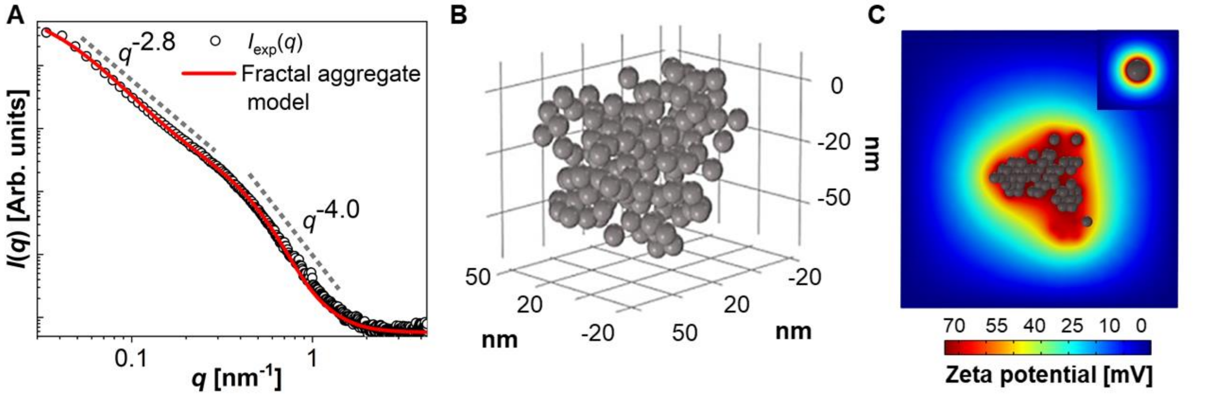

Figure 1. **A**) SAXS curves for the Fe_3O_4 NPs dispersion. **B**) Mass fractal aggregate formed by the primary particles of Fe_3O_4. **C)** Electric potential distribution in the central plane of the Fe_3O_4 NPs aggregate. The electric potential distribution around the equivalent spherical particle is shown in the upper corner of the image.[1]

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Acknowledgments

This work was undertaken in collaboration with the National Institute on Advanced Eco-Efficient Cement-Based Technologies and was supported by the following Brazilian funding agencies: CNPq, CAPES and FAPESP.

Main Menu

3D printing

Drug-loaded mesoporous silica on carboxymethyl cellulose hydrogel: development of 3D printed films for oral mucosal drug delivery

Laís M. Schmidt [1], Juliana dos Santos [1], Thayse V. de Oliveira [1], Edilson V. Benvenutti [2], Monique Deon [1,3], Ruy Carlos Ruver Beck [1]

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ABSTRACT:

3D printing has emerged in recent years as a versatile and disruptive approach for manufacturing and personalizing drug delivery systems. Triamcinolone acetonide (TA) is a synthetic glucocorticoid widely used in the treatment of oral lesions, however, TA presents low water solubility and low permeability, which affect its bioavailability and limit its formulation options for hydrophilic environments as the oral mucosa. Mesoporous silicas, such as SBA-15, are highly porous drug carriers that can host high loads in their nanopores and can increase the drug's apparent solubility by dispersing it through its large surface area, enabling water-based formulations of lipophilic drugs. In this study, the nanoencapsulation of TA in SBA-15 was carried out to improve its apparent solubility and allow its further incorporation on a carboxymethyl cellulose (CMC) hydrogel to develop 3D printed oral films. SBA-15 was synthesized and characterized, presenting the typical rod-like morphology and hexagonal pore arrangement. A reduction in the surface area and pore volume of SBA-15 was observed after incorporation of the drug. Release studies of TA indicate that the formulation (SBA-TA) showed *in vitro* release profile comparable with an ethanolic TA solution, evidencing the increase in the apparent solubility of TA in aqueous environment. A film composed of CMC and SBA-TA was produced by 3D printing, for oral mucosa application. TA release profile from the 3D printed film showed a similar behaviour compared with the SBA-TA, reaching close to 100% of drug release in 12 h. Moreover, the presence of the SBA-TA nanostructured material improved the *in vitro* mucoadhesiveness of the polymeric film. Therefore, SBA-TA is a promising intermediate product for the development of TA water-based formulations and the 3D printed dosage form containing drug-loaded mesoporous silica represented an innovative strategy to develop personalized formulations, with faster dissolution profile, better palatability and greater patient acceptance.

Acknowledgments: Financial support from CNPq/Brazil, Fapergs and CAPES/Brazil (Finance Code 001).

3D printed Nanofibrillated Cellulose Hybrid Aerogels with Anisotropic Thermal Insulation Properties

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ABSTRACT:

Aerogels have different market applications owing to their exceptional properties but currently available solution are limited to the field of thermal insulation in the form of blankets, renders and composites. Silica aerogels are by far the most common material, but recent research points to biopolymer aerogels as an exciting alternative, as they contain different surface functional groups, which provide avenues for derivatives, hybrids and applications. In our current study, we apply our know-how on silica aerogel and CNC-based additive manufacturing [1–3] to successfully 3D print pure cellulose aerogel consisting of nanofibers (CNF) and nanocrystals (CNC). Our reference NFC-CNC inks have a unique range of mechanical and thermal properties and we achieve contrasting anisotropic thermal conductivities (25 $mW.m^{-1}.K^{-1}$ *v/s* 120 $mW.m^{-1}.K^{-1}$; for the same sample) as well as an order of magnitude greater mechanical strength in the longitudinal versus transverse direction. To improve the performance further, hydrophilic silica was introduced, which lowers the thermal conductivity down to 21 $mW.m^{-1}.K^{-1}$. These biopolymer hybrids, and the possibility to 3D print them, introduces customizability of aerogel thermal and mechanical properties, along with anisotropy, to extend the potential for oil-water separation, CO_2 capture, catalysis, and medicine, beyond aerogel's well-established thermal management applications.

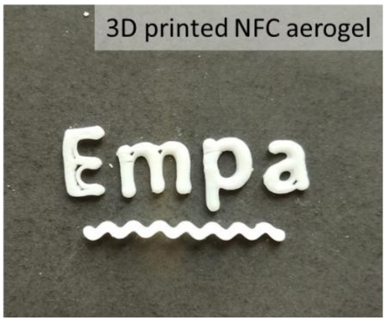

Figure 1 : 3D printed NFC-CNC aerogel

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Characterization techniques

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RHEOLOGY OF SOL-GEL TRANSITION

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ABSTRACT:

Sol-gel transition is associated with the formation of spatial chains, which permeate the whole volume of the sol. It is manifested several new physical properties: elasticity, critical shear stress, the ability to preserve shape. Viscosity and yield point - two macroscopic integral characteristics of Newtonian medium (sol) and Bingham medium (gel) that are responsive to changes in the colloidal system, occurring in the process of gelation. Therefore, the study of these processes requires using of special rheological methods. A convenient model for such studies is silica-sols.
To study the rheology of gelation, we have developed a measuring system consisting of several measuring cells such as Weiler-Rebinder. This measurement complex is designed to measure the dependence of the critical shear stress versus time, from the beginning of the sol-gel transition to the complete conversion of the sol into a gel.
For the developed system, the range of measured values of the critical shear stress is equal to . The device, as mentioned above, has allowed establishing the form of the initial part of the curve $\tau = f(t)$ and to develop a methodology for a more accurate definition of gelation time.
We found that the classical method determining the sol-gel transition start time based on the intersection point determination a tangent to the linear portion of rheological curve τ=f(t) gives much distorted results. Carried out analysis of experimental data has allowed finding a new phenomenon: the kinetic curves in coordinates of Avrami-Erofeev-Bogolyubov’s equation are complex and have a point of inflection. The constant in Avrami-Erofeev-Bogolyubov’s equation was defined as not dependent on the temperature and is the same for both the initial and final parts of the kinetic curve. It depends only on the chemical nature of the reacting system.

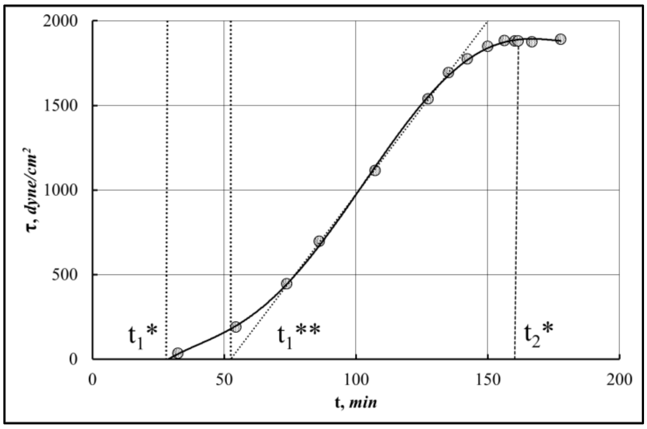

Figure 1 : View the full curve of the critical shear stress versus time during gelation of silica sol with a concentration of 3% at pH 6.0 and T = 20 °C.

For the initial section of the kinetic curves, the value of the parameter n in Avrami-Erofeev-Bogolyubov’s equation amounted to n=23.4±2.8. The large value of this parameter can be interpreted as the average number of growth directions of a fractal aggregate. The observed behavior of the kinetic curves is responsible for changing the process mechanism and decreasing the number of possible directions of fractal aggregates growth.
Based on general considerations, these critical points can be classified as points of 2nd order phase transitions. Phase transitions of the second kind are phase transitions in which the dependences of the second derivatives of thermodynamic potentials, depending on external factors, change abruptly, and their first derivatives - gradually.

New method for determining mechanical moduli of disordered materials with hierarchical porosity on different structural levels

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ABSTRACT:

Knowledge on the impact of synthesis parameters and structural properties, respectively, on mechanical properties of the respective porous material on different structural levels provides information for targeted materials design serving specific applications.

We investigated two non-standard approaches, i.e. deformation upon mercury porosimetry and in-situ dilatometry during nitrogen adsorption analysis, for determining the mechanical properties of the mesoporous backbone phase in a series of disordered, sol-gel-based monolithic SiO_2-materials possessing hierarchical meso-macroporosity. Using ordered porous model materials, the latter method has been recently proven to provide reliable mechanical moduli [1,2]. Within our present study, this concept was applied to a monolithic SiO_2-material developed for HPLC exhibiting disordered hierarchical meso- and macroporosity, as well as a series of analogue phenyl-modified meso-macroporous SiO_2 monoliths with up to 36.1 at% organic modification. The aim of the investigations was to identify correlations between the organic modifications and their impact on the morphology of the porous solid and the resulting mechanical properties.

The study shows that both, Hg-porosimetry and in-situ dilatometry performed during N_2 adsorption at 77 K provide similar and reasonable moduli of compression for the mesoporous backbone of the silica materials investigated. These data were compared with bulk moduli as determined from sound velocity measurements by describing the fully connected macroporous backbone with a foam model. The analysis of the results reveals an otherwise overseen side effect of the organic modification of the silica framework: In contrast to the reference SiO_2 meso-macroporous monolith, the hybrid material is composed of a more particulate morphology on the mesoscale i.e. mesoporous particles and corresponding necks between them are formed, which results in a significant softening of the porous solid on the macroscale.

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GAS PHYSISORPTION – SOME ARTIFACTS AND MISINTERPRETATIONS OF THE RESULTS

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ABSTRACT:

Gas physisorption method is one of the most widely used tools for the textural characterization of micro- and mesoporous materials. Despite the commercial availability of hi-tech gas physisorption instruments as well as software for evaluation of sorption isotherms, a correct interpretation of results may still be problematic.

This contribution focuses on an overview of selected examples of misinterpretations of obtained isotherms and the results. For example, pore size distributions (PSDs) can vary significantly depending on whether they are derived from the adsorption or desorption isotherm. A typical example is H2(a) [1] hysteresis, which is a characteristic consequence of the complex network of interconnected inkbottle pores present in the test sample. Under certain conditions, so-called cavitation of the adsorbate in the porous system can occur. If a desorption isotherm is chosen for the calculation of the PSD, there is a significant risk of misinterpretation due to the presence of an artifact at approximately 4 nm (pore diameter).

Commercially available software for the calculation of textural data usually includes the ability to obtain the pore size distribution from the experimental isotherm using DFT methods. Although these are advanced approaches that (simply stated) take into account the properties of the adsorbed phase at the molecular level, the resulting PSD curves still need to be critically examined. This paper will present other issues that can be commonly encountered in the context of the gas physisorption method.

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Understanding VOC-adsorption-induced Sol-gel coating deformation: a complete study by ellipsometry

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Understanding the adsorption of gases into microporous thin film is a key factor in the development of Volatile Organic Compounds (VOC) detectors. However, given how little is known about the behaviour of such gases in nanopores (< 2 nm) where the Kelvin model doesn't apply, an empirical study of the theoretical works concerning this subject must be undertaken beforehand. Thus, this work will aim at evaluating the mechanical properties of a microporous thin film of hybrid silica though the measurement of its refractive index and thickness, via Ellipsometry Porosimetry (EP), during the adsorption isotherm of various VOC. The use EP as a method for evaluating the quantity of gas adsorbed into a porous thin film is already well verified and validated. However, including the evolution of thickness is novel and allows for more precise measurements. The present experimental work is dedicated to the empirical verification of the theorical work laid by Gennady Y. Gor & Noam Bernstein regarding the use of Bangham's law and the Brunauer–Emmett–Teller (BET) model as a mean to quantify adsorption-induced deformation. This verification consists in recording the evolution of refractive index and thickness of the sample throughout an adsorption isotherm using a variety of VOC (typically organic solvents with different surface tension), using the Bruggeman Effective Medium Approximation (BEMA). Besides, the evolution of thickness as a parameter was introduced in the model to determine the quantity of adsorbed VOC. Finally, the method described by Gennady Y. Gor & Noam Bernstein was used to deduce the pore load modulus of the microporous film. The comparison of the results obtained for each measurement was in agreement with what was predicted by the theory.

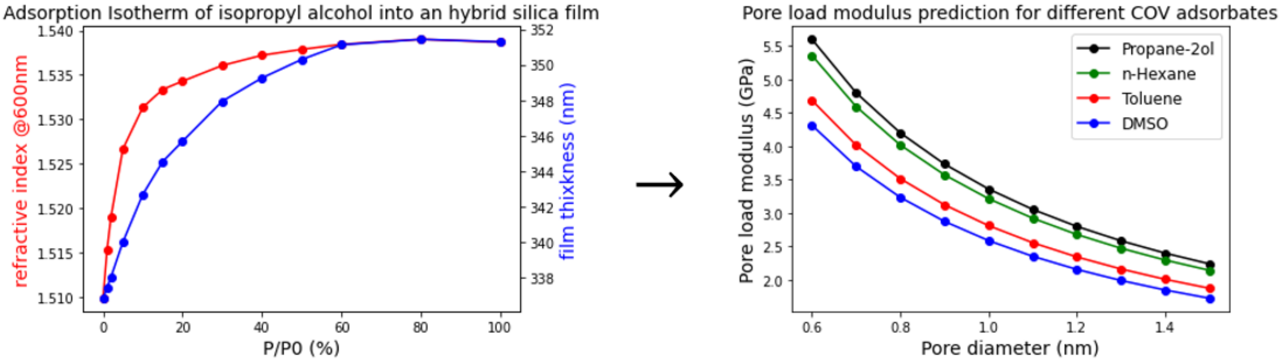

Figure 1: Extraction of pore load modulus from adsorption isotherm

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Modelling techniques for sol-gel materials

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CONTRIBUTIONS OF NETWORK ANALYSIS FOR UNDERSTANDING THE COMPLEX SOL-GEL PROCESS. THE CASE OF STOBER SYNTHESIS

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ABSTRACT:

Stöber process [1] is a widely used and effective method for synthesizing monodisperse SiO_2 particles. However, it is a complex system where synthesis variables are interdependent, and the relevance of different synthesis factors on the final diameter is still controversial [2]. Moreover, none of the proposed models cover all experimental results. This work aims to describe the Stöber method with a non-reductionist analysis that exposes this complexity of the process.

A network representation was constructed considering the main reactions involved: hydrolysis, condensation, and interactions. The importance of each relationship between variables that influence the synthesis was defined based on previous works, leading to a highly connected network diagram. The network topology was analyzed using graph theory metrics (degree distribution, betweenness centrality, average shortest path length, PageRank) [3].

Graph analysis provides a more comprehensive and unifying vision of the synthesis and interrelation of the variables involved, as it allows a complete visualization on a single plane. In this way, it helps to unravel the complexity of the links between the parameters, taking into account minor factors that have not been reported. This opens up the opportunity for combining graphs with data analysis tools, machine learning, and artificial intelligence to generate a predictive model of the Stöber process.

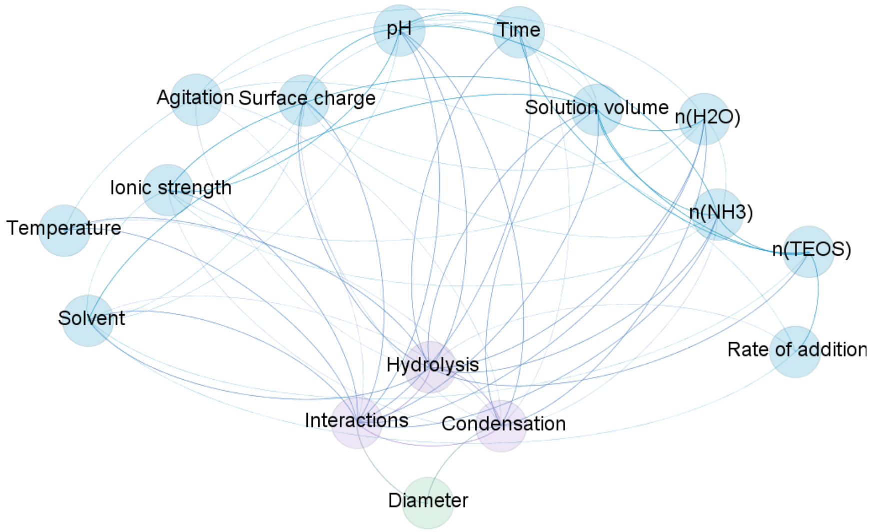

Figure 1: Graph representation of the Stöber process

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CELLULAR AUTOMATA COUPLED WITH LATTICE BOLTZMANN MODEL FOR MODELING OF SILICA AEROGEL FORMATION AND STRUCTURE

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ABSTRACT:

The formation of silica aerogels and the kinetics of condensation were investigated numerically. There was used the cellular automata method coupled with two-color lattice Boltzmann Model (LBM) (1). The latter method was applied to track the microscopic phase separation during the aerogel synthesis. The original LBM method has been widely used for modeling of various problems concerned with fluid dynamics. In this method there is tracked the evolution of the particle distribution function (PDF). In two-color LBM, we have two PDF's for two fluids (which are usually referred to as two "colors"). These two PDF's are evolving separately but the equations of evolution are linked by means of surface tension term.

In parallel to the evolution of two liquid phase, the gelation kinetics in one of the phase is investigated by means of cellular automata (CA) method. The model of gelation is based on model proposed by Rege et al. (2-3) The main difference is that in current work it is performed in domain region occupied by the condensing phase. Each cell can be described by one of two possible states: (i) a cell occupied by a particle or (ii) an empty cell. An initial state of the system was pseudo-randomly generated. Then, the particle start to move in pseudo-random walking, imitating diffusion. Some of them, called "seeds" are however fixed. Any other ("walkers") are moving to the neighboring cell in every time step. However, they cannot leave the gelling phase.

As an effect of proposed algorithm we obtain the dynamics of kinetics of gelation which appears in good agreement with experimental results. Also, the final structures are similar to those observed experimentally.

Acknowledgement: Research was funded by POB Technologie Materiałowe of Warsaw University of Technology within the Excellence Initiative: Research University (IDUB) programme (IDUB-TM-2-3).

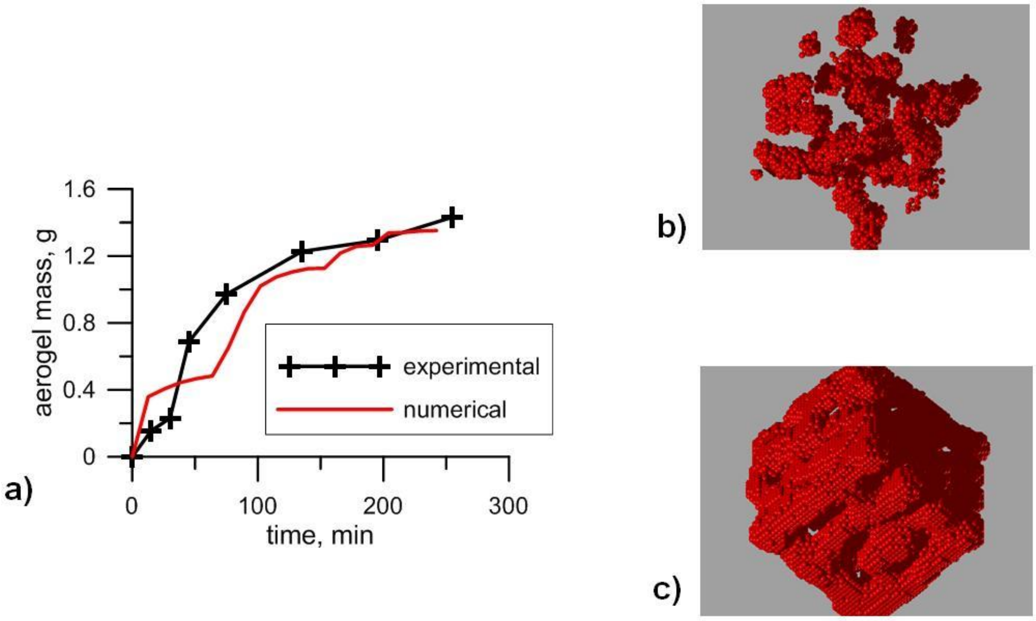

Figure 1 : (a) kinetics of silica aerogel formation – experimental and numerical; (b) and (c) exemplary structures of aerogel obtained by means of numerical model.

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Main Menu

Materials for catalysis and photocatalysis

THE SOL-GEL METHOD FOR PREPARATION OF ALUMINA SUPPORTED IRON CATALYST FOR BIGINELLI REACTION

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ABSTRACT:

Heterogeneous catalytic systems usually exhibit high activity in organic reactions. Many studies have been reported concerning the preparation methods [1]. The sol-gel is one of this method. The use of sol–gel method for catalyst preparation has been described by Pajonk [2]. The method has several advantages such as a well-defined pore size distribution, high purity control of reactants, homogeneity, high thermal stability… [3]. This latest method may use a variety of supports rather than alumina and silica to prepare mixed oxide supports [4].

The goal of the present study was to use sol gel method in order to prepare alumina supported iron catalyst (Fe/Al2O3-SG) calcined at 500°C and the investigation of surface parameters (BET), morphology (SEM), composition (XRD) and catalytic activity. The catalytic performances of the samples were evaluated in the Biginelli reaction with a ratio of 2:2:3 of benzaldehyde, ethylacetoacetate, and urea, respectively, to obtain 5-ethoxycarbonyl-4-phenyl-6-methyl-3,4-dihydropyridin-2(1H)-one known by the DHPM acronym. The reaction was performed under solvent free conditions. The catalyst gives good performance after 1 hour reaction time with 61% of DHPM yield.

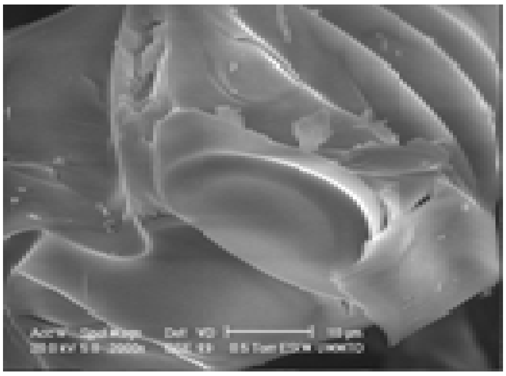

Figure 1 : SEM image of calcined catalysts at 500°C of Fe/Al2O3-SG

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USING OF VANADIUM POLYOXOMOLYBDATE AS GREEN CATALYST IN THE NITRATION OF 7-HYDROXY-4-METHYLCOUMARIN

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ABSTRACT:

The nitration of organic compounds is a very active and rewarding area of research because they are basic elements in the field of synthetic organic chemistry. Moreover, nitro-aromatic compounds have been extensively used as chemical feedstock for a wide range of useful materials, such as dyes, pharmaceuticals, perfumes and plastics [1]. They also can be employed as precursors for various amines synthesis via reduction process[2].

Therefore, much attention has been drawn to the development of efficient and practical methods for the synthesis of aromatic nitro compounds. As conventional electrophilic nitration of aromatics generally requires the use of excess nitric acid or a mixture of nitric and sulfuric acids, this results in excess acidic waste streams coupled with frequent low selectivity due to the formation of polynitro derivatives and oxidative by-products along with the desired mononitro product.

In this study, vanadiumpolyoxomolybdate $H_4PMo_{11}VO_{40}$ was used as acid catalyst in the nitration of 7-Hydroxy-4-Methylcoumarin as green process. Many salts are also used as nitrating reagents. Very interesting results were obtained in mild conditions.

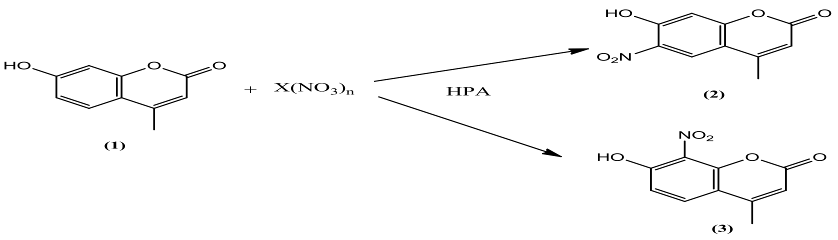

Figure 1: Nitration of 7-Hydroxy-Methylcoumarin

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Ethanol dehydrogenation over Cu-SiO_2 catalysts prepared by sol-gel, impregnation, and deposition techniques

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ABSTRACT:

Ethanol dehydrogenation to acetaldehyde represents the first step in the ethanol-to-butadiene process and is effectively catalysed by copper. This reaction is critical for the future due to the ongoing changes in the oil industry: the possible sustainable production of butadiene from bioethanol would be highly desired. However, catalysts used for this modern purpose mainly suffer from low stability with time-on-stream [1].

In this study, different Cu-SiO_2 catalysts were prepared by several techniques: hydrolytic and non-hydrolytic one-pot sol-gel, dry impregnation technique, strong eletrostatic impregnation, and deposition of pre-made (by hot injection) Cu NPs on silica [2–4]. Both sol-gel prepared catalysts were highly porous (up to 560 $m^2\ g^{-1}$) and exhibited highly homogeneous ("atomic") copper dispersion (STEM-EDS). Other synthetic techniques (i.e., impregnation) led to surface area decrease and provided larger nanoparticles (e.g., 1-3 nm for strong electrostatic impregnation; 10-20 nm for pre-made Cu NPs) on the catalysts' surface. Samples were thoroughly characterized both before and after catalytic tests (TGA, XPS, P-XRD, ICP-OES).

Catalysts were tested in a gas-phase fixed-bed catalytic reactor in ethanol dehydrogenation. Samples with atomically dispersed Cu prepared by one-pot sol-gel method were highly active. The stability with time-on-stream was a major issue for all catalysts; severe deactivation was observed. Catalysts suffered from both particle sintering and coking. The Cu NPs alloying with Ni and Co was suggested as a possible solution to the deactivation phenomena.

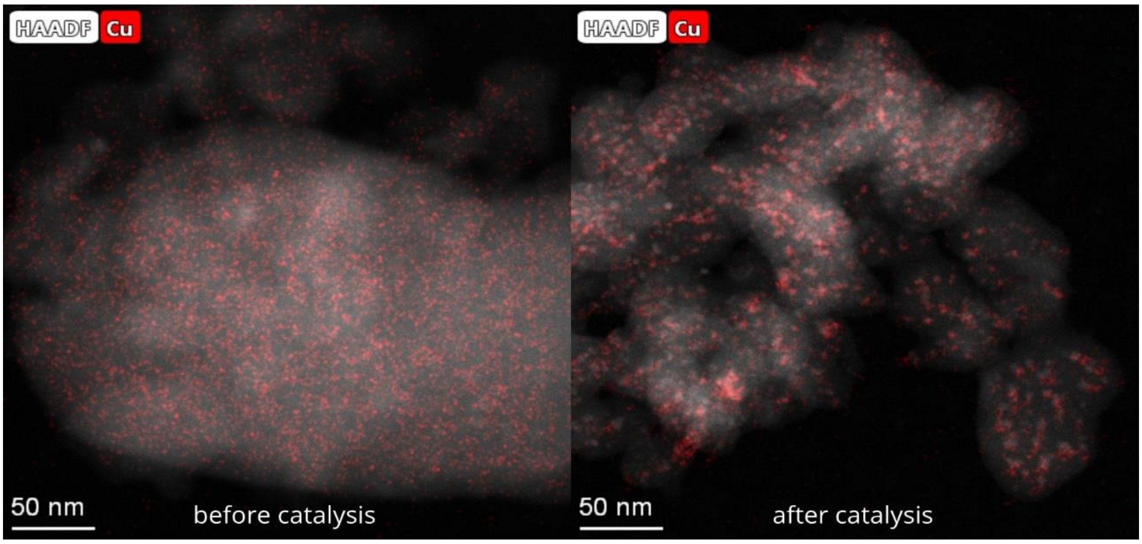

Figure 1: Sintering of Cu nanoparticles (red color) prepared by strong electrostatic impregnation during catalysis (STEM-EDS).

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Synthesis of lithium metasilicate catalysts using non-conventional silicon sources for biodiesel production from waste oils.

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In the last decade, several strategies have been developed to limit the use of fossil fuels in order to tackle climate change.[1] One of the approaches developed is the use of renewable fuels to mitigate these effects. Being biodiesel one valuable alternative, which is produced from transesterification reactions of animal or vegetable fats.[2] Conventional processes to produce biodiesel involve the use of homogeneous alkaline catalysts under mild temperatures and atmospheric pressure.[3] In this study, we present the synthesis and characterization of lithium metasilicate (using non-conventional precursors) and its use in transesterification reactions to obtain biodiesel. The lithium metasilicate (catalyst) was synthesized from non-conventional silicon sources by a solid-state method (fuse reagent) and basic extraction followed by hydrothermal treatment. Subsequently, biodiesel production was carried out by heterogeneous catalysis using three alcohol/oil molar ratios (6:1, 12:1 and 18:1), three catalyst concentrations of 1%, 3% and 5% (wt.) with respect to oil, and a temperature range from 30 to 60 °C, finding an optimum temperature of 60 ºC for biodiesel production. XRD analysis of the synthesized catalyst displayed a difference in materials purity, depending on the type of synthesis used (fuse reagent or basic extraction). Structural characterizations (SEM) showed amorphous agglomerated crystals of about 30 m. Gas chromatography analysis demonstrated that the molar ratio of 18:1 and a concentration of 5% (wt.) of lithium metasilicate as a catalyst, resulted in biodiesel conversion of up to 95 % in the transesterification reactions.

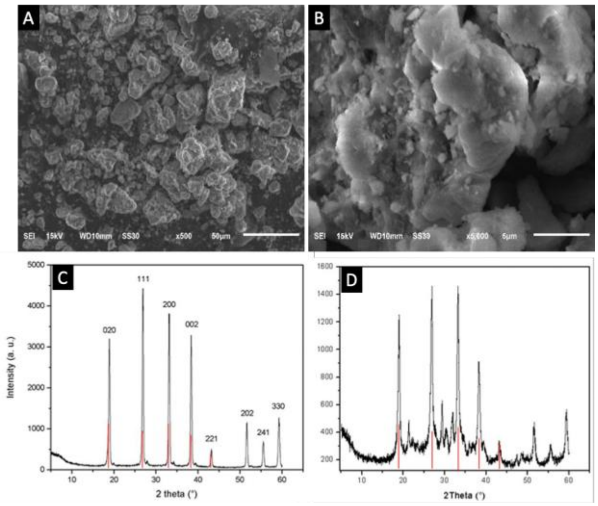

Figure 1: SEM and XRD structural analysis of the lithium metasilicate (Li_2SiO_3) catalyst. A and B SEM micrographs of amorphous crystals of Li_2SiO_3; C diffractograms of catalyst synthesized by basic extraction, and fuse reagent (D).

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NOVEL CeWTiO$_x$ CATALYST FOR LOW TEMPERATURE SELECTIVE CATALYTIC REDUCTION

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NO$_x$ is a major part of acidic rains and contributes also to formation of tropospheric ozone. For this reason, NO$_x$ emissions from both stationary and mobile sources are currently under great supervision not only in the EU, and the USA but also in countries that have historically adopted older European or American emission standards and limits.[1] The most common method for NO$_x$ removal is a selective catalytic reduction (SCR), which uses ammonia as a reducing agent (NH_3-SCR).[2] The most frequently used catalysts for NH_3-SCR are mixed-metal oxides based on V_2O_5 or Fe, Cu exchanged zeolites.[3] Cu, Fe exchanged zeolites are generally used for applications where high-temperature conversion and stability (above 500 °C) is required. However, the conversion at low temperatures of these materials is insufficient and the highest emissions of current both low-duty and heavy-duty vehicles, and machinery are during cold starts, i.e., low catalyst temperatures. Mixed-metal oxides catalysts based on vanadium pentoxide have better conversion at low temperatures, but the conversion at higher temperatures decreases significantly and poses poor thermal stability.

A promising alternative are mixed-metal oxides based on CeO_2, WO_3 and TiO_2.[4] Between 220-450 °C, this material shows NO$_x$ conversion higher than 90 %, and remained high conversion even under high GHSV. Unlike commercial de-NO$_x$ mixed-metal oxide catalysts, this material does not contain vanadium, which is toxic and can be released into the environment. In this work the CeWTiO$_x$ mixed-metal oxide catalyst was synthesized by several chemical routes (hydrothermal synthesis, electrospinning and non-hydrolytic sol-gel[5]) with a constant stoichiometric ratio of 2:1:10, forming $Ce_{0.2}W_{0.1}TiO_x$. Different synthetic routes gave rise to different morphologies of the material such as nanofibers, xerogel, and bulk which affect its key properties such as thermal stability, specific surface area, porosity, and strength of the material. These factors were compared among different synthetic routes and morphologies in order to find the best approach for this application.

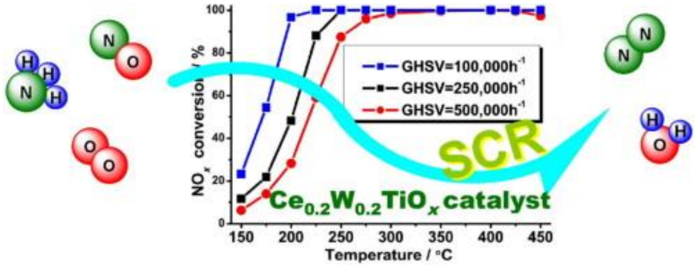

Figure 1 : CeTiWO$_x$ catalyst conversion[4]

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USING OF VANADIUM POLYOXOMOLYBDATE AS GREEN CATALYST IN THE NITRATION OF 4-METHYLCOUMARINS

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[2]Laboratoire LCAGC, Département de Chimie, Faculté des Sciences, Université Mouloud Mammeri, 15000, Tizi-Ouzou, Algeria

ABSTRACT:

The nitration of organic compounds is a very active and rewarding area of research because they are basic elements in the field of synthetic organic chemistry[1]. Moreover, nitro-aromatic compounds have been extensively used as chemical feedstock for a wide range of useful materials, such as dyes, pharmaceuticals, perfumes and plastics. They also can be employed as precursors for various amines synthesis via reduction process.

Therefore, much attention has been drawn to the development of efficient and practical methods for the synthesis of aromatic nitro compounds. As conventional electrophilic nitration of aromatics generally requires the use of excess nitric acid or a mixture of nitric and sulfuric acids, this results in excess acidic waste streams coupled with frequent low selectivity due to the formation of polynitro derivatives and oxidative by-products along with the desired mononitro product.

In this study, vanadiumpolyoxomolybdate $H_4PMo_{11}VO_{40}$ was used as acid catalyst in the nitration of 7-Hydroxy-4-Methylcoumarin(1) as green process (Figure1). Many salts are also used as nitrating reagents. Very interesting results were obtained in mild conditions.

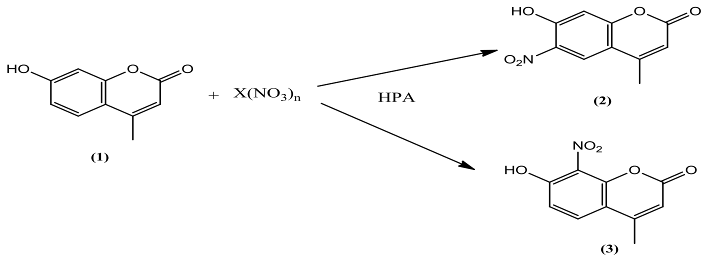

Figure 1: The nitration of 7-Hydroxy-4-Methylcoumarin

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Innovative sol-gel routes to mesoporous bifunctional catalysts for the upgrading of bioethanol to butadiene

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ABSTRACT:

Bioethanol production has been promoted by strong political and incentives and is technologically sound. In parallel, butadiene is one of the compounds that is expected to suffer future shortage due to the shift towards shale gas from the traditional steam cracking of naphtha. Therefore, intensive research is currently conducted towards the direct catalytic conversion of ethanol to butadiene. The reaction is long known, and consists of a complex network of dehydration and dehydrogenation reactions catalysed respectively by acid and redox active sites that must operate in a controlled and balanced fashion to maximize the butadiene yield.[1]

In the highly versatile toolbox of sol-gel chemistry, non-hydrolytic sol-gel (NHSG) is particularly effective to synthesize mesostructured materials with tailored properties (texture, homogeneity, surface chemistry) and has already shown its potential to obtain effective catalysts.[2-4]

Here, NHSG was used to prepare bifunctional Ta-Cu-SiO_2 catalysts via the acetamide elimination route (“Ac”) and compare them with similar compositions obtained through the ether route (“Et”). Both pathways yielded mesoporous materials (Figure 1A; SSA≈600 $m^2\ g^{-1}$; V_p≈0.1 mL g^{-1}; D_p≈4.0 nm for the acetamide elimination route, SSA≈700 $m^2\ g^{-1}$; V_p≈0.02 mL g^{-1}; D_p≈7.0 nm for the ether route), with similar CuO crystallite size of around 20 nm. IR spectroscopy and XPS pointed to a successful Ta incorporation inside the silica matrix. The catalysts obtained through the acetamide elimination route perform systematically better than those synthesized by the ether route (Figure 1B). After optimization of the Cu and Ta loading, the best formulation (Ac-2Ta4Cu) reached an ethanol conversion of 75 % and a butadiene selectivity of 50 %.

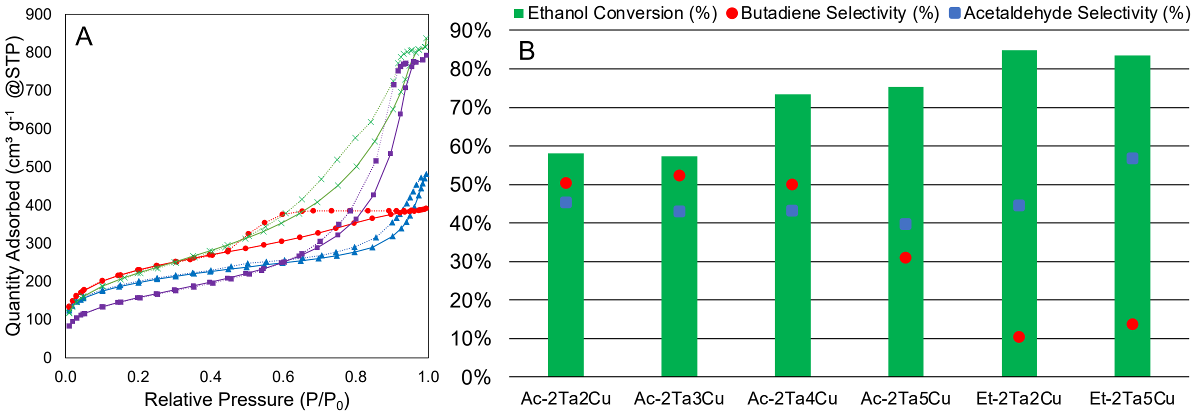

Figure 1 : (A) N_2-physisorption isotherms of Ac-2Ta2Cu (blue Δ), Ac-2Ta5Cu (red ○), Et 2Ta2Cu (green ×), Et-2Ta5Cu (purple ◊). Adsorption isotherms are plotted as solid lines, desorption isotherms are plotted as dotted lines; (B) Catalytic data at 325 °C, WHSV=1.10h^{-1}

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GREEN SYNTHESIS OF HETEROGENOUS CATALYSTS BY SOLVENT-FREE REACTIVE EXTRUSION

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ABSTRACT:

We present a new strategy for the sustainable manufacturing of catalysts, which combines the sol-gel process with the principle of reactive extrusion. This method allows the synthesis and shaping of the active phase and the support simultaneously, at room temperature in a solvent-free continuous mode. Reactive extrusion has been intensively developed for the synthesis and processing of polymeric materials but it is still in its beginning stage with metal oxides.

We focused on the synthesis of bohemite (γ-AlOOH) which is converted upon calcination into mesoporous alumina (γ-Al_2O_3) with high specific surface area. The developed material exhibits good catalytic properties regarding ethanol dehydration activity comparable to those observed in literature. This oxide is widely used in industry as catalyst and catalyst support. Afterwards, we developed reactors and processes for the synthesis of Ruthenium-based catalysts supported on γ-AlOOH and γ-Al_2O_3 for CO_2 methanation. In order to quickly evaluate the influence of the experimental parameters (concentrations, temperature and hydrolysis), the simultaneous synthesis of the support and the active phase of the catalyst was developed in a stirred reactor tank (outside the extruder). The Ru precursor (solid) is mixed with the aluminum precursor (viscous liquid) without addition of solvent then the mixture was hydrolyzed. Ru/AlOOH and Ru/γ-Al_2O_3 catalysts with different weight contents of Ru (Wt%Ru: 1, 2, 4 and 6% relative to the γ-Al_2O_3 support) were prepared. As prepared materials were heated under air and dihydrogen with different temperatures.

The X-ray diffraction and transmission electron microscopy shows very small Ru nanoparticles (2-3 nm) well dispersed on nanoplatelets of aluminum hydroxide and oxide. The specific surface area increases with decreasing amount of Ru (from 506m^2/g for Wt%Ru=6% to 818m^2/g for Wt%Ru=1%). The most interesting samples will be evaluated in CO_2 methanation catalysis (A.Kim *et al.* 2019) [1].

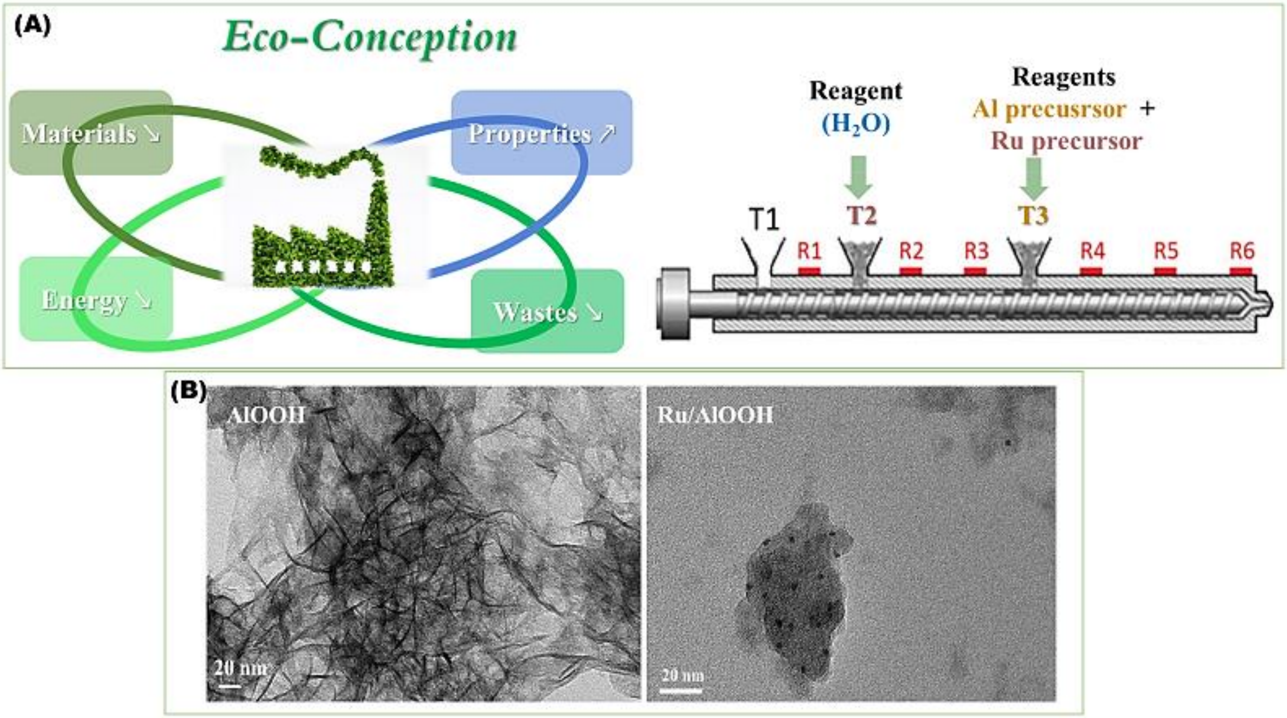

Figure 1: (A) The principle of the synthesis at left and the scheme of the experimental set-up of Reactive extrusion at right; (B) TEM images of γ-AlOOH synthesized by solvent-free reactive extrusion at left and Ru/AlOOH (Wt% Ru = 4%) prepared by solvent-free synthesis in a stirred reactor tank

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Influence of organic solvent and pH in sol-gel synthesis of TiO_2 powder on the photocatalytic Low-Pressure Cold Spray coatings properties

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ABSTRACT:

The rapid increase of the demand for clear water over the years roots the growth of the global photocatalyst market. Typically, the photocatalyst is utilized as powder, distributed in a volume of the liquid. The high specific surface of the powder photocatalysts is an indisputable advantage. But, on the other hand, the regeneration of the dispersed photocatalyst is a clear disadvantage of the powder photocatalysis process. Therefore, simple and efficient methods that allow immobilizing the photocatalytic material are constantly progressing. One of them are thermal spraying techniques, in which melted/deformed powder material is sprayed onto a substrate. To produce an efficient photocatalytic coating of desirable crystalline structure and high specific surface, one has to avoid overheating of the TiO_2 powder. Hence, choosing a low-temperature process such as low-pressure cold spray (LPCS) is most suitable. The quality of TiO_2 cold-sprayed coatings highly depends on the TiO_2 powder properties used for its creation. Powder particle size and shape, crystallinity degree, agglomeration all are conditioning the spraying process. Thus, to study the powder features, the sol-gel synthesis conditions were modified: by changing the solvent to a few chosen ones and applying different pH values. Powders were investigated concerning morphology, crystallinity, chemical composition, particles size and shape. Selected powders were sprayed onto a substrate. Mechanical and physicochemical properties, including the photocatalytic activity of the coatings, were examined.

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PHOTOCATALYTIC INDOOR AIR PURIFICATION DRIVEN BY PRISTINE AND METAL-MODIFIED TIO_2 OBTAINED BY SOL GEL METHOD

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ABSTRACT:
The aim of this research is to investigate and evaluate the ethanol gas phase oxidative degradation assimilated to the indoor air purification. Pristine and metal (Au, Pt)-modified TiO_2 photocatalysts (powders and films) were obtained by sol gel method. The metal precursors were added both directly during the synthesis process but also as surface modifiers of the pre-synthetized TiO_2. The presence of gold and platinum nanoparticles on TiO_2 can mainly trigger the red shift of light absorption edge, energy band bending and separation of the photo generated charges. The structural, morphological and optical characterizations of the as obtained photoactive materials were analyzed in accordance with their functional properties depicted from the photocatalytic assays. These allow the hierarchization of the investigated materials based on their photoactivity for the mineralization of organic compound (ethanol) under simulated solar and visible light. Also, the photocatalytic measurements were meant to give a complete picture of the whole oxidative process. Accordingly, the mild oxidation products generated by successive reactions have been analyzed and quantified. The photo degradation mechanism relative to the photocatalyst type (pristine/metal-modified TiO_2, powders/films) was also investigated.

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SOL-GEL SYNTHESIS OF NANOCRYSTALLINE MgO FOR CATALYSIS APPLICATION

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ABSTRACT:

MgO has many catalytic applications, since its basicity is very useful for the reforming of various organic compounds to produce hydrogen [1], as well as for condensation reactions [2]. This study presents an easy route to induce pores formation, increase the specific surface area and control the crystallite size of magnesium oxides using the sol-gel method with addition of Pluronic P123 surfactant. Sol-gel MgO was prepared in the presence of the Pluronic P123 surfactant and details of preparation can be found in the publication [2]. Samples prepared without surfactant and using Pluronic P123/MgO molar ratios of 0.004, 0.008, 0.016, and 0.032, were denoted MgO, S1, S2, S3, and S4, respectively. The characterization of catalysts by X-ray powder diffraction (Fig. 1a) showed a decrease of the intensity of all the reflections by increasing the Pluronic proportion. Additionally, the crystallite size decreased from 78 nm (MgO) to 17nm (S4) and the surface area increased from 2 m^2/g (MgO) to 50 (S4) m^2/g. The catalytic properties of samples were evaluated through the Knoevenagel condensation reaction using the condensation of benzaldehyde and ethyl cyanoacetate. The catalytic conversions revealed different rates of product formation for MgO and samples S2 and S4 (Fig. 1b). The slowest rate was observed using MgO, which presented the lowest surface area. The activity of sample S2 was between the values for MgO and S4 sample, in accordance with the values for the surface area and basic sites (32 m^2/g). The fastest conversion was achieved for S4 sample, with 80% product formation after 2 min, in agreement with the highest value for the surface area.

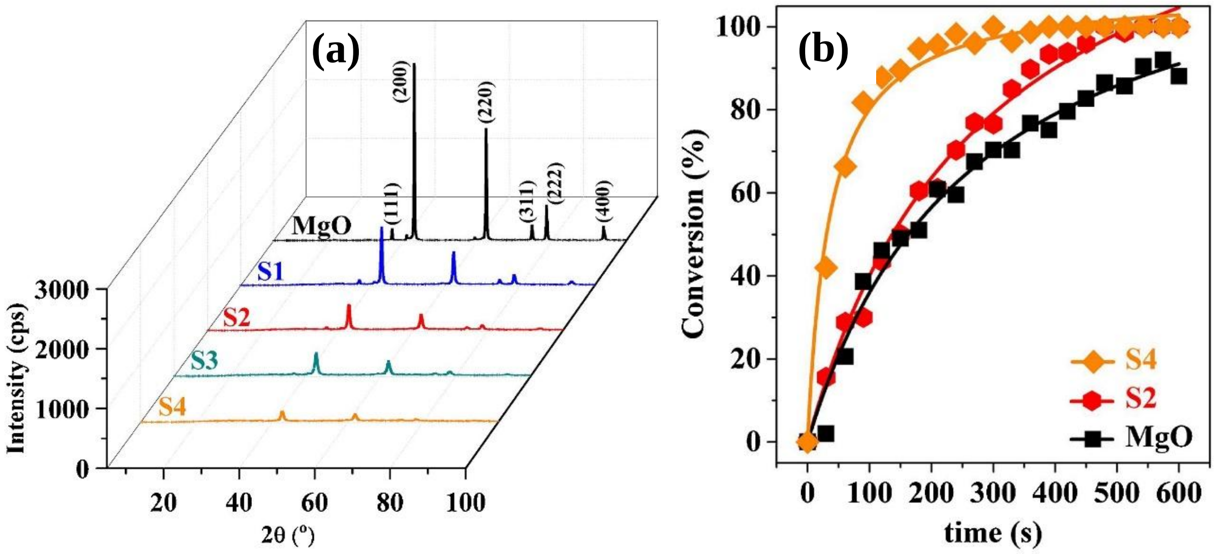

Figure 1: (a) XRD diffraction patterns of the MgO samples prepared by the sol-gel method using Pluronic P123/MgO molar ratios of 0.000 (MgO), 0.004 (S1), 0.008 (S2), 0.016 (S3), and 0.032 (S4) and (b) Conversion of reagents in the Knoevenagel condensation reaction as a function of time.

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HYBRID ACID CATALYSTS PREPARED VIA TRIMETHYLSILYLATION OF ALUMINOSILICATES SYNTHESIZED BY NON-HYDROLYTIC SOL-GEL

Lucie Leonova[1], **Jiri Pinkas**[1], **Ales Styskalik**[1]

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ABSTRACT:

Hybrid materials based on aluminosilicates are extensively studied for their enhanced catalytic performance. Organic groups can change acidity, hydrothermal stability, and porosity. First, we have shown, that non-hydrolytic sol-gel (NHSG) provides highly homogeneous and porous aluminosilicate materials exhibiting superior activity and long-term stability in ethanol dehydration [1]. Second, the ethylene selectivity was improved by one-pot incorporation of organic groups [2]. Interestingly, this approach did not display the direct influence of hydrophobicity on alcohol dehydration in contrary to other reports [3].

In this study, the NHSG-prepared aluminosilicate catalysts (fully inorganic) were post-synthetically modified by grafting trimethylsilyl groups onto their surfaces. Trimethylsilyl groups were attached to the surface using trimethylchlorosilane or trimethyl(methoxy)silane. The number of reacted ≡Si−OH moieties and thus the trimethylsilyl groups loading was controlled via a temperature-vacuum pretreatment of aluminosilicate samples. Trimethylsilyl groups loading was evaluated by ^{29}Si MAS NMR measurements (Figure 1). Structure, porosity, acidity, and hydrophobicity of NHSG-prepared catalysts were closely followed by MAS NMR studies, N_2 physisorption, IR-pyridine analyses, and water adsorption. Moreover, aluminosilicates were tested in a gas-phase fixed-bed catalytic reactor in ethanol dehydration and in a batch reactor in aminolysis of styrene oxide (liquid phase). These tailored NHSG-prepared aluminosilicate catalysts exhibited varying catalytic activity and selectivity in both catalytic reactions depending on trimethylsilyl groups loading in the samples.

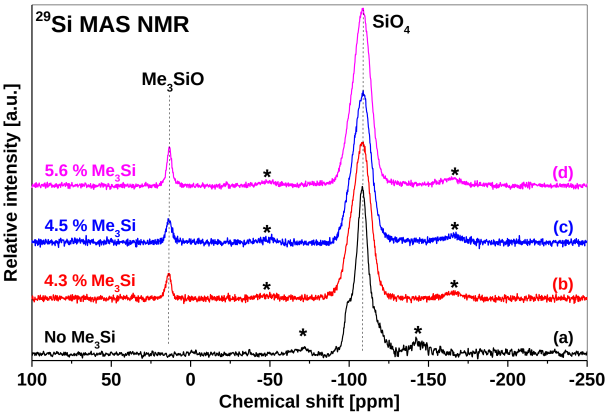

Figure 1: Comparison of pristine aluminosilicate with post-modified aluminosilicate samples. Trimethylsilyl groups loading was controlled by different conditions during temperature-vacuum pretreatment of pristine aluminosilicate. (a) Pristine aluminosilicate without Me_3Si groups; (b) Pretreatment at 500 °C under vacuum, then silylated; (c) Pretreatment at 150 °C under vacuum, then silylated; (d) Pretreatment at room temperature under vacuum, then silylated. Asterisks denote spinning sidebands.

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Photocatalysts based on perovskite-like $Bi_2Si_{1-x}TixO_5$ composites prepared via gelation process

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ABSTRACT:

Hydrogen production with means of solar power is favourable for environment due to low (or zero) emissions of CO_2. However, to date there are major challenges (low efficiency of charge carriers generation, their fast recombination, etc.) that reduce the photocatalytic performance. Heterojunction or Z-scheme is the most attractive technique to solve the stated issues. The family of bismuth silicates [1] and titanates are perspective for hydrogen production due to the position of valence and/or conduction bands.

The samples were prepared via simple gelation process from ethylene glycol solution with consistent thermal treatment. BS series was synthesized with 3 variations of Bi/Si atomic ratio, namely, 2.09/1, 2/1, 2/1.5, based on Bi_2SiO_5 substance. The BST was prepared under similar conditions, but a part of Si-containing precursor was replaced with Ti-containing one.

The samples prepared were investigated with XRF, XRD, SEM EDS, TEM, FTIR, Raman spectroscopy, simultaneous thermal analysis, and UV-Vis DRS. Positions of conduction and valence bands for the prepared photocatalysts as well as detailed results of photoelectrochemical measurement (EIS, CVC) in different media are in progress and will be discussed in the report.

Synthesis via gelation leads to the formation of the composite materials regardless of the Bi/Si atomic ratio and the thermal treatment mode used. It was shown that the final phase composition directly depended on conditions of temperature treatment. In addition, the heating mode allows to prepare composites with variation of specific surface area (2-100 m^2/g). It was also shown in Rhodamine B photodegradation that phase composition impact photocatalytic activity more than S_{BET} value. Under the same experimental conditions, the amount of evolved H_2 in presence of prepared photocatalyst in 19.6 times ($\mu mol*S_{BET}^{-1}*m_{Ti}^{-1}$) higher than one of TiO_2 Hombifine.

This work was supported by the Russian Science Foundation, grant No. 19-73-30026.

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P207

Influence of the porosity of silica carrier material on the performance of immobilised DMAP in flow catalysis

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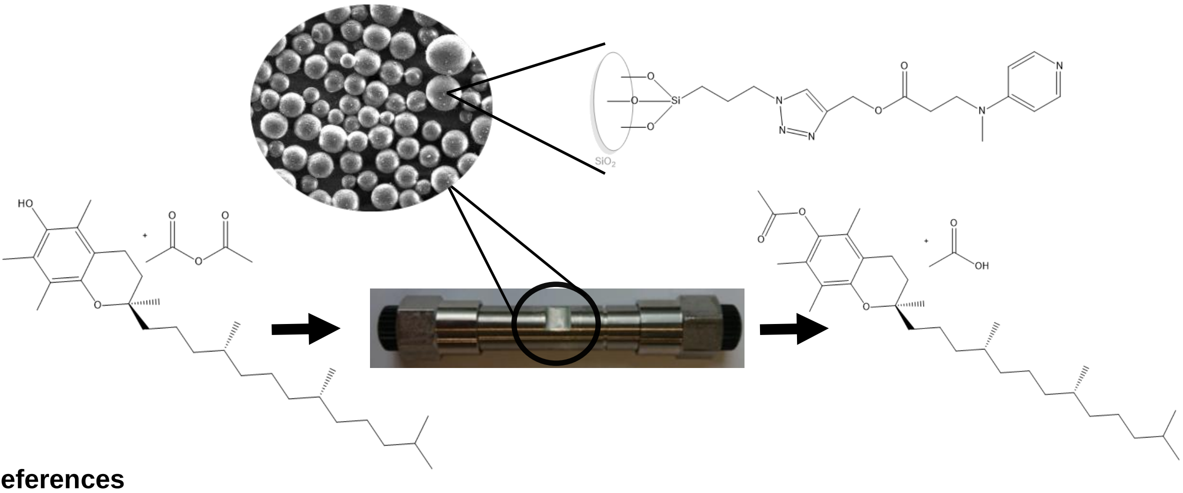
ABSTRACT:

4-Dimethylaminopyridine (DMAP) and derivates are known as a high performing catalyst in many organic reactions such as acylation, ester rearrangement and silylation.[1] Due to its efficiency, immobilised DMAP is even used in heterogenous flow catalysis. In this report we investigated the influence of the mesopore size of the silica carrier material on the catalytic potential. The catalytic activity was tested through the acylation of the sterically demanding α-Tocopherole with acetic anhydride, which is quite challenging according to literature.[2,3] For the study, commercially available silica particles (LiChrospher Si60, LiChrospher Si100 and PerfectSil300) with three different mesopore sizes (6, 10 and 30 nm) were functionalised with DMAP in a two-step synthesis. First, an azide linker was introduced to the mesoporous SiO_2 material by post-synthetical grafting. Second, the DMAP derivate was coupled by a copper(I)-catalysed Click-reaction. The success of each step was monitored not only by physisorption and IR measurement, but also by elemental analysis for the calculation of achieved catalyst loading. The resulting functionalised particles were packed in commercial HPLC columns and used in flow catalysis experiments for the acetylation of α-Tocopherole. The particles containing 10 and 30 nm-sized mesopores produced yields up to 75 % after one hour each at a flow rate of 0.5 mL/min, while the 6 nm particles only archive a conversion of 37 %. Although particles with larger mesopore sizes show a decreased catalysator loading due to their smaller surface area, the corresponding catalytic experiments show a higher catalytic efficiency. In conclusion, we show that the mesopore size of the silica carrier material needs to be quite large (ca. 30 nm) to achieve optimum catalytic performance, even for medium-sized organic reactants.

Figure 1: Catalysed acetylation of α-Tocopherole with DMAP immobilised on Silica particles with different mesopore sizes.



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Zn-Cu MIXED ALUMINATES FOR PHOTOCATALYTIC HYDROGEN PRODUCTION

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ABSTRACT:

Fossil fuels as primary energy sources have existed for centuries. It begun with the burning of coal, then oil replaced it becoming the most used energy source to date. This resource is in limited quantity and once what is available is used up, and can not be regenerated. There are estimates in which it is indicated that in a hundred years the existing reserves will be exhausted therefore, it is necessary to look for alternatives to produce light fuels from renewable fuels[1,2,3]. Photocatalysis is one of the cleanest and safest methods for obtaining it. The process starts with the division of the water molecule. In this chemical process, water is converted into hydrogen and oxygen. The process begins when the photocatalyst is dispersed in water and irradiated with UV or visible energy[4]. Therefore, the search for materials with potential use in these photocatalytic processes is of great interest. In this work, mixed aluminates of Cu and Zn $(\mathrm{Cu_{1-x}Zn_xAl_2O_4})$ with different concentrations $(\mathrm{x} = 0.1, 0.5 \text{ and } 0.9)$ have been developed. The photocatalysts were synthesized using the sol-gel method and calcined at 800°C in air. XRD, SEM and Diffuse Reflectance were used as techniques for characterization. Also, the band gap was obtained to determine the values of the energy potentials of valence and conduction bands. As a result, materials with a cubic crystalline phase were obtained whose peaks belong to spinel of Zn and Cu aluminates[5]. SEM confirms the formation of semi-spherical nanoparticles[6] with crystallite size between 15 and 50 nm. The diffuse reflectance spectra confirm the arrangement in octahedral and tetrahedral sites of the spinel[7] according to the increase in the concentration of copper in the samples. The band gap values determine that the materials can be exited in the UV and visible. The calculated potentials show more negative values for the reduction of hydrogen $(\mathrm{H^+/H_2})$, and more positive than the oxidation potential of water $(\mathrm{OH^-/O_2})$. These results suggest the developed mixed aluminates are potential candidates for the photocatalytic production of hydrogen. The best Hydrogen production rate of $231\,\mu\mathrm{mol\,g^{-1}h^{-1}}$ was achieved with the photocatalyst $\mathrm{Cu_{0.1}Zn_{0.9}Al_2O_4}$, sinterized at 800°C.

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Design of yellow TiO_2 powders for photocatalytic applications

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ABSTRACT:

Sol gel method as a low-cost, simple approach enabling control over produced material in the atomic scale and modifications is particularly recommended for highly photocatalytic active substances. There are many sol-gel and sol-gel related TiO_2-based materials produced and modified for working as efficient photocatalysts [1]. Traditionally, TiO_2, with band gap approximately 3.2 eV, responds only to UV light which significantly limits its applications as photocatalyst. Of prior importance is to design material that exhibits photocatalytic activity triggered by visible light. One method is to produce surface and intrinsic defects in TiO_2 structure, such Ti^{3+}, oxygen or titanium vacancies, which lead to formation of mid-gap bands and hence improvement of photocatalytic efficiency in the visible light [2]. Usually, the crystallin structures, such as anatase and anatase-rutile mixtures, are recognized as most efficient in pollution degradation. The latest literature states that well-designed amorphous structures can exhibit high photocatalytic activity [3].

In this research work, the focus is laid on the partially amorphous or amorphous TiO_2 powder activated by H_2O_2 synthesis itself. The series of powders synthesized with different volume of hydrogen peroxide, H_2O_2 added in different time regarding to the synthesis start and then either heat-treated in temperatures up to 100 °C or dried in the air is investigated to obtain lowest mid-gap bands.

The powders are planned latter to be deposited using low-pressure cold spray technique.

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DiZyme: open-access expandable resource for quantitative prediction of nanozyme catalytic activity

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ABSTRACT:

Natural enzymes, being extremely effective, suffer from high cost, complex purification, and low stability. Development of artificial enzymes mimicking their activities being easy-to-produce, low cost, and of comparative or higher effectiveness is desired. Given system complexity, it is desired to presume their activities quantitatively prior to synthesis, which is the synthesis-by-design approach. Current research focuses on the peroxidase activity of metal- and metal oxide-based nanozymes, since these two classes are the most common among existing nanozymes, have unique mechanical, electronic, and optical properties. Despite the growing demand for customized nanozymes, to date, there is no open-access nanozyme database. In this work, a user-friendly expandable database of >300 existing inorganic nanozymes, which are represented by inorganic materials, is developed for the first time by data collection from >100 articles. Data analysis was performed on the collected data to reveal what nanomaterial features are responsible for their catalytic activities and what descriptors could be used for its ML-assisted prediction. To develop for the first-time synthesis-by-design approach for nanozymes, a random forest regression model for quantitative evaluation of nanozyme peroxidase activity achieving performance up to $R^2 = 0.80$ for the catalytic rate constant (K_{cat}, s^{-1}) and $R^2 = 0.63$ for Michaelis-Menten constant (K_m, mM) based on physicochemical parameters, elemental descriptors as well as reaction conditions was built and optimized by correlation-based feature selection and hyperparameter tuning. Moreover, DiZyme (dizyme.net) expandable and open-access resource containing the database for quantitative nanozyme peroxidase activity prediction, intuitive data analysis, and visualization were developed. This resource will facilitate the design and optimization of nanomaterials with the desired catalytic activity and open new frontiers for nanozyme design. With an expandable database, the resource will be augmented, the model will improve the accuracy of the qualitative prediction of catalytic activity, which will also apply to more types of enzyme-mimicking activities in the future.

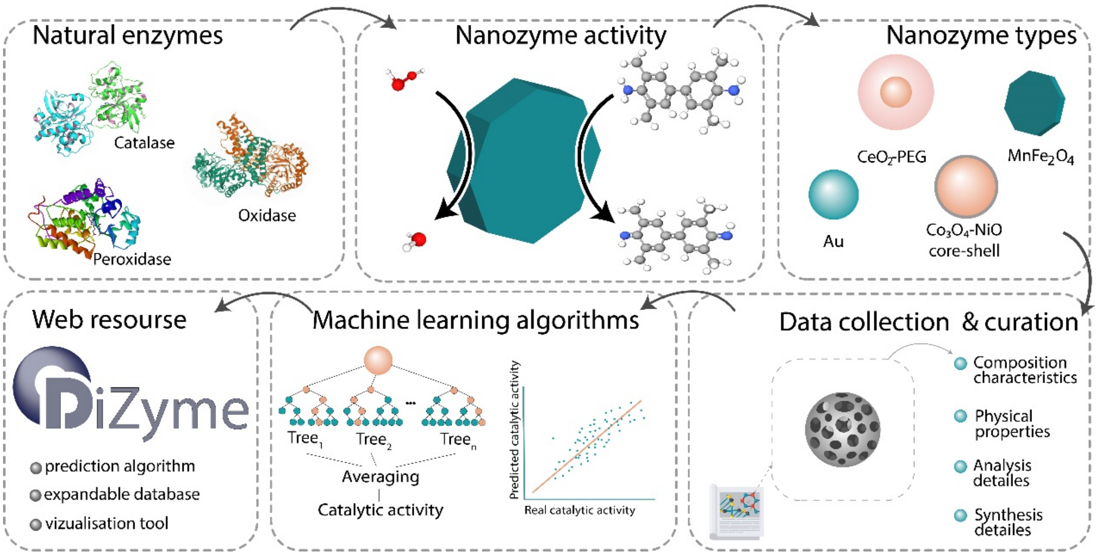

Figure 1: Resource development pipeline from natural enzymes to collecting nanozymes database, building ML algorithms for quantitative prediction catalytic activity, and developing open resource DiZyme, that combines a predictive ML algorithm, an extensible nanozyme database, and an interactive visualization tool.

LOW TEMPERATURE CURABLE TITANIUM-BASED SOLS FOR VISIBLE LIGHT PHOTOCATALYTIC COATINGS

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ABSTRACT:

Titanium oxide (TiO_2) is a widely used material in photocatalytic coatings in which efficiency generally lies in the ultraviolet (UV) spectrum of light. Sol-gel method provides a simple and versatile synthesis route to shift the bandgap of TiO_2 into the visible region by doping the sol formulation. In this study, hybrid transparent films based on 2-aminobenzene-1,4-dicarboxylate (NH_2BDC) ligand and titanium(IV) oxide were deposited on glass and polycarbonate substrates by immersion into a sol and annealed at 80 and 150 °C. Doped coatings exhibited a meaningful redshift of the band gap (2.37 eV) compared to that provided by neat TiO_2 coatings (3.29–3.36 eV). The photocatalytic study of the films was carried out by assessing the photodegradation of a dye in aqueous solution. In this sense, when NH_2BDC-sensitized coatings were illuminated with visible light, they surpassed the dye removal ability provided by neat TiO_2 cured at 450 °C even when the latter was activated with UV light. Besides, low temperature cured neat TiO2 coating (150 °C) were fully inactive towards the dye degradation. The SiO_2 protective layer is not necessary as the low synthesis temperatures prevent the photocatalytic inhibition caused by the migration of Na^+ into the titania film. Type of substrate and heat treatment influence the final roughness of the film. Rougher films exhibit greater dye-adsorption capability, whereas denser coatings proved to be more effective in dye photo-degradation. All doped coatings showed good adhesion with the substrates and medium hardness, despite the low annealing temperature.

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KINETIC MODELING OF STRONTIUM ASSISTED PHOTOCATALYTIC DEGRADATION OF MB USING g-C_3N_4-TiO_2 NANOCOMPOSITES

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ABSTRACT

Heterojunction between TiO_2 and graphitic carbon nitride (g- C_3N_4) offers additional interesting electrical and optical properties. However, it led to limited success to improve the photocatalytic activity. One way to enhance the efficiency of photocatalytic materials is to develop "assisted" photocatalysis processes''[1]. In this respect, ferroelectric polarization by strontium (Sr) might be a promising strategy to modify band structures and charge transport performance in heterojunction-based semiconductors (to the best of our knowledge, not used up to now). Hence, we designed ''one-pot'' in situ g-C_3N_4-TiO_2 nanocomposite synthesis via sol gel method coupled with solvothermal method. Firstly, a solution of g-C_3N_4 was sonicated and added to sol solution of TiO_2 as described by Livage and al [2]. The mixture was transferred into Teflon-lined autoclave (15h, 140 °C). Secondly, the sample was collected by filtration, dried overnight under vacuum at 50°C and calcined at 400 °C for 2 h. Finally, 0.8wt% Sr was added to g-C_3N_4-TiO_2 nanocomposite by dry impregnation followed by new calcination at 400°C. Attention was therefore paid here to the influence of strontium on the structural, textural, optical and morphological properties of the resulting material named as Sr g-C_3N_4-TiO_2. The correlation was then performed with photodegradation of methylene blue (MB) under visible light (Figure 1).

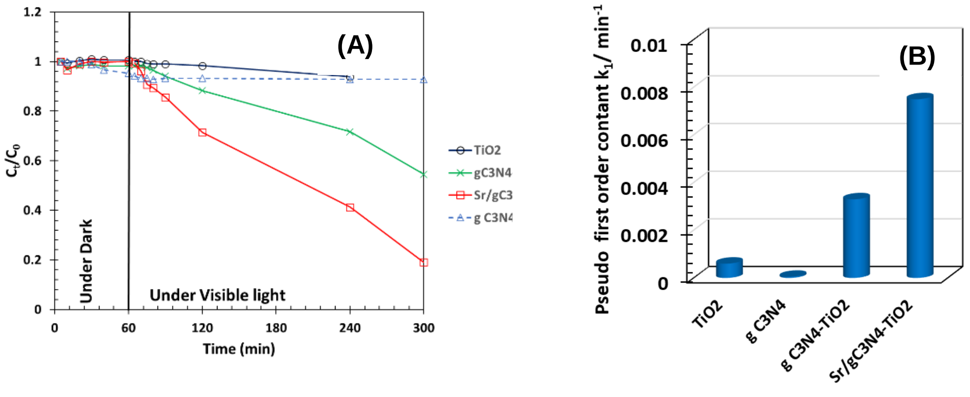

Figure 1: A) Photodegradation of MB onto g-C_3N_4-TiO_2 and 0.8wt%Sr- g-C_3N_4-TiO_2 nanocomposites, TiO_2 and g-C_3N_4 are given as references. B) pseudo first-rate constants.

Results clearly underlined that the strontium addition strongly enhanced the photocatalytic response of the g-C_3N_4-TiO_2 system by 127%. This improvement is even more remarkable if the comparison is made with the TiO_2 reference, the activity enhancement reaches 1150%.

Acknowledgement

The authors would like to acknowledge the funding from Ministry of Education (IF-2020-018-BASRC).

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P213

PREPERATION, CHARACTERISATION, ACTIVITY AND STABILITY OF ZIRCONIUM OXIDE FOR SUPERCRITICAL WATER GASIFICATION OF FORMALDEHYDE

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Zirconium oxide (ZrO_2) material, which is transparent, resistant to heat and electrical conductivity, chemically stable and has ionic conductivity at high temperatures[1], was selected to be tested in the gasification of formaldehyde in supercritical water (SCW)[2]. ZrO_2 catalyst was synthesized by sol-gel method and characterised at 500, 900 and 1400 °C. Stability of ZrO_2 samples used in the catalytic gasification of formaldehyde in SCW along with fresh ZrO_2 was determined by various methods such as FT-IR, XRD, TEM, SEM, BET, TPO, H_2-TPR,and zeta potential. In addition, the effect of catalyst amount, temperature, reactant concentration and retention time on the yield of SCW gasification of formaldehyde with ZrO_2 catalysts was studied. XRD results in Fig 1. show that ZrO_2 samples calcined at 500 and 1400 °C mostly have monoclinic and tetragonal phase, respectively and have nono-sized particles. The surface area and porosity of samples prepared with the sol-gel increased significantly in catalytic gasification of formaldehyde in SCW, but decreased in commercial ZrO_2. The increase in surface area and porosity may be explained by the formation of defects by dissolutionof material under hydrothermal conditions. The thermal stability study of ZrO_2 catalysts by thermogravimetric method showed that the ZrO_2 sample calcined at 1400 °C with high crystal size has high thermal stability. The presence of carbon-containing compounds prevents the adsorption of hydroxyl ions on the ZrO_2 surface. H_2-TPR results show that the tetragonal and monoclinic phases of ZrO_2 samples have different H_2 reduction properties. O_2-TPD results show that the ZrO_2 catalysts calcined at 1400 °C have undergone foramldehitin gasification in SCW and have lost oxygen desorption properties at high temperatures (600 °C). The highest percentage of hydrogen was obtained in the presence of 0.5 g ZrO_2 catalyst calcined at 500 °C and 10% formaldehyde concentration at 400 °C for 30 minutes, which is approximately 64%.

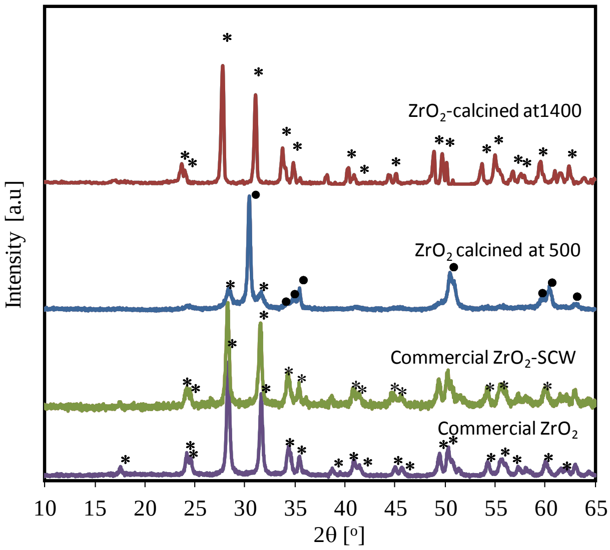

Figure 1: XRD pattern of ZrO_2 samples (●:Tetragon phase and *: monoclinic phase)

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SOL-GEL SYNTHESIS AND STABILITY OF MOLYBDENUM TRIOXIDE WITH ORTHORHOMBIC CRYSTAL STRUCTURE

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ABSTRACT:

Molybdenum trioxide (MoO_3) is a transition metal oxide and has a variety of industrial applications such as photocatalyst, the anode in lithium-ion batteries, and gas sensors, because of their electrochemical and optical properties [1]. Crystallite MoO_3 has mainly three structures; one stable orthorhombic (*α*-phase), and two metastable phases namely hexagonal (h-phase) and monoclinic (*β*-phase), respectively [2]. In this study, MoO_3 with orthorhombic crystal structure was synthesized by the sol-gel method and tested in the gasification of formaldehyde in SCW (SCWG). The presence of supercritical water (SCW) in the gasification of biomass leads to the decomposition of biomass into CO, H_2, CO_2, CH_4, and other organic compounds through acid and base catalyst action of SCW. In this system, to increase the selectivity and formation rate of H_2, MoO_3 as a heterogeneous catalyst was chosen. Structural and morphological changes of MoO_3 with SCWG were investigated using XRD, FT-IR, SEM, BET, TPO, H_2-TPR, and zeta potential. XRD results show that MoO_3 has an orthorhombic crystal structure. Its structure was not changed under SCWG. The surface area of SCWG exposed MoO_3 increased from 35.4 m^2/g into 60.1 m^2/g via the comminution of particles under high pressure and temperature. Based on the SEM pictures in Fig. 1, the MoO_3 synthesized has rod-shaped particles. After the SCWG of formaldehyde, thin planar plates formed. According to H_2-TPR analysis results, it was determined that the reduction properties of MoO_3 changed via the formation of defects. Compared to homogeneous gasification, in the presence of MoO_3 catalyst, percentages of CO_2 and CH_4 decreased and the percentages of H_2 and CO increased via changing of decomposition mechanism.

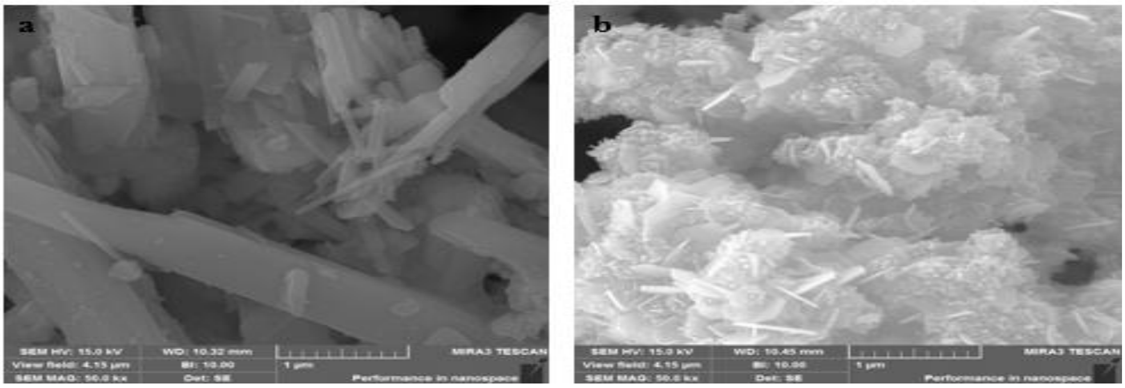

Figure 1: SEM images of MoO_3 before (a) and after (b)SCWG of formaldehyde

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Hybrid bacterial cellulose/silica aerogels modified with photocatalytic nanomaterials for decontamination of flowing water.

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ABSTRACT:

Currently, environmental protection and guaranteeing the supply of quality drinking water are major contemporary challenges of modern society. Research aimed at developing new materials is of paramount importance to combat the growing pollution caused by the industrial and agricultural sectors and to guarantee the quality of drinking water for the world population. To solve this problem, the heterogeneous photocatalysis promoted by semiconductor nanomaterials has been considered as a low-cost, sustainable and ecological approach, using solar energy to occur. In this work we report the development of new routes for the preparation of photocatalytic hybrid aerogels of bacterial cellulose/silica modified by photoactive TiO_2 nanoparticles. The surface modification of the organic biopolymer with the double layer of inorganic components occurred through the hydrolysis-polycondensation of precursors tetraethyl orthosilicate (TEOS) and tetrabutyl orthotitanate (TBOT), respectively. Crystallization of amorphous TiO_2 occurred via mild hydrothermal treatment (150°C, 24 h) with subsequent drying under supercritical conditions using CO_2 as solvent. The detailed characterization of the aerogels was carried out by a wide range of techniques that enabled to correlate the high photocatalytic activity achieved (99% of total degradation of the MB dye in 30 minutes of UV illumination) with its physicochemical and structural properties. Therefore, macroscopic photocatalytic membranes with macro/mesoporous internal structure and high surface area were synthesized and are able to synergistically contribute to the high performance of effluent decontamination and water purification in flow systems.

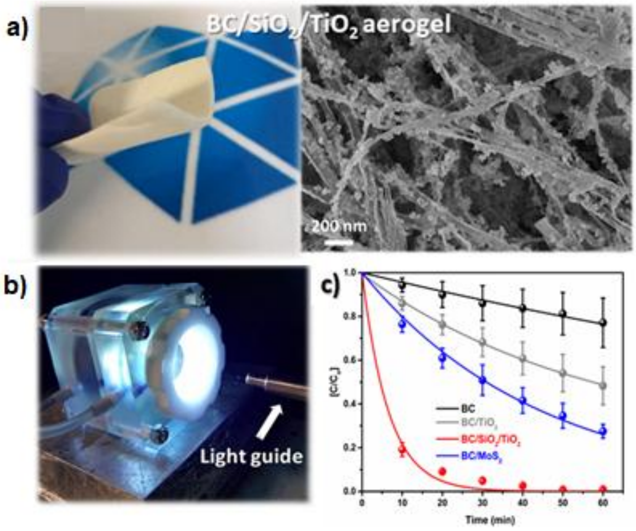

Figure 1 - Digital photos and FEG-SEM micrographs of a) $BC/SiO_2/TiO_2$ hybrid aerogel membranes; b) Digital photo of membrane photoreactor used to evaluate photocatalytic activity of hybrid aerogel; c) In-flow photo-assisted removal of Methylene Blue dye in aqueous solution using different aerogel membranes. Adapted from reference [1].

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CHARACTERIZATION OF CU OXIDE NANOCLUSTER CATALYST PREPARED FROM PVP-STABILIZED CU COLLOID

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ABSTRACT:

The development of base metal catalysts is expected from the viewpoint of elemental strategy. Copper is abundant and shows catalytic activity for many reactions. However, its catalytic activity is not sufficient compared to precious metal catalysts. To solve this problem, nanoclusterizing the copper is one of the promising methods, since nanocluster exhibits the so-called nanosize effect and high atomic efficiency. Recently, we succeeded in showing high catalytic activity for 1-phenylethanol oxidation reaction by nanoclusterizing the base metal oxides[1,2].

In this work, supported copper oxide nanocluster was prepared by using polyvinylpyrrolidone (PVP) stabilized Cu colloid as a precursor (col). Silica (SiO_2), alumina (Al_2O_3), hydrotalcite (HT) or activated carbon (AC) was used as a support. Cu K-edge X-ray absorption fine structure (XAFS) measured at BL-12C at PF.

From XAFS measurement, it was revealed that obtained col and imp catalysts was composed to the divalent copper species as shown in Fig. 1. Among them, only col CuO_x/AC showed the catalytic activity for 1-phenylethanol oxidation reaction to acetophenone at 373 K. The active Cu structure will be discussed based on a detailed analysis of Cu K-edge XAFS.

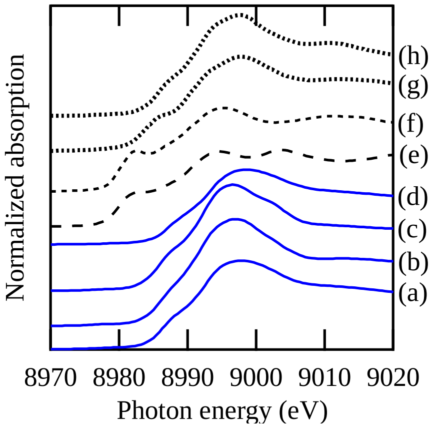

Figure 1: Cu K-edge XANES spectra for (a) col CuO_x/SiO_2, (b) col CuO_x/Al_2O_3, (c) col CuO_x/HT, (d) col CuO_x/AC, (e) Cu foil, (f) Cu_2O, (g) CuO and (h) $Cu(OH)_2$.

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THE SOL-GEL METHOD FOR PREPARATION OF ALUMINA SUPPORTED METAL (Co, Fe, Ni) AS EFFICIENT CATALYST FOR BIGINELLI REACTION

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ABSTRACT:

Heterogeneous catalytic systems usually exhibit high activity in organic reactions. Indeed, many studies have been reported concerning the preparation methods [1]. The sol-gel is one of this method. The use of sol–gel method for catalyst preparation has been described by Pajonk [2]. The method has several advantages such as a well-defined pore size distribution, high purity control of reactants, homogeneity, high thermal stability… [3]. This latest method may use a variety of supports rather than alumina and silica to prepare mixed oxide supports [4].

In this work, a new clean and recyclable alumina supported metal (M) (M: cobalt, iron and nickel) catalyst prepared by sol/gel method noted (MAl-SG) calcined at 500°C with 10% of metal was reported. Therefore, an efficient and green method for dihydropirimidinone (DHPMs) synthesis according to Biginelli condensation catalysed for the first time by MAl-SG in free solvent conditions was developed. The surface parameters (BET), morphology (SEM), composition (XRD) and catalytic activity (Fig.1) was invistigated. The catalytic performances of the samples were evaluated in the Biginelli reaction with a ratio of 2:2:3 of benzaldehyde, ethylacetoacetate, and urea, respectively, to obtain 5-ethoxycarbonyl-4-phenyl-6-methyl-3,4-dihydropyrimidin-2(1H)-one (DHPM). The CoAl-SG catalyst gives a good performance after 1 hour reaction time with 71% of DHPM yield. Indeed, this result can be explained by the presence of a CoAl2O3 spinel phase as observed by XRD diffraction. Also, FeAl-SG and NiAl-SG catalysts have proven to be efficient in DHPM synthesis with 67 and 46% yields respectively. On the other hand, the use of MAl-SG (M: Co, Fe and Ni) as a supported catalyst prepared by the sol/gel method for the synthesis of the DHPM has been proved reusable with no great decrease in yield, as cited in the literature [5,6].

Very interesting results were obtained with MAl-SG oxide catalyst in mild and green conditions compared to the conventional method: high DHPMs yield, short reaction time, no solvent and lower energy costs.

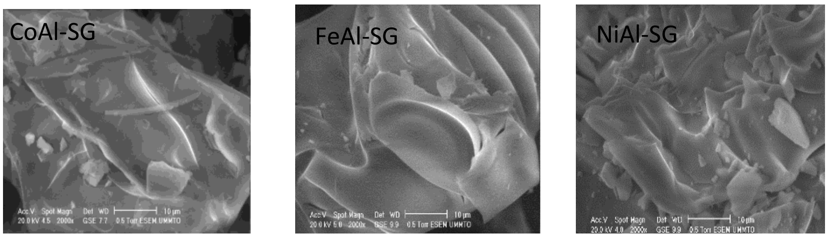

Figure 1. SEM images of calcined MAl-SG

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Mn-, Co-, and Cu-doped Ni/SiO$_2$ catalysts prepared by sol-gel chemistry for the CO$_2$ methanation reaction: deciphering the role of dopant

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ABSTRACT:

Ni-based catalysts are the most widely studied catalysts for CO$_2$ methanation reaction due to the high selectivity of Ni towards CH$_4$ and to its cost effectiveness.[1] However, Ni-based catalysts exhibit lower activity when compared with Ru-based counterparts.[2] Adding a dopant is a promising way to promote the activity of Ni-based catalysts.[3] Herein, the effect of different dopant (Mn, Co, and Cu) on mesoporous Ni-SiO$_2$ catalysts prepared by sol-gel method was investigated. In term of CO$_2$ conversion, both Mn and Co addition improved the catalyst performance in the whole test temperature range (200 – 400 °C). Notably, Mn addition has a better effect at lower temperature ($\leqslant$ 250 °C), while Co addition has a better effect at higher temperature ($\geqslant$ 300 °C). On the contrary, Cu addition has a negative effect on the catalytic activity. In situ DRIFTS revealed that CO$_2$ methanation on all prepared catalysts followed the formate pathway and RWGS-CO hydrogenation pathway with a predominance of the former at low temperature and a predominance of the latter at high temperature. The rate determining step of RWGS-CO hydrogenation pathway is the formation of methoxy from formaldehyde, and we show that Mn dopant could facilitate this step. The rate determining step of the formate pathway is the formation of formate, and Co dopant has the strongest enhancement effect on this step. This work provides a new theoretical understanding of CO$_2$ activation and methanation, and a practical way to address the existing problem for Ni-based catalysts.

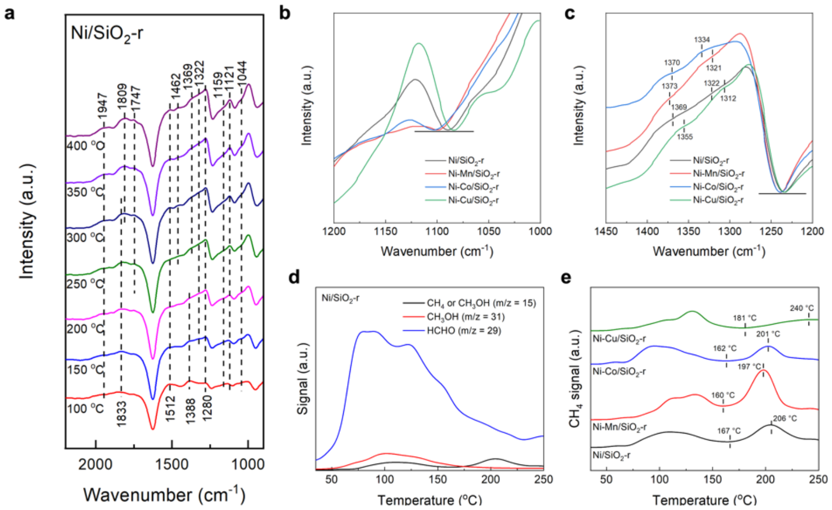

Figure 1: (a) CO$_2$ methanation DRIFTS experiments on reduced Ni/SiO$_2$; Comparison of peak intensity of (b) formaldehyde intermediate and (c) formate intermediate; (d) HCHO-TPSR over reduced Ni/SiO$_2$, (e) HCHO-TPSR over reduced Ni/SiO$_2$, Ni-Mn/SiO$_2$, Ni-Co/SiO$_2$, and Ni-Cu/SiO$_2$.

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CO_2 methanation with high-loading mesoporous Ni/SiO_2 catalysts prepared by sol-gel chemistry

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ABSTRACT:

The power-to-gas (PtG) concept, which stores surplus renewable energy in the form of methane, has attracted much attention, but hydrogenation of CO_2 to methane at a lower temperature is still challenging and requires the development of high-performance catalysts.[1-3] Herein, we disclose the preparation of a new kind of high loading Ni/SiO_2 catalysts via sol-gel method for CO_2 methanation. The method allows us to increase the Ni loading to high values (30-60 wt%) while maintaining an excellent Ni dispersion (small Ni particles in a highly porous silica matrix). With our best catalyst, 96% selectivity of CH_4 with 79% CO_2 conversion were obtained at 300 °C, corresponding to a maximum specific activity of XXX $mmol.g_{cat}^{-1}.s^{-1}$. Catalysts were characterized by N_2-physisorption, TEM, XRD, XPS, H_2-TPR. High dispersion and small Ni nanoparticles could be obtained for those high Ni loading catalysts, which was responsible for their high CO_2 methanation performance. Besides, DFT calculations, CO_2-TPD, in-situ CO_2 desorption DRIFTS and TPSR were also carried out to investigate the reaction mechanism. CO_2 methanation on Ni/SiO_2 catalysts followed the RWGS+CO-hydrogenation and the formate pathway, with the former being dominant at low temperature and the latter dominant at high temperature. CO_2 adsorbs on the Ni/SiO_2 in different forms, carbonyl formed from the bicarbonate reacts with H_2 to form CH_4 via RWGS+CO-hydrogenation pathway, while monodentate carbonate is hydrogenated to CH_4 via formate pathway.

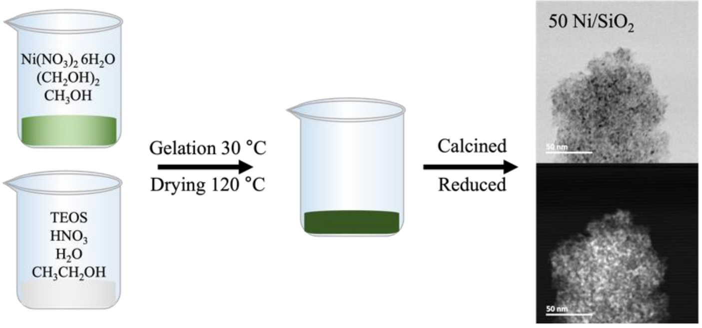

Figure 1: Schematic illustration for fabricating Ni/SiO_2 by sol-gel method.

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A thermoreversible sol-gel synthesis of mixed ceria-zicronia catalysts for the effective ketonization of valeric acid

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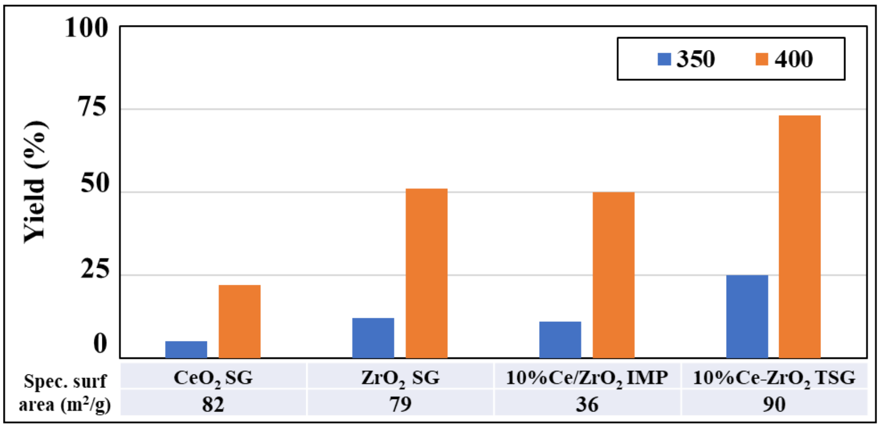
ABSTRACT:

The ketonization of carboxylic acids is highly relevant for upgrading bio-based streams. Valeric acid is an easily accessible lignocellulose-derived C-5 compound and an important platform chemical for producing bio-based fuels and fuel additives [1]. In the ketonization of valeric acid, oxygen content and acidity are reduced while forming C-C bonds in order to produce 5-nonanone. Developing high-performance heterogeneous catalysts for the ketonization reaction is needed. Amphoteric metal oxides (e.g., ZrO_2, CeO_2) owning high lattice energy have been shown as excellent candidates for ketonization. It could be explained by the redox properties, reducibility, and highly-exposed surface area [2]. Zirconium alkoxides such as n-butoxide and n-isopropoxide have been conventionally used as the precursors for sol-gel synthesis. Besides being expensive, alkoxides are also very reactive, and tailoring their micro- and mesostructure is challenging [3]. In this research, an innovative thermo-reversible sol-gel (TSG) method has been implemented for the synthesis of porous ZrO_2 materials using nitrate salt. Moreover, the addition of 10% of Ceria to ZrO_2 was studied using sol-gel and impregnation methods. For the comparison, ketonization was also performed over pure CeO_2 and ZrO_2.

Leveraging on the TSG method, we obtained a higher surface area for the 10%Ce:ZrO_2 (90 vs. 36 m^2/g for impregnation). These textural properties match with XRD data, showing very small crystallite sizes. At 400℃, it showed the highest yield (~73%). Selectivity to 5-nonanone remained very high (>95%), and the total quantity of by-products (cis-4-nonene, 2-hexanone, 3-heptanone, and 2-octanone) was negligible. Furthermore, stability tests were carried out over 40h where 10%Ce-ZrO_2(TSG) showed outstanding stability, sustaining its catalytic activity throughout the testing time. Here, GHSV was relatively high (~80000 h^{-1}) compared to previous reports [4]. We report a record specific productivity toward 5-nonanone for our developed sol-gel Ce-Zr-based catalyst ($0.063\ \text{mol}_{5\text{-nonanone}}.\text{g}^{-1}.\text{h}^{-1}$).

Figure 1: Catalytic performance for CeO_2, ZrO_2, and 10%Ce-ZrO_2 in the valeric acid ketonization.



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Materials for energy and environment

REMOVAL OF ARSENIC (III, V) FROM AQUEOUS SOLUTION BY IRON OXIDE COATED CTAB

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ABSTRACT:

In the present work, synthetic nanoscale iron oxide stabilized with cetyltrimethylammonium bromide (CTAB) was examined for ability in removing of arsenic from aqueous solutions. Iron oxide such as magnetite and maghemite are the most promising iron nanoparticles for arsenic removal.

The crystal structure and phase purity of the synthesized CTAB coated iron oxide (IO-CTAB) composite were examined by XRD analysis. The calculated value of lattice parameter of IO-CTAB is in agreement with the previously reported value [1]. The average crystal size of IO-CTAB was 17.26 ± 3 nm. No obvious XRD peaks corresponding to other phases were found in the XRD model of the analysed sample, which shows a good purity of the IO-CTAB prepared sample. The shape and morphology of IO-CTAB was examined by TEM and SEM analysis. The TEM analysis demonstrated that the sample was composed of a number of nanoparticles with spherical shapes. The observed IO-CTAB nanoparticles had the sizes between 10 and 25 nm. The mean particle size was 19.86 ±1.7 nm which is in accordance with the result achieved from the XRD analysis.

The efficiency of the IO-CTAB nanoparticles in the removal of arsenic ions from aqueous solutions was investigated using flame atomic absorption spectroscopy. The best removal efficiency of As (III) from aqueous solutions using IO-CTAB nanoparticles was obtained for pH 5. These results are in good agreement with studies regarding the „applications of CTAB modified magnetic nanoparticles for removal of chromium (VI) from contaminated water" conducted by Elfeky et al [2]. The XPS analysis showed that during the adsorption process As (III) can be oxidized simultaneously to As(V) which has contributed to the decrease of arsenic toxicity. The data determined using the Langmuir and Freundlich models emphasized that IO-CTAB nanoparticles were favourable for the adsorption of As (III) ions from aqueous solutions.

Acknowledgments: This work was supported by the Romanian Ministry of Research and Innovation through the project PN-III-P2-2.1-PED-2019-0868 contract no. 467PED ⁄ 2020 and project PN-III-P2-2.1-PED-2019-1375 contract no. 331/PED/2020.

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REMOVAL OF Pb (II) IONS FROM CONTAMINATED WATER USING NEW HYDROXYAPATITE-CTAB COMPOSITE AS ADSORBENT

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ABSTRACT:

Hydroxyapatite (HAp) nanoparticles coated with cetyltrimethylammonium bromide (CTAB) are very promising biocompsite for wastewater treatment. The first goal of this study was to prepare HAp-CTAB composite by an adapted method [1] keeping constant the stoichiometric ratio Ca / P stoichiometric ratio at 1.67. The second objective was to examine the performance of HAp-CTAB biocomposites as an adsorbent for lead removal from aqueous solutions. The morphological and structural properties were evaluated by various analysis such as X-ray diffraction (XRD), transmission electron microscopy (TEM), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX). The ultrasonic measurements conducted in order to evaluate the efficacy of HAp-CTAB biocomposites as an adsorbent for lead removal from aqueous solutions. On the other hand, the Langmuir and Freundlich models underlined that HAp-CTAB biocomposite were favorable for the adsorption of lead ions from aqueous solutions. Moreover, the toxic effect of lead ions adsorbed by HAp-CTAB biocomposites from contaminated water on fibroblast cells was assessed. The ultrasound measurements as a non-destructive method used in decontamination proces of wastewater will lead to essential advances in the complex analysis of the effectiveness of various materials used in different environmental applications. Furthermore, the present study clearly shows the efficacy of HAp-CTAB biocomposite in removing lead ions from contaminated solutions.

Acknowledgments: This work was supported by the Romanian Ministry of Research and Innovation through the project PN-III-P2-2.1-PED-2019-0868 contract no. 467PED ⁄ 2020 and project PN-III-P2-2.1-PED-2019-1375 contract no. 331/PED/2020.

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Efficient nitrous oxide recovery from incineration leachate by a nosZ-deficient strain of Pseudomonas aeruginosa

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Nitrous oxide (N_2O) is a strong oxidizer that can serve as a potential energy source in co-combustion with other fuels such as methane generated during anaerobic digestion. It is also an intermediate generated during biological nitrogen removal processes carried out at wastewater treatment plants. Therefore, recent studies are trying to identify methods to harvest N_2O from WWTPs. However, the high solubility of N_2O in water means that N_2O only accounts for a small proportion of biogas being produced.

Two approaches should help achieve higher N_2O production rates and increase the proportion of N2O found in biogas: (1) increasing denitrifying loads in the wastewater, and (2) increasing the proportion of N_2O-forming incomplete denitrifiers in the bacterial community. One type of wastewater that has high denitrifying loads is fresh incineration leachate formed from municipal solid waste (MSW) incineration plants. While nitrite can serve as an electron acceptor during denitrification to N_2O, its protonated form, free nitrous acid (FNA), inhibits microbial activity and impairs the denitrification process. Therefore, after partial nitrification of incineration leachate to nitrite, it is necessary to adjust the pH to minimize the formation of FNA.

In this study, N_2O was recovered from a lab-scale moving-bed biofilm reactor treating partial nitrification-treated leachate supplemented with a *nosZ*-deficient strain of *Pseudomonas aeruginosa* after determining the threshold for free nitrous acid (FNA) inhibition. High nitrite removal and N_2O conversion efficiencies (> 95%) were achieved with long-term operation of this MBBR. N_2O accounted for the majority of biogas (80%) produced when the MBBR was fed partial nitrification-treated leachate with high nitrite concentrations and the drainage ratio was adjusted to 30%. Bacterial community analysis revealed that the nosZ-deficient Pseudomonas strain remained metabolically active and was primarily responsible for denitrification processes in the reactor. This study presents a promising method for N_2O recovery from incineration leachate.

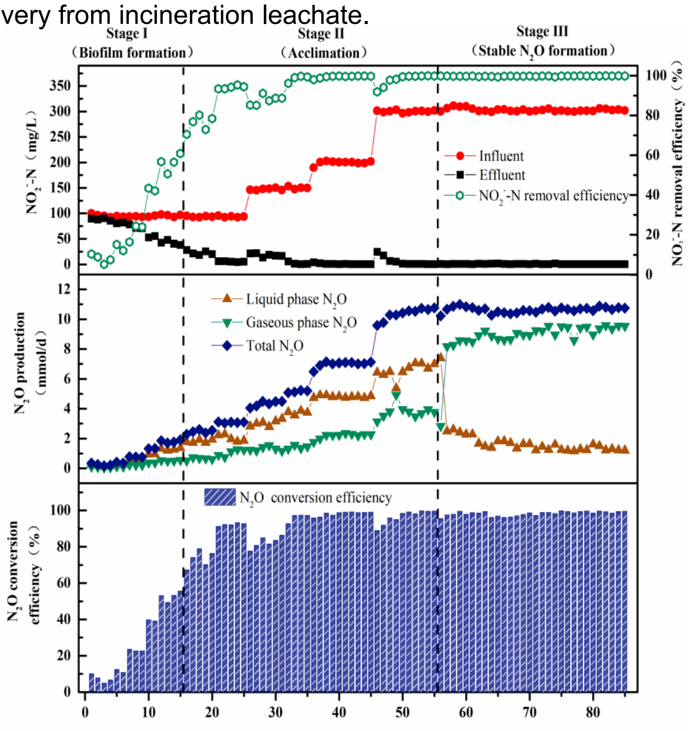

Figure. 1. Performance of the MBBR supplemented with the *nosZ*-deficient *P. aeruginosa* strain.

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SOL-GEL ROUTE FOR MAGNESIUM SILICATE GLASSES - TECHNIQUES AND APPLICATIONS

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Human advancement has led to an increase in greenhouse gases (e.g., CO_2, N_2O) in the atmosphere, which results in the rise of surface temperature. Cement industry is responsible for about 8% of the global CO_2 emissions[1]. About half of the CO_2 from cement industry is due to energy requirements for processing and the remaining comes from the starting material $CaCO_3$.

Eq. 1

According to Eq. 1, to produce 1 ton of Portland cement, there is approximately 0.9-ton CO_2 footprint from starting materials[2]. Reactive synthetic glasses can offer solutions to the present CO_2 problems from cement industry. The chemical composition is the key factor while designing the glasses with cementitious activity. The requirement of high energy for melting during their production has been identified as the major bottleneck of the conventional melt-quenching method for glass synthesis. The sol-gel technique involves much lower heat treatment temperatures, which significantly contributes to energy saving[3–6]. Synthetic magnesium silicate glasses are considered a good alternative to current concrete technology due to their reactivity[7, 8]. In this work, we synthesize magnesium silicate glasses via sol-gel method and measure their reactivity towards cementitious material through the dissolution experiments. In the present study, we observe that the reactivity of glasses, directly related to the ratio of glass former to glass modifier. This work is the preliminary evaluation of the practicality of the sol-gel technique in the large-scale synthesis of cementitious materials in further study, with the aim of reducing CO_2 emissions compared to traditional cement manufacturing methods[9].

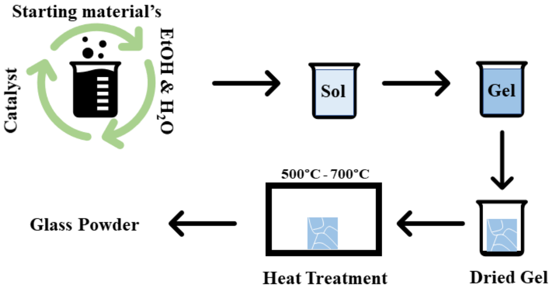

Figure 1 : Procedure flow chart for glass preparation by sol-gel technique

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CREATION OF MATERIALS AND APPLICATION OF SOL-GEL PROCESSES FOR WASTEWATER TREATMENT

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ABSTRACT:

Aluminum-silicon flocculant-coagulant ASFC is one of the few binary compositions, composed of only inorganic components: a coagulant - aluminium sulphate and an anionic flocculant - active silicic acid. The action of ASFC is based on the effect of the interaction of the primary components of ASFC - the composition with coagulants and the flocculant. Coagulant is aluminium compounds and flocculant - active silicic acid. When dissolved in water, the sol-gel synthesis reaction is activated, and complex compounds with higher flocculation ability are formed. The resulting gel consists of zeolite-like nanoscale structures with a developed sorption surface. There is a synergistic effect - increasing exposure effectiveness because of the integration of individual processes into a single system. The water purification mechanism is realized due to the volume of sorption of pollutants on self-assembled aluminium-silicon complexes.

However, existing methods to date allowed receiving such materials only in the form of solutions. Thus, their lifetime is not more than 2-3 weeks. This factor is holding back the practical use of ASFC in industrial practice for wastewater treatment.

The task was solved by processing aluminium-silicon raw material with sulfuric acid, separating the liquid phase from the solid and liquid phase dehydration. Processing raw materials were carried out with concentrated sulfuric acid under conditions effective to obtain a concentrated 20-30% or more of an aqueous solution of flocculant-coagulant. Dehydration of the resulting solution to obtain a dry product, carried out at a temperature below the boiling point of water by evaporation under vacuum or by dispersing in a high-temperature, high-speed gas stream of coolant. The resulting product is dried and separated from the coolant at a temperature below the boiling point of water.

These technological methods allowed “freezing” and isolating in the matrix of the solid phase the components of the flocculant-coagulant - acid salts of aluminium sulfate and active silicic acid, located in the nanodisperse state. Quick translation of the active components in the solid-state can dramatically reduce the rate of diffusion processes and, at the same time, preserve the activity of the material.

Experiments have shown that the material thus obtained can be stored for a long time. During the warranty period of storage, for 0.5 years, there are no noticeable changes in the material's properties, for some samples were observed to preserve 90% of the activity for over two years. The aqueous solution in a concentration of 0.1÷2.0 % ASFC is stable long-term storage. For effective water treatment, the reagent is required in much smaller quantities. An important feature is the use of powdered ASFC in water treatment from oil and heavy metal compounds.

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FABRICATION OF SODIUM METAL PYROPHOSPHATES SINTERS DERIVED FROM SOL–GEL PRECURSORS

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ABSTRACT:

Sodium-ion batteries (SIBs) have attracted increasing interest as one of the promising next-generation energy storage devices due to the use of abundant Na^+ ions as a charge carrier. In addition, the increasing attention to the safety issue motivate researchers to develop all-solid-state batteries (ASSBs) and thereby to study Na^+-ion conducting properties of solid electrolytes. On the other hand, there are very few reports on those of electrode materials despite the fact that the electrical properties of electrodes have significant influence on the battery performance. This is probably due to the difficulty in obtaining pellets dense enough for the electrical measurements in the case of electrode materials, which often requires reductive or inert atmosphere for calcination.

The objective of this research is to fabricate dense sinters of SIB cathode materials, sodium metal pyrophosphates (*e.g.* $Na_2MP_2O_7$; M = Mn, Fe, Co)[1-3]. Our previous research revealed that the conventional solid-state synthesis yielded the $Na_2MP_2O_7$ pellets with the relative densities of <85%. In this study, we have prepared the green bodies from the sol–gel precursors, which allow the crystallization of $Na_2MP_2O_7$ at relatively low temperatures. The epoxide-mediated sol–gel process[4] provided the amorphous gels involving Na, M, and P, and the following calcination under N_2 atmosphere gave rise to the single-phase $Na_2MP_2O_7$ powders. In addition, we have employed the spark plasma sintering (SPS) technique to fabricate highly dense pellets. The electrical measurements of the sintered pellets are ongoing to acquire insights into the ionic conduction in a series of $Na_2MP_2O_7$.

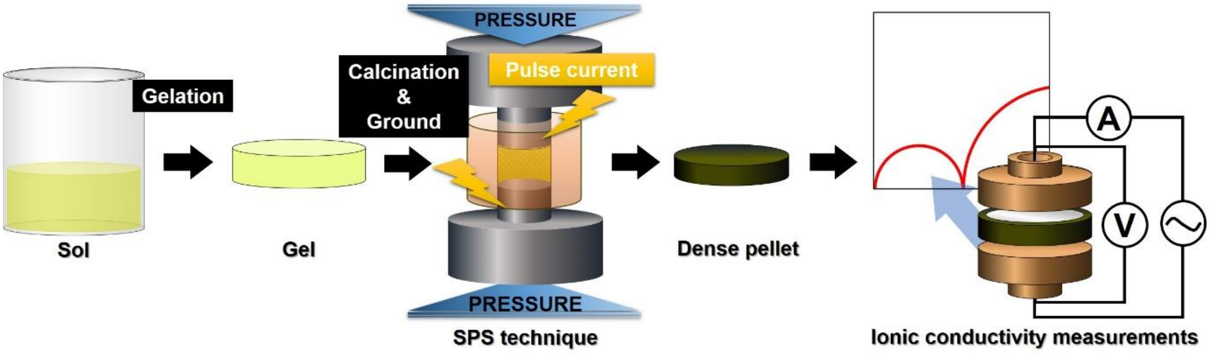

Figure 1 : Overview of the synthetic approach to fabricate $Na_2MP_2O_7$ sinters.

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Mg and Al lamellar double hydroxide nanoparticles for the development of intelligent cementitious materials

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ABSTRACT: Cement is the most used synthetic material worldwide due to the high demand in the construction of infrastructure. Despite its versatility, the cement production process leads to several environmental problems, especially with high levels of CO_2 emissions[1]. This has motivated the development of intelligent and eco-efficient cementitious materials based on the use of functional additives. In this context, synthetic clays known as layered double hydroxides (LDH) are a class of multifunctional materials that, when added to cement, can contribute to the formation of the microstructure of hydrated cement. The thermal decomposition of LDH at moderate temperatures leads to the formation of mixed oxides (MO) that can regenerate the lamellar structure in contact with water and anionic solutions, through the memory effect[2]. The LDH structure regeneration mechanism was elucidated from time-resolved wide-angle X-ray scattering (WAXS) analysis. The results suggest that the memory effect occurs through the dissolution and precipitation process of LDH particles inside the pores formed during the consolidation of the cement (Fig.1a). It was possible to observe a reduction in porosity of up to 20% with the addition of 2.0 wt.% of MO and a decrease in the specific surface area of the cement from 60 to 36 m^2g^{-1} after 28 days of hydration (Fig.1b). Thus, the incorporation of MO can be used as a strategy to reduce the porosity of the cement matrix. The study of the rheological behavior of cement containing different MO contents showed that the regeneration of the lamellar structure contributes to the increase of the elastic modulus (G´), Figure 1c. This feature was attributed to the aggregative growth, that induces the conversion from 2D to 3D LDH particles (sol-gel transition), favoring the consolidation of the paste. These results evidence the potential application of these cement formulations for 3D printing.

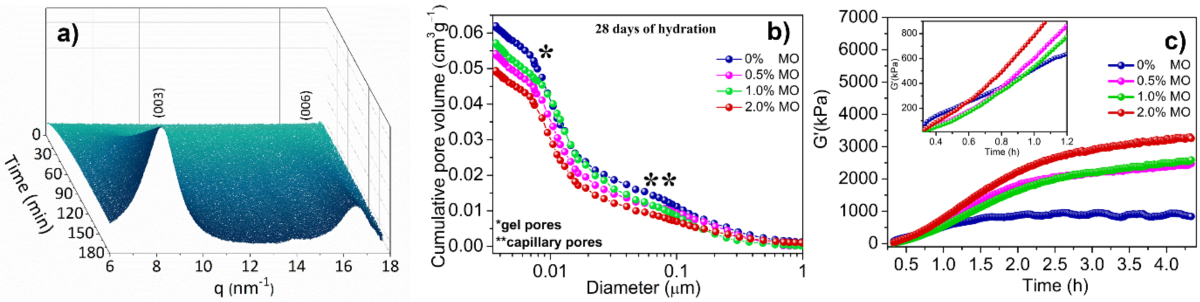

Figure 1: a) *In situ* WAXS monitoring of the LDH recovery after addition of cement pore water to the MO, b) Cumulative volumetric pore size distribution for cement specimen prepared with different contents of MO (0, 0.5, 1.0, and 2.0 wt.%) and c) Elastic modulus (G ') as a function of time for different formulations of cement paste containing MO.

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Acknowledgements: This work was undertaken in collaboration with the National Institute on Advanced Eco-Efficient Cement-Based Technologies and was supported by Brazilian funding agencies CNPq, FAPESP, CAPES and Synchrotron Brazilian Light Laboratory (LNLS).

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Comparative study between cement pastes and nanotechnologically additives pastes with lamellar double hydroxides (HDL)

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ABSTRACT:

The search for sustainable means, coupled with reducing environmental impacts caused by human exploitation, has required massive investments from sectors such as the cement industry to obtain more efficient and ecological materials[1]. We presented the investigation about the prepation of $Mg_{0.66}Al_{0.33}(OH)_2(NO_3)_{0.32}\cdot mH_2O$ lamellar double hydroxides (HDL) by co-precipitation method applied as precursor of nanostructured agregates to be used as additive in cement pastes[2]. The HDL were decomposed at 500°C to obtain mixed oxides (MO) with different surface areas (Figure 1a and b). When exposed to water, the MO quickly restructures due to the HDL memory effect, thus allowing the additive incorporated into the paste to fill pore regions, densifying the cementitious composite, and removing harmful ions such as carbonate and chloride present in the mixture, and accelerating hydration kinetics[3]. The fundamental differences in the viscoelasticity between HDL and high early strength cement (HE) paste were evaluated. The effects of the surface area and the amount of additive on the rheological behavior of HE pastes were studied. The additive significantly affected the HE paste viscosity due to microgel formation. The high surface area of the additive activator increased the plastic viscosity by at least 42% times higher than that of cement paste (Figure 1c), accelerated the chemical reactions, and allowed the pastes' setting quickly, improving the paste's workability using a meager amount of additives (0.7 – 1.5 % weight). The results obtained in this study describe the short-term viscosity evolution of the HE and additive high early strength cement paste (AHE) from the fresh condition to the initial setting.

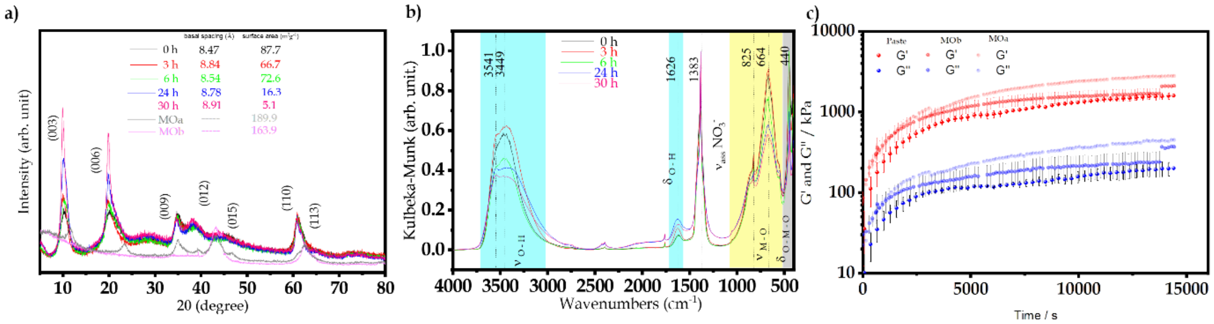

Figure 1: a) XRD of the LDH samples as-synthesized and after MO formation under calcination at 500°C, inserted are the basal spacing of each additive and its surface area. b) FTIR spectra of LDH confirming the incorporation of nitrate ions inside the lamellae. c) Elastic and viscous moduli as a function of time for pure cement pastes and with additives (MOb 1.5% and MOa 1.0%).

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Acknowledgments

This work was undertaken in collaboration with the National Institute on Advanced Eco-Efficient Cement-Based Technologies and was supported by the following Brazilian funding agencies: CNPq, CAPES and FAPESP

SYNTHESIS AND CHARACTERIZATION OF LEAD- FREE FERROELECTRIC THIN FILMS IN COMPOSITION $Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3$

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ABSTRACT:

Materials in composition $Pb(Zr_xTi_{1-x})O_3$ (**PZT**) are extensively used in ferroelectric random access memory, dynamic random access memory, actuator, sensor and other applications due to their excellent ferroelectric and piezoelectric properties. However, the high toxicity of lead, led to development of environmental friendly piezoelectric materials. In this work we present a sol-gel route for the synthesis of $Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3$ thin films. This lead-free composition is regarded as one of the most promising for the replacement of PZT in practical applications. Our synthesis method, avoid the use of the highly toxic 2-methoxyethanol, and offers the advantage of to be a simple and rapid preparation process. A precursor solution was prepared using alkoxide and acetate compounds as starting reagents, acetoin as chelating agents, and ethanol as solvent. By deposition on Pt/TiO2-x/SiO_2/Si substrates, were obtain thin films with thicknesses of 130 and 240 nm. After annealing treatment at temperatures between 700 and 900°C the thin films exhibited a single-phase perovskite structure. The electrical properties measurements show that the films have ferroelectric behaviour with a weak frequency dependence for the dielectric constant and low dielectric loss.

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SYNTHESIS OF h-MoO_3 COMPOSITES WITH GRAPHITE, GRAPHENE AND GRAPHENE OXIDE FOR LITHIUM ION BATTERIES

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ABSTRACT:

Molybdenum oxides are a family of functional and adaptable materials with an overwhelming portfolio of real and potential applications in different fields like photocatalysis, sensing, optoelectronics, energy storage, phototherapy and chromic devices. One of the most investigated members of this family is MoO_3, a polymorphic material which is mainly obtained in the orthorhombic, thermodynamically stable, α-phase. Some authors have reported on the pseudocapacitive performance of this oxide, frequently in composites with conductive polymers or other materials [1]

In this work, we report the synthesis of hexagonal MoO_3 microrods and its composites (with graphite, graphene and graphene oxide –GO-), by a soft chemistry route which preserves the structure and properties of the carbon material while yielding phase pure, highly crystalline oxide microstructures [2], as evidenced by XRD, SEM-EDX, TEM, synchrotron XPS and micro-Raman spectroscopy. A comparative electrochemical assessment of the samples as lithium batteries (LIBs) anodes reveal that h-MoO_3 graphene and GO composites show greatly improved electrochemical performance as compared with bare h-MoO_3 microrods or h-MoO_3 - graphite samples.

The obtained data evidence that this behavior can be mainly attributed to an enhanced conductivity and lithium diffusion coefficient, together with the effective wrapping of the oxide microrods by the GO layers which effectively hinder volume changes upon Li insertion.

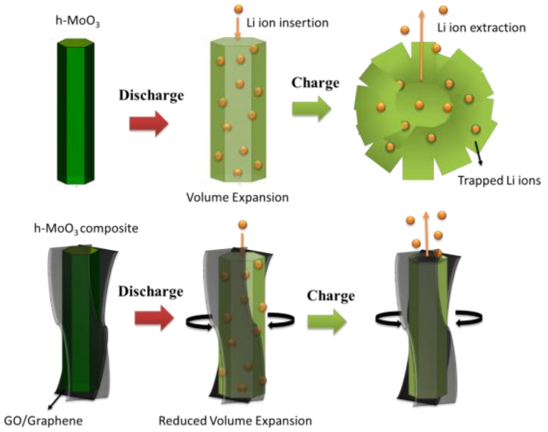

Figure 1: Scheme of the electrochemical processes observed for h-MoO_3 and composites

The uniformly dispersed h-MoO_3 on graphene and GO layers increase the structural stability of the composites and create a conductive network ensuring effective ambipolar diffusion of electrons and Li^+ ions (Figure 1), as revealed by electrochemical impedance spectroscopy measurements and scanning electron microscopy of the cycled electrodes. These results expand the potential applications of h-MoO_3 composites towards LIBs, paving the way for future improvements in this energy storage field.

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Electrochemical redox behavior of sol-gel derived Co-Al layered double hydroxide thin films

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ABSTRACT:

Layered double hydroxides (LDHs) have been studied as anion exchangers, catalysts, and electrode materials. Among them, transition metal-containing LDHs have been considered as new electrode materials for various electrochemical devices. LDHs are usually prepared by the co-precipitation process and obtained as powders. However, for the application of LDHs to electrochemical devices, it is desirable to obtain LDHs in thin-film form. On the other hand, electrochromic devices, which can change their optical transmittance reversibly according to the external electric field by a combination of electrolytes, have drawn attention for their applications in smart windows, display devices, and thermal control devices.

In the present study, the electrochemical redox behavior of Co-Al LDH thin films was evaluated. Co-Al LDH thin films were prepared by the hot water treatment of sol-gel-derived precursor gel films [1]. Precursor gel films of CoO-Al_2O_3 were prepared on ITO substrate from cobalt nitrates and aluminum tri sec-butoxide by the sol-gel method. Then, the precursor gel films were immersed in NaOH solution at 100 °C. Nanocrystallites of Co-Al LDH were precipitated by the hot water treatment with NaOH. From the XRD measurements, it was confirmed that CO_3^{2-} intercalated LDHs were formed in this process. The color of the obtained Co-Al LDH thin films was changed depending on the potential sweep. Oxidation and reduction current was observed in the cyclic voltammogram of the Co-Al LDH thin film electrode.

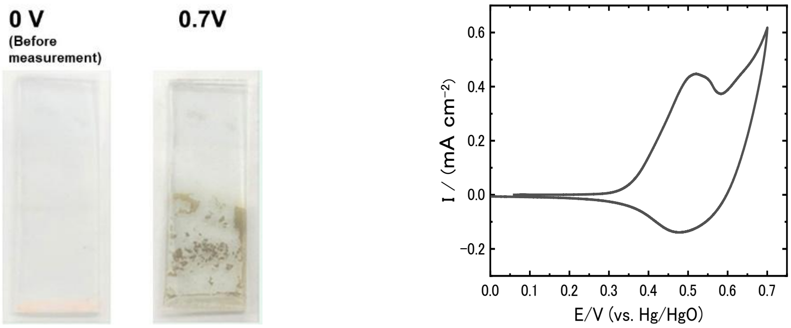

Figure 1 : Photograph of the Co-Al LDH thin film electrode before (0 V) and after application of potential (0.7 V), and cyclic voltammogram in NaOH solution.

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Incorporation of a lithium salt and an ionic liquid into a co-condensed d-U(600)/d-U(900) hybrid matrix

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ABSTRACT:

In the last few decades, the design and development of organic-inorganic hybrid (OIH) materials prepared by the sol-gel method [1] has not ceased to increased. The most remarkable properties of such OIH materials include chemical and thermal stability, suitable dielectric properties, selective ion binding, and ion conducting ability, depending on their organic and inorganic components. A wide range of potential applications including advanced batteries, fuel cells, energy and data storage, sensors and electrochromic devices, have been explored.

The main goal of the present work was to produce an ion conducting ormolyte through the co-condensation of two di-urea cross-linked poly(oxyethylene) (POE)/siloxane (di-ureasil [2]) networks and the incorporation of a lithium salt plus an ionic liquid. The di-ureasil frameworks used were d-U(600) and d-U(900), where d stands for di, U denotes ureasil, and 600 and 900 correspond to the average molecular weight of the starting diamine precursors (8.5 and 15.5 oxyethylene repeat units, respectively). The resulting ormolytes were identified using the notation [d-U(600)-co-d-U(900)]-Li-IL, where d-U(600)-co-d-U(900) represents the co-condensed host hybrid framework.

The characterization of the hybrids produced was performed using Fourier Transform Infrared Spectroscopy (FT-IR), Polarized Optical Microscopy (POM) and Atomic Force Microscopy (AFM. The wettability of the hybrids was analyzed by the static contact angle (CA) using the sessile drop method. The ionic conductivity of the [d-U(600)-co-d-U(900)]-Li-IL sample was determined by means of complex impedance spectroscopy.

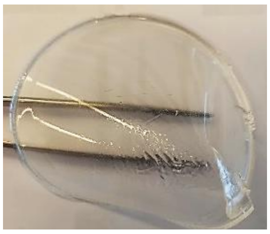

Figure 1: d-U(600)/d-U(900) hybrid material

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Acknowledgments

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Main Menu

Materials for health applications

DEVELOPMENT OF IRON SUBSTITUTED HYDROXYAPATITE FOR MEDICAL APPLICATIONS

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ABSTRACT:

Iron substituted hydroxyapatite (FeHAp) magnetic nanoparticles have been little studied. Magnetic nanoparticles of FeHAp could be a new alternative for numerous biomedical applications. This study presents both the method of synthesis and the physico-chemical and biological properties of FeHAp. FeHAp magnetic nanoparticles were obtained by an adapted co-precipitation method in an aqueous solution by adding different concentrations of Fe^{2+}.The stability of FeHAp magnetic nanoparticles suspension was evaluated by dynamic light scattering (DLS), ultrasonic measurements (US) and zeta potential (ZP). Physico-chemical properties were assessed by X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS) were conducted. The purity of the FeHAp magnetic nanoparticles was appraised by Energy-dispersive X-ray spectroscopy (EDS) and the presence of the constituent elements such as Calcium, Phosphorous and Iron in the analyzed sample were confirmed. The positions of the peaks correspond to the structure of the pure hydroxyapatite. XRD studies have shown that there is no individual peak that matches the γ-Fe_2O_3 peak which shows that Fe^{2+}/Fe^{3+} were substituted in HAp. On the other hand, the crystallinity decreased with increasing iron ion concentration. Our results are in agreement with previous studies presented by Zuo et al. [1] which proved that the presence of Fe^{2+} ions with a lower ionic radius (0.0835 nm) than that of Ca^{2+} affects the network parameters. The *in vitro* cytotoxicity of the FeHAp magnetic nanoparticles suspensions was evidenced using osteoblast cells. The MTT assay showed that the FeHAp magnetic nanoparticles suspensions exquisite excellent biocompatible properties.

Acknowledgments: This work was supported by the Romanian Ministry of Research and Innovation through the project PN-III-P2-2.1-PED-2019-0868 contract no. 467PED ⁄ 2020 and project PN-III-P2-2.1-PED-2019-1375 contract no. 331/PED/2020.

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EFFECT OF CERIUM DOPED HYDROXYAPATITE NANOPARTICLES ON THE BIOLOGICAL PROPERTIES

Alina-Mihaela Prodan[1,2], Simona Liliana Iconaru[3], Steluta Carmen Ciobanu[3], Mihai-Valentin Predoi[4], Stefania Raita[5], Cristian Catalin Petre[6], Mircea Beuran[1,2], Daniela Predoi[3,*]

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ABSTRACT:

In the last years the cerium doped hydroxyapatite (Ce:HAp) coatings were very little investigated. The Ce:HAp composite coatings was obtained by dip coating method. The $Ca_{10-x}Ce_x(PO_4)_6(OH)_2$ with x_{Ce}=0.05, stable suspensions were obtained at room-temperature by an adapted sol-gel method. This research presented the stability of Ce:HAp gels from which the coatings were made were obtained. The stability of suspension was evaluated by dynamic light scattering, zeta potential and ultrasound measurements. Zeta potential and ultrasound measurements on the suspension of Ce-HAp composite coatings revealed a good stability. The value of stability parameters of Ce:HAp suspension obtained by ultrasound measurements was in good agreement with the value of bidistilled water used as reference fluid. The complex studied such as transmission electron microscopy, scanning electron microscopy, Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy were conducted on suspension and coatings. A uniform distribution of all the constituent elements on the surface Ce:HAp coating was observed. The optical spectroscopy, atomic force microscopy and metallographic examination on Ce:HAp composite coatings were also performed. Cell culture and MTT (3-[4,5-dimethylthiazol-2-yl]-2,5-diphenylte-2H-tetrazolium bromide) assay and antimicrobial studies were also conducted on Ce:HAp suspension and coating. The biological studies such as cell culture and MTT assays highlighted that the Ce:HAp suspension and coating have no negative effect on the cell viability and proliferation. The antimicrobial assays have demonstrated that both Ce:HAp suspension and 5Ce-HAp coating have successfully inhibited the development of CFU for gram-positive *Staphylococcus aureus* ATCC 25923, gram-negative *Escherichia coli* ATCC 25922 and fungal *Candida albicans* ATCC 90029. More of that, the antimicrobial assays showed that the Ce:HAp suspensions had a biocide effect against *E. coli* and *C. albicans* microbial strains after 72h of incubation.

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PTX COMPLEXED PH-RESPONSIVE DISULFIDE CORE-CROSSLINKED CARBON DOTS FOR TARGET DRUG DELIVERY

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ABSTRACT:

Targeted drug delivery systems for tumor death and diagnosis were investigated in the study. Current drug delivery systems have the limitation that there is no high dose release and the ability to selectively realize only the tumor site. There is a need to develop a target drug delivery system that effectively delivers drugs to target sites and has high sensitivity and selectivity for tumor detection. We prepared a pH / Redox sensitive fluorescent on / off system based on disulfide core-crosslinked polymer dots (PD) encapsulated with fluorescent dye for tumor targeting. PTX was also loaded into the matrix for tumor death. In the extracellular condition of the tumor, the boronate ester bond of the polymer dots decomposes to release the dye attached to the system, and fluorescence is recovered again. Fluorescence signal of polymer dots can be confirmed by the recovered fluorescence, and drug release monitoring is visualized. It is expected that the polymer dot uptake into the tumor cell will result in efficient cancer therapy by the release of the loaded PTX as the disulfide bond is destroyed by the reducing agent GSH (about 4 times more than normal cells). Even after GSH treatment, there was no significant increase in the fluorescence intensity of the PTX loaded matrix under physiological environment, and it proved the stability of system quenching behavior and drug release prevention. This system enables the development of a matrix that can be used as a drug delivery system for diagnosis and death by selectively distinguishing only tumors in response to GSH and pH.

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Cancer Cells-Targeted MnO_2 Decorated Polymer Dots Coated Wireless Electrochemical Biosensor

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ABSTRACT:

Herein, a wireless electrochemical biosensor for cancer detection based on carbonized catechol conjugated poly ethylene glycol (C-PEG) immobilized manganese oxide (MnO_2) polymer dots (C-PEG/MnO_2) was fabricated. The biosensor not only provided fluorescence-based approach, but it also exhibited highly electrochemical response due to the interaction of cancer cells with C-PEG/MnO_2 on the coated surface. By MnO_2 immobilized into C-PEG that caused quenching effect by FRET, the electroconductivity of the system increased, thus decreased the resistance of the biosensor. In the presence of expressed alkaline phosphatase (ALP) in cancer cells following by the addition of 2-phospho-L-ascorbic (AAP), MnO_2 complex was reduced to Mn^{2+} due to the formation of ascorbic acid (AA) which resulted in the recovery of C-PEG, simultaneously, increased the resistance of the biosensing platform. On contrary, there was no significant changes in electrochemical signals after normal cells were cultured on C-PEG/MnO_2 coated biosensors which proved the sensitivity and selectivity of the biosystem towards cancer cells. Furthermore, the biosensor showed low LOD (3.98 cells/mL) compared to fluorescent approach or colorimetric assays (1995 cells/mL) displaying its potential in early detection of cancer. The electrochemical signals generated could be obtained through a wireless electronic device connect with a smart phone which enabled the detection process to be rapid and simple. Therefore, with highly efficient sensing ability and non-time-consuming feature, the C-PEG/MnO_2 wireless electrochemical biosensor demonstrated its potential in early cancer detection and medical application in the future.

Unravelling the effect of metal ions leaching from bioactive glasses on wound associated biofilms.

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ABSTRACT:

Chronic wounds (principally pressure sores, venous leg ulcers and diabetic foot ulcers) are a drain on global health services and remain a major area of unmet clinical need. Bioactive glass fibres, which have a “cotton-wool” like appearance, offer a promising treatment for chronic wounds. Fibres are created by electrospinning inorganic sol-gel solutions made up of SiO_2 and CaO. Fibres form a 3D structure that mimics the fibrin clot and is both mesoporous and macroporous with large inter-fibre spaces. This morphology makes the fibres ideal for packing into wounds, even with complex geometries. Moreover, fibres have a high surface area to volume ratio which makes them highly reactive. When fibres are placed in fluid they undergo multiple chemical reactions such as: leeching, dissolution and precipitation. Si^{4+} and Ca^{2+} ions, released during dissolution, are able to promote wound healing. Here we investigate doping fibres with other inorganic ions, namely Ag^{+} and Cu^{2+}, which are known to have antimicrobial activity. The antimicrobial activity of doped fibres is being investigated against wound-associated bacteria both in planktonic and biofilm form. Furthermore, an *in vivo* mathematical model is being developed to investigate the importance of certain parameters, such as ion releases rates and ion potency on the effectiveness of bioactive glass fibres healing chronic wounds. Experimental data is used to fit and validate the model. Initial solutions from the model have identified fibre-associated parameters that are critical for chronic wounds to heal. These include: the increased secretion of growth factors by fibroblasts due to uptake of released ions, and the death rate of bacteria by antimicrobial ions. Model solutions imply that a chronic wound must be cleared of any infection first to be able to heal fully. Therefore, the antimicrobial activity of bioactive glass fibres is a key focus of this project.

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MAGNETIC MESOPOROUS SILICA NANOPARTICLES CONTAINING MITOXANTRONE FOR TUMOUR TARGETING

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ABSTRACT:

Cancer is the second cause of mortality worldwide and it is only outnumbered by cardiovascular diseases [1]. The intrinsic diversity and complexity of the disease entails that the treatment is highly challenging. Nanomedicine has appeared as a powerful tool to overcome these problems. Several nanomaterials have been investigated to be used as drug delivery systems (DDS). Among them, mesoporous silica nanoparticles (MSNs) present interesting properties such as high pore volumes, large surface areas or good biocompatibility, which make them suitable as drug carriers. Additionally, it is possible to take advantage of the ease of functionalization of these materials to prevent drug leaking, prolonging blood circulation time and permitting tumour targeting [2].

In this work, we have synthesized a novel type of magnetic mesoporous silica nanoparticles incorporating the anticancer drug Mitoxantrone (Fe_3O_4@MSNs@MTO), with a high relation Mitoxantrone/MSN, good textural properties and homogeneous sizes in the range 50-200 nm. Besides, they can be easily carried to the target by using magnetic fields. Several Fe_3O_4@MSN samples, with different amounts of MTO (from 6.2 to 65 mg of MTO per 100 mg of MSNs), have been assayed both *in vitro* and *in vivo*. The results allowed us to conclude that not only is important the amount of MTO loaded, but also the textural properties of the materials to ensure a sustained delivery of the drug and a high therapeutic effect. In this way, nanomaterials carrying 12.4 mg of mitoxantrone per 100 mg of MSNs presents the highest therapeutic effect.

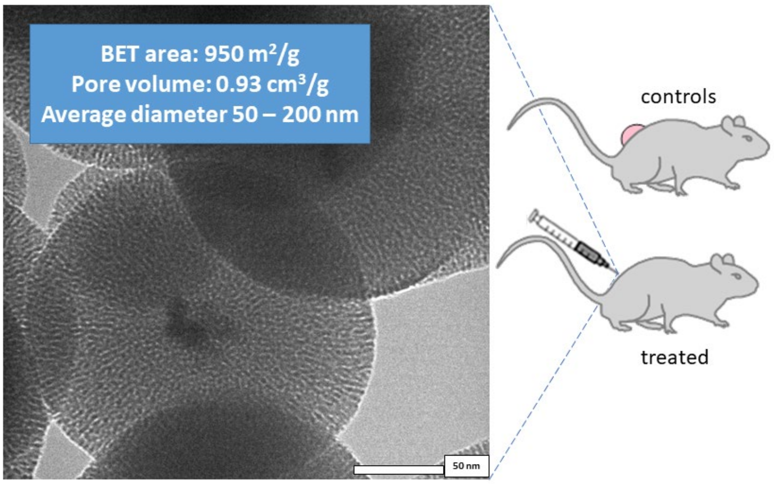

Figure 1 : Magnetic mesoporous silica nanoparticles carrying mitoxantrone and its textural properties.

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LUMINESCENT GARNET-TYPE NANOCRYSTALS FOR NANOMEDICINE

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ABSTRACT:

Neodymium-doped garnets have been widely developed during roughly the last sixty years and have been an outstanding fluorescent material. Yet, the successful downsizing of this system into the nano regimen has been elusive, so far. Indeed, the synthesis of a garnet structure at the nanoscale, with enough crystalline quality for optical applications was found to be quite challenging.

First, we will present an original solvothermal synthesis method, involving mild pressure (200-600 bar) and temperature (300-400°C), developed to produce Nd^{3+}-doped $Y_3Al_5O_{12}$ ($YAG:Nd^{3+}$) and $Gd_3Sc_2Al_3O_{12}$ ($GSAG:Nd^{3+}$) nanocrystals of remarkably good structural quality and controlled size in the range 50 to 200 nm [1]. These features allow for high photoluminescence efficiency, leading to the development of thermosensitive near-infrared (NIR) light-emitting nanoparticles.

Second, we will show how to stabilize these garnet-type nanocrystals in aqueous solutions, a key requirement for use in biomedical applications. Stabilization was successfully achieved thanks to the use of asymmetric double-hydrophilic block copolymers such as Poly(acrylic acid)-b-Poly(acrylamide) copolymers (PAA-b-PAM), constituted of a metal-binding block and a neutral water-soluble block. The quantification of the number of copolymers on the nanocrystal surface was performed using ThermoGravimetry Analysis coupled with Mass Spectrometry (TG-MS). It shows that the length of the copolymer PAM block has an influence on the amount of copolymer adsorbed on the nanoparticle surface.

These newly stabilized $YAG:Nd^{3+}$ nanoprobes offer long lifetimes and, more importantly, narrow emission lines that have been exploited by differential NIR fluorescence imaging, thus achieving an autofluorescence-free *in vivo* readout at the deep tissue level [2].

Finally, nanothermometry measurements, based on the ratiometric fluorescence of the $YAG:Nd^{3+}$ and $GSAG:Nd^{3+}$ nanocrystals, will be presented. $GSAG:Nd^{3+}$ nanocrystals exhibit a maximal relative thermal sensitivity of 0.20% $°C^{-1}$, higher than that of $YAG:Nd^{3+}$ nanocrystals due to the difference in the crystal field of the host matrices [3]. In addition, we show that adding a codopant such as Cr^{3+} ions leads to significantly higher thermal sensitivity (2.5%.C^{-1}) [4].

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SYNTHESIS AND CHARACTERIZATION OF SILICA-BASED MESOPOROUS NANOPARTICLES: THE PH STUDY

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ABSTRACT:

Mesoporous silica nanoparticles (MSNs) are considered promising drug carriers due to their ordered pore structure that allows high drug loading and release capacity. Si and Ca represent important components of bone biology and bone metabolism. The dissolution of such ions from MSNs can lead to osteogenic differentiation of stem cells in the direction of extracellular matrix calcification[1]. Moreover, Ce ions have received a lot of attention due to their desirable properties, such as antioxidant, anti-inflammatory, and antibacterial properties, which are considered to be prerequisites for tissue regeneration[2]. The aim of this work was to study the effect of different pH values on the physicochemical properties of sol-gel derived MSNs. The synthesis of pure silica MSNs and Ca/Ce-doped MSNs MCM-41 type was performed via the CTAB-assisted Sol-Gel method. The synthesis of the MSNs was conducted via the Sol-Gel method using tetraethyl orthosilicate (TEOS) as the silica source and Cetyltrimethylammonium bromide (CTAB) as the pore directing agent in an alkaline environment (for pH values=11.00, 11.75, 12.22, and 12.50). For the synthesis of Ca/Ce-doped MSNs, the ions were added to the solution as nitrate salts ($60SiO_2$, 35CaO, $5CeO_2$ % mol). The physicochemical properties of MSNs were investigated by S.A.XRD, SEM/EDS, TEM, FTIR, and N_2 porosimetry. Different pH values affected the particle size and the mesoporous structure. As it is shown in the isotherm plots (Fig.1), pH 11.75 is the ideal value for the formation of both neat and doped-MSNS with tubular meso- and micro-pores.

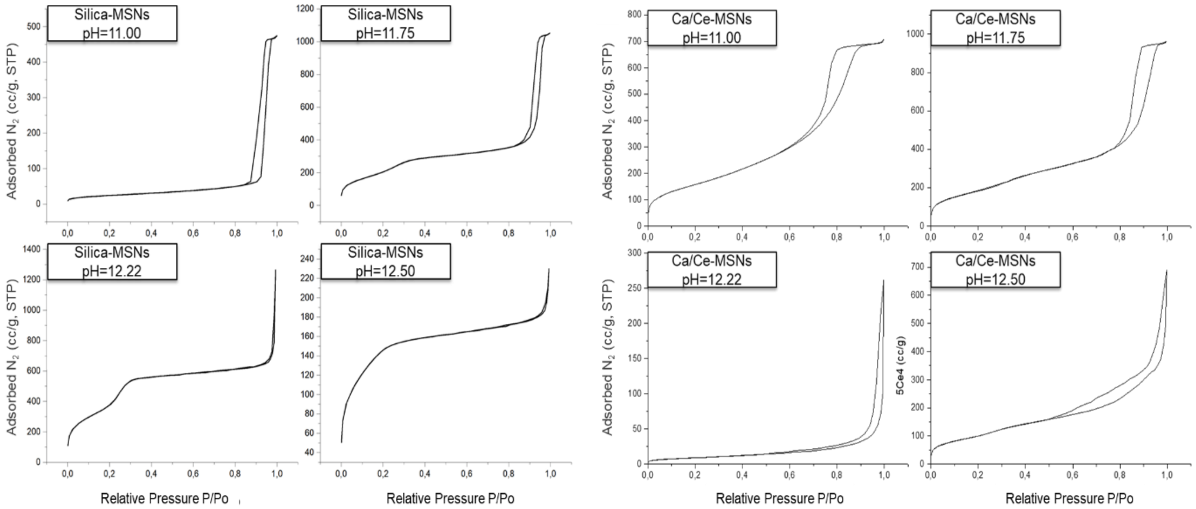

Figure 1: N_2 adsorption/desorption isotherms of Silica-MSNs (left) and Ca/Ce-doped MSNs (right)

Acknowledgments: This work is supported by European Union's Horizon 2020 research and innovation programme under grant agreement No 953128, project: Smart, Multifunctional Dental Implants: A solution for peri-implantitis and bone loss.

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SYNTHESIS AND CHARACTERIZATION OF AKERMANITE SCAFFOLDS TOWARDS BONE TISSUE REGENERATION

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ABSTRACT:

Various glass ceramics have been used as scaffold materials, especially Si-based ceramics doped with Ca and Mg. Akermanite ($Ca_2MgSi_2O_7$) has attracted interest for bone regeneration due to its controllable biodegradation rate, improved mechanical properties, and high apatite forming ability[1,2]. The aim of this study was to produce Akermanite scaffolds through the Foam Replica Technique combined with the Sol-Gel method to improve the overall effectiveness towards potential hard tissue regeneration. The methodology followed was similar to the one proposed in the literature[1]. Briefly, tetraethyl orthosilicate (TEOS), d.d.H_2O, and HNO_3 were mixed for 30min. Then, Mg and Ca were added to the solution as nitrate salts and stirred for 5h. The solution was aged and dried to produce a xerogel, sieved, and heated up to 700°C. The powder was thermally characterized before the fabrication of the scaffolds with TGA/DSC. The scaffolds were produced by the immersion of PU foams to Sol-Gel solution several times, then dried, heated up to 700°C, and sintered at 1300°C. The scaffolds were loaded with Moxifloxacin, an antibiotic with antimicrobial activity. The characterization was performed by FTIR, XRD, and SEM/EDS. The bioactivity, degradability, and mechanical properties were also investigated. Drug loading/release profiles were assessed with HPLC. The fabricated highly-porous scaffolds presented a high drug loading capacity (84%) and controlled release rate, while the *in-vitro* bioactivity evaluation indicated the formation of a Ca-P layer on the surface of the samples after 14days of immersion.

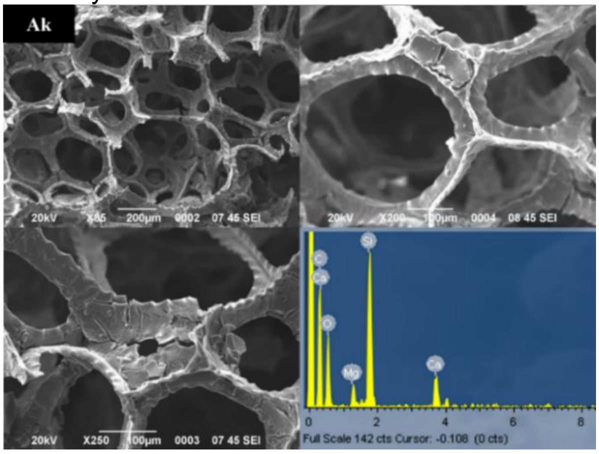

Figure 1: SEM microphotographs of the synthesized Akermanite Scaffolds and EDS analysis.

Acknowledgments: This research is co-financed by Greece and the European Union (European Social Fund- ESF) through the Operational Programme «Human Resources Development, Education and Lifelong Learning» in the context of the project "Strengthening Human Resources Research Potential via Doctorate Research" (MIS-5000432), implemented by the State Scholarships Foundation (IKY).

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MESOPOROUS SILICAS WITH VARYING PORE SIZE AND SURFACE FUNCTIONALITY AS CARRIERS OF BIOACTIVE MOLECULES

Dimitrios Gkiliopoulos[1], Ioannis Tsamesidis[2], Georgia K. Pouroutzidou[2,3], Anna Theocharidou[2], Evi Christodoulou[1], Dimitrios Bikiaris[1], Konstantinos Triantafyllidis[1], and Eleana Kontonasaki[2]

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ABSTRACT:

Mesoporous silicas are nano- or microparticles with large surface areas and pores with diameters between 2 and 50nm. Due to their unique properties, they are used in many applications, such as catalysis, adsorption, and drug delivery[1-2]. In this study, sol-gel chemistry was applied to synthesize SBA-15 mesoporous silicas, that were tested for their effectiveness as bioactive molecule carriers. The syntheses were conducted via the cooperative self-assembly route, in acidic environment, using tetraethyl orthosilicate (TEOS) as Si-source and Pluronic® P123 as the pore directing agent. Three SBA-15 variants were produced: i) SBA-15(8) with large (8 nm) and long pores, ii) SBA-15(4) with small (4 nm) and short pores, and iii) SBA-15(sc, *short channel*) with large (8 nm) and short pores. Additionally, the surface of SBA-15(8) was organically modified with amino or phenyl moieties. SBA-15 silicas were loaded either with *artemisinin*, a lactone able to stimulate the generation of reactive oxygen species (ROS) or with *rhBMP-2*, a bone morphogenic protein. The biocompatibility and haemolytic activity of neat and drug-loaded mesoporous silicas, as well as the bioactive molecule release profiles, were evaluated and the results were correlated with the morphological, structural, and textural properties of SBA-15 silicas. The N_2 adsorption/desorption isotherms of the samples are presented in Fig.1. All samples had Type IVa isotherms with Type H1 hysteresis loops. The surface area values of SBA-15(8), SBA-15(4), SBA-15(sc), p-SBA-15(8), and a-SBA-15(8), were 820, 650, 800, 716, and 474 m^2/g, respectively.

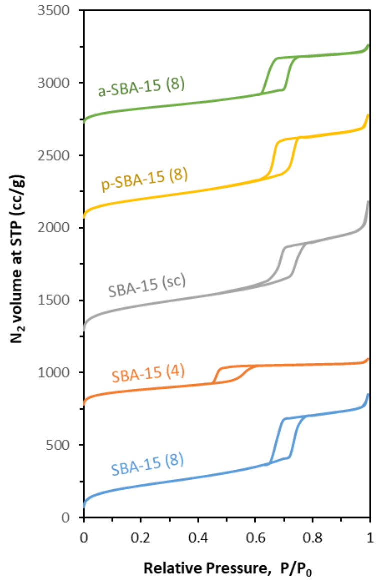

Figure 1: N_2 adsorption/desorption isotherms of SBA-15 mesoporous silicas

Acknowledgments: This work is supported by European Union's Horizon 2020 research and innovation programme under grant agreement No 953128, project: Smart, Multifunctional Dental Implants: A solution for peri-implantitis and bone loss.

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UV PHOTOLITHOGRAPHY OF A HYBRID POLYMER FOR *IN VITRO* MODELING OF MUSCLE REGENERATION AFTER AN INJURY.

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ABSTRACT:

At a human muscular level, there is a great inter-variability in response to the same mechanical exercise. As a matter of fact, two athletes with the same age, the same medical history, and the same training, may develop different muscle pathologies. The objective of the project is to propose a precise and reproducible model to evaluate the muscle regenerative capacities after an injury. To this purpose, EETMOS (for 2-(3,4) epoxycyclohexylethyltrimethoxysilane) a hybrid polymer is synthesized by sol-gel process in soft acidic condition(*1*) with a mixture of photoinitiator. Then, the polymer solution is applied on a PDMS membrane by spin coating and microstructured by UV photolithography to create a network of parallel lines. This support will act as a mimetic scaffold to culture primary human quadriceps satellite cells. The network of parallel lines can be optimized to produce aligned myofibers with a controlled diameter in order to model the original muscle morphology (Figure 1). After biofunctionalization with adhesion peptide grafting(*2*), those silicone membranes can then be uniaxially mechanically stretched to mimic the stress applied to the quadriceps during an intense physical activity. The muscle contractions can be followed by Ca^{2+} release measurement inside the environment and the regeneration process can be assessed in the laboratory by immunofluorescence. The outlook of this project is to individually predict the muscular response of each athlete in order to individually adapt his training to prevent injuries.

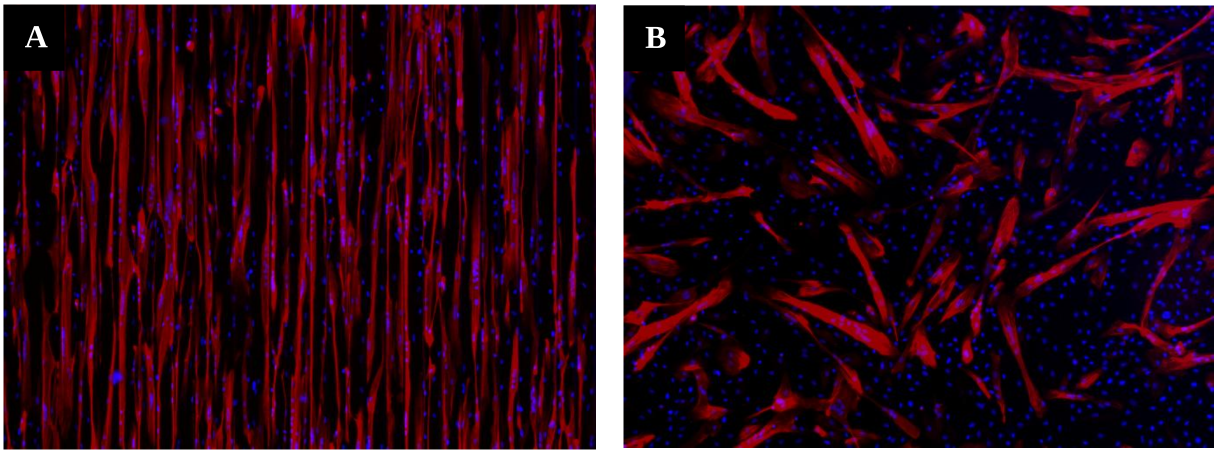

Figure 1: Fluorescence microscopic observation of the myofibers created on A) microstructured PDMS and B) bare PDMS.

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Sustainable antibacterial activity of polyamide fabrics containing modified ZnO nanoparticles obtained by sol-gel process

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ABSTRACT:

Microbial infections caused 700.000 deaths worldwide according to the World Health Organization (OMS)[1].We present an unprecedented study about the influence of parameters such as dyeing, softening and number of washes on the maintenance of antibacterial activity of polyamide fabrics containing zinc oxide nanoparticles (ZnO NP) impregnated by a simple and easy to scale technique. ZnO NP was synthesized by the sol-gel method at different reaction times (1h, 3h and 24h) followed by surface modification with (3-glycidyloxypropyl) trimethoxysilane and water dispersion. The reaction time of ZnO NP synthesis were modified to evaluate their influence on the size of particles and antibacterial activity after impregnation on polyamide fabrics treated with softener, without softener, with dyeing and without dyeing, before and after 20 washing cycles. The presence of ZnO NP in fabrics was evidenced by different techniques as X-ray diffraction, Scanning Electron Microscopy and Energy-dispersive X-Ray Spectroscopy. The mean diameter of the ZnO NP remained in 5 nm independent of the reaction time revealing the efficient control of the nanoparticles size, important once ZnO with particle size smaller than 10 nm can present improved antibacterial activity. The antibacterial activity of fabrics containing ZnO NPs indicated that polyamide fabrics after impregnation with NP ZnO synthetized with reaction time of 1 hour have high biocidal potential against *S. aureus* and *E. coli* both with and without the presence of fabric softener or dye. The antibacterial behaviour remained intact after 20 washing cycles demonstrating the resistance of antibacterial performance of fabrics both to usual chemical treatments employees in industries and several washing cycles The low reaction time of 1 hour used for the synthesis of ZnO NP and the versatility of polyamide fabrics in the manufacture allow the application of the studied fabrics in different environments to contain the proliferation and transmission of microorganisms.

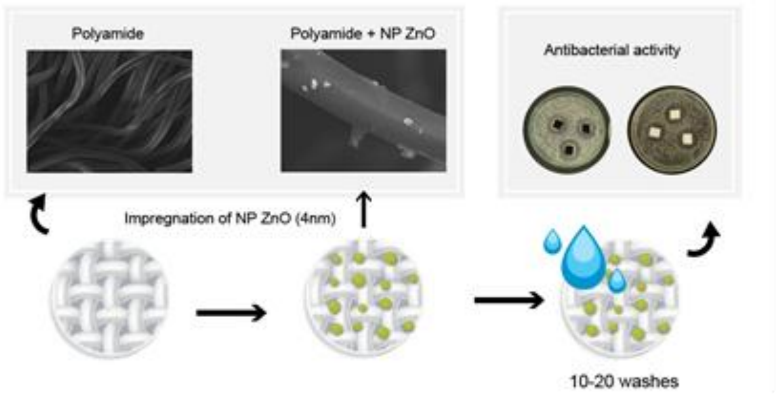

Figure 1 : Representation of the impregnation of ZnO nanoparticles in fabric fibers and of the antimicrobial activity of impregnated fabrics.

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SYNTHESIS OF VIRUS-LIKE MESOPOROUS SILICA NANOPARTICLES FOR DRUG DELIVERY ACROSS THE BLOOD BRAIN BARRIER

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ABSTRACT:

Neuronal damage resulting from infectious brain disease, such as Tuberculous meningitis, is challenging to treat due to the selective permeability of the blood-brain barrier (BBB) that the therapeutic target (neurons) is behind [1]. Mesoporous silica nanoparticles (MSNPs) are emerging as drug delivery candidates due to their tunable morphology and biocompatibility. Virus-like mesoporous nanoparticles (VMSNPs) use the unique shape to enter cells and evade clearance mechanisms longer than other types of MSNPs [2]. To evaluate the potential of VMSNPs for drug delivery across the BBB, suitably sized VMSNPs with a range of spike lengths is synthesized using a sol-gel method with surfactant-mediated templating. The effect of synthesis parameters, including temperature, co-solvent, stirring rate, aging time, and surfactant concentration, on particle size and shape is investigated. The morphology of particles is determined with transmission electron microscopy (TEM), dynamic light scattering (DLS) and Brunner-Emmett-Teller (BET) analysis. Encapsulation of rifampicin and cerium oxide is achieved by post-synthetic impregnation and confirmed using high performance liquid chromatography (HPLC) and inductively coupled plasma mass spectrometry (ICP-MS). The permeability of the BBB to the VMSNPs is confirmed and compared to spherical MSNPs.

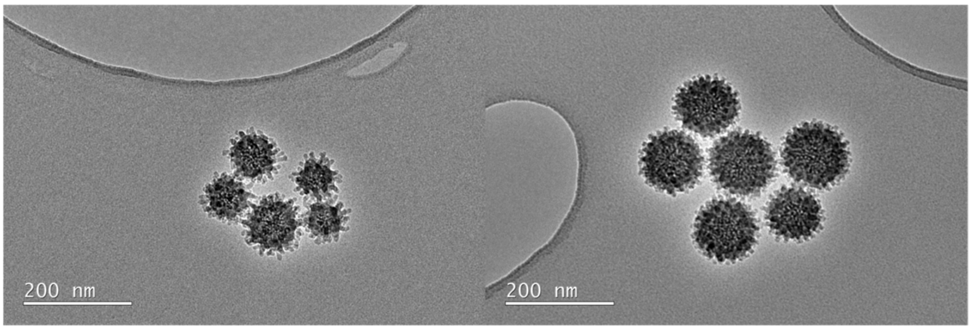

Figure 1: TEM images of two types of VMSNPs synthesized: 18 nm spikes (left) and 9 nm spikes (right).

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TAILORED POROUS SERS SUBSTRATES CONTAINING GOLD NANOPARTICLES: SIZE-DEPENDENT DETECTION OF MOLECULES OF MEDICAL INTEREST

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ABSTRACT:

The detection at low concentrations of drugs or molecules with an impact on health is a major societal issue and an important challenge in the field of analytical chemistry due to the high demand in fields such as pharmacology, toxicology and forensics. At the moment, a method that detects in a fast, simple, specific, sensitive and low-cost way, does not exist yet.

The detection using Surface Enhanced Raman Spectroscopy (SERS) is considered as one solution to face this demand as it combines all these parameters. In this context, the design of efficient and adaptable substrates remains the main challenge. This technological barrier was overcame, in this work, by developing tailored porous substrates containing gold nanoparticles using a new synthesis method[1] and by using them to detect molecules via the coupling of their adsorption properties and their Raman response[2].

Mesoporous substrates with controlled architecture (size and amount of Au nanoparticles) have been, in this way, successfully developed. These solids were first used to detect an anxiolytic (oxazepam). For this molecule, it was shown that the larger the size of the nanoparticles the higher the sensitivity of the substrate. In a second step, the detection of a pesticide (imidacloprid) was performed and, this time, it seems that a certain size is necessary to detect the molecule.

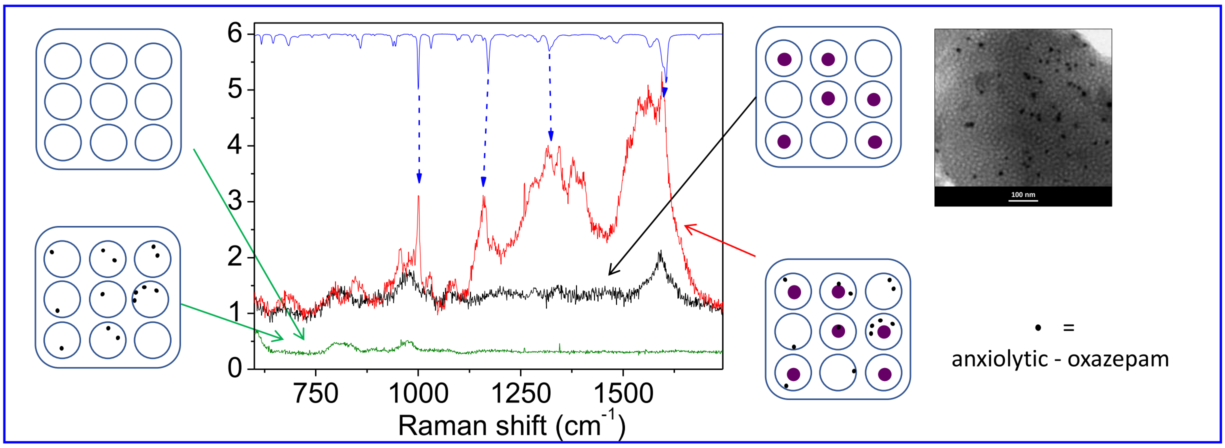

Figure 1 : SERS Detection of oxazepam using porous substrates containing gold nanoparticles

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IRON OXIDE NANOPARTICLES FUNCTIONALIZATION FOR NANOMEDICINE APPLICATIONS

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ABSTRACT:

Iron oxide nanoparticles or SPIO (Superparamagnetic Iron Oxide) are widely used in the field of nanomedicine thanks to their numerous properties (small size, high magnetic moment, biocompatibility…).

Medical imaging and treatment of diseases are the two main domains concerned by the use of SPIO. For such applications, it is imperative to create a stable and biocompatible nanohybrid used as a backbone for the conjugation of functional molecules addressing relevant properties (selective cell/organ targeting agent, imaging agent, drug…).

Herein, we report such a MRI-active nanohybrid that contains an inorganic Fe_3O_4 core and may host such functional molecules. Hence, a photosensitizer/fluorophore was grafted to an inorganic bi-functional platform, where the second function remains available for subsequent conjugation with a partner of interest (such as, biomolecules for site-selective delivery to cells/organs, molecular moieties to allow nanohybrid stabilization in a given medium, etc..)

These magnetic nanohybrids were prepared in collaboration with SON SAS. It consisted in an iron oxide (Fe_3O_4) based inorganic core and the subsequent grafting of any organic molecule onto their surface. Both structure and purity were confirmed by several analytical techniques: XRD, TEM, XPS, IR and Fluo-X.

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In vivo Evaluation of a Sustained Release in situ gelling Risperidone Delivery System Based on Lipid Liquid Crystal

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ABSTRACT:

Risperidone is an antipsychotic drug used in the treatment of schizophrenia and acute phase of mania. Conventional risperidone drug delivery systems have side effects, risk of abuse and patient inconvenience. A modified release risperidone delivery system, which releases drug in a prolonged manner, is desirable. Here, oil phase was prepared with mixing of phosphatidylcholine and glycerols. Then Risperidone in N-methyl 2-pyrrolidone (NMP) was dispersed and oil phase and the dispersion mixed to make the drug delivery system. In next step, animal experiments were done on rabbit. The study groups were: group 1, control group (non-injected), group 2, rabbits receiving commercial formulation of Resperidon (Risperidal Consta®) (intramuscular injection), group 3, rabbits receiving lipid liquid crystal formulation without risperidone, and group 4, rabbits receiving lipid liquid crystal formulation containing risperidone (25 mg), which were subcutaneously injected into the back of the rabbits' necks. Each group consisted of three rabbits. The results showed the Cmax of the lipid-liquid-crystal formulation is lower than the Risperidal Consta®, indicating a uniform release of the drug from the lipid-liquid-crystal formulation. The lipid-liquid-crystal formulation creates a uniform serum drug concentration from the beginning of the injection in spite Risperidal Consta®. In addition, the time to reach to maximum plasma concentration (Tmax) in lipid liquid crystal formulation was significantly less than the Risperidal Consta®, which indicates that the new formulation reached the maximum concentration faster than Risperidal Consta®. The disadvantage of Risperidal Consta®, which is in form of sustained release risperidone microspheres, is a delay of 2 or 3 weeks to reach to the Cmax. This forces patients to use oral formulations during couple of days after first injection.

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ZIRCONIA-BASED BIOMATERIALS:

COMPOSITION *VS* STRUCTURAL STABILITY

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ABSTRACT:

Due to its mechanical properties similar to metals and its compatibility with tooth color, in addition to its superior wear resistance and biocompatibility, tetragonal zirconia-based ceramics generated a considerable interest as dental materials [1]. Good mechanical properties due to phase transformation toughening were evidenced for yttria-doped tetragonal zirconia polycrystals (Y-TZP). However, under wet environment, Y-TZP ceramics develop low-temperature degradation (LTD) [2]. Nanostructured zirconia-based powders with various dopants (alkaline earth cations, titanium, cerium) were synthesized by a sol-gel procedure. Their thermal behaviour was investigated by dilatometry measurements, wit te aim to optimize the sintering procedure. Structure, composition, and morphology of sintered co-doped zirconia ceramics were evidenced using X-ray diffraction, Raman spectroscopy, SEM/EDXS analysis. Experimental evidence on phase transformation in different zirconia co-doped materials obtained by sol-gel procedure after biocompatibility tests and accelerated ageing tests will be provided.

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DELIVERY OF ANTIVIROTIC AGENTS USING Fe_3O_4_SiO_2 MAGNETIC NANOPARTICLES FOR POTENTIAL TREATMENT OF CORONAVIRUS DISEASE (COVID-19)

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ABSTRACT:

The global impact of viral infections, the development of resistance to current drugs, and the emergence of new viruses all translate into the incessant scientific challenge of drug discovery and formulation development. Moreover, with the ongoing COVID-19 pandemic still escalating, many researchers are turning to nanotechnology as a method of treatment not only for this pandemic but in preparation for the pandemics of the future [1]. Nanoparticles are very well-known for their use in drug delivery systems as they can improve the physicochemical properties of drug molecules by modifying their pharmacokinetic profile, solubility, and bio-distribution and thus maximize therapeutic efficacy and minimize drugs side effects [2]. Carbon-based, inorganic metallic-based, lipid-based, and polymeric-based nanoparticles have been already successfully employed to deliver antiviral drugs [3]. Their size and surface properties make them suitable and preferred candidates to be loaded with different antiviral agents [4]. The novel sever acute respiratory syndrome coronavirus 2 (SARS-CoV-2) is similar to the size of these nanoparticles, which are in nano-size of 60-140 nm. Hence, loading these nanoparticles with antiviral drugs may provide effective therapeutic outcomes [5]. In present work, we synthetized magnetic mesoporous silica nanoparticles composed by magnetic core and nonporous/porous silica shell using different synthetic routes. These nanoparticles were loaded with antiviral drugs (ivermectin, lopinavir). Nanoparticles were characterized by N_2 adsorption/desorption measurements, thermal analysis, transmission electron microscopy and infrared spectroscopy. *In vitro* and *in vivo* drug release experiments and the amount of released drugs were determined by UV-Visible spectroscopy. Biocompatibility and cytotoxicity of prepared nanoparticles on the cells will be tested using the microscopic techniques, MTT assay and apoptosis assay. Prepared magnetic mesoporous silica nanoparticles loaded with antiviral drugs will be tested *in vivo* in model animals, wistar rats.

Acknowledgement: This work was supported by APVV-20-0512, ITMS 2014+:313011AUW7 and MESRSSR Triangel - Top Research Teams in Slovakia.

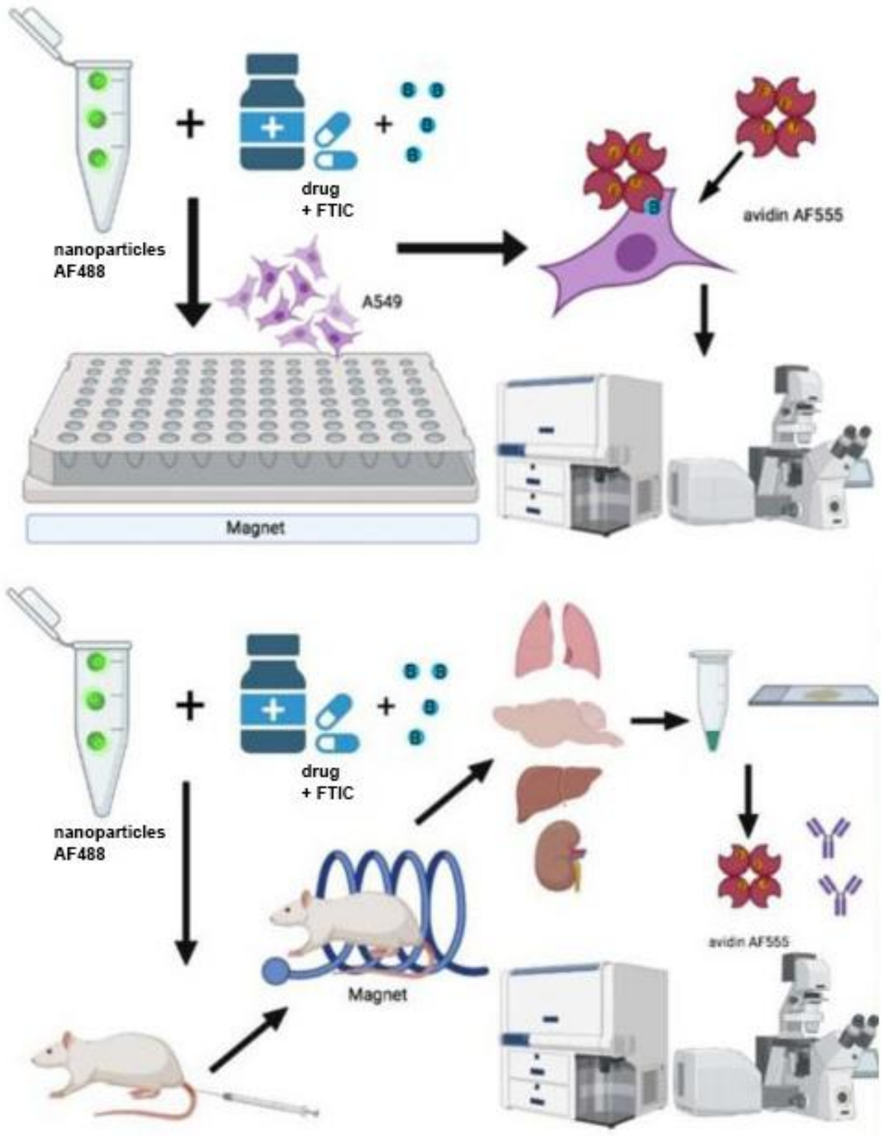

Figure 1 : Analysis of transport efficiency and method of drug nanoparticles crossing the cell membrane in *in vitro* and *in vivo* environment.

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Interaction of Nano Titania in Hybrid Wound Dressings with Blood Proteins[1]

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ABSTRACT:

Wound management is critical for preventing infections and promote healing processes. Today, passive wound dressings, e.g. gauzes and bandages, are the most common dressings. These, however, only provide a physical barrier between the wound and the surrounding. Active wound dressings are receiving increasing attention as these possess antibacterial properties and/or stimulate healing processes [2]. Nanocellulose dressings have proven efficient bandage materials to promote wound healing and pain relief, particularly for burn wounds. Nanocellulose, however, is not by itself antibacterial and the risk for infection remains. Nanotitania has previously been reported as an efficient material for delayed drug delivery [3, 4] and also in promoting blood coagulation and stimulating wound healing by initiating moderate inflammatory responses [5]. Based on this, we developed three novel potential nanocellulose-titania dressings containing different kinds of nanotitania. Two of them, using hydrothermal and colloidal titania, induced strong blood coagulation and moderate complement activation, properties that can be useful for stopping bleeding and initiate healing processes. The other material, utilizing ammonium oxo-lactato titanate ("TiBALDH") as titania source, inhibited blood coagulation and complement activation through a lowered surface pH. This material could be of interest for applications where coagulation is undesired, like in drug delivery. Thus, by modifying the surface properties of titania, blood coagulation could either be promoted or inhibited (Figure 1). This could open up for new advanced wound dressings with tailored properties.

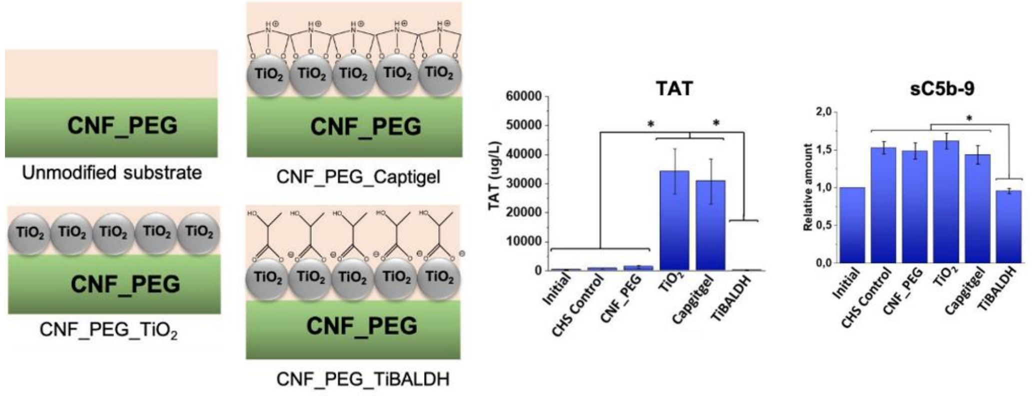

Figure 1. Surface structures of the different hybrid materials and levels of thrombin-antithrombin complex (TAT, indicator of blood coagulation) and the sC5b-9 (indicator of inflammation) after incubation of the materials with human whole blood.

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Iron oxide nanoplates design guided by artificial intelligence and impact of shape and defects of Iron Oxide Nanoparticles on Photothermal and Magnetothermal therapies

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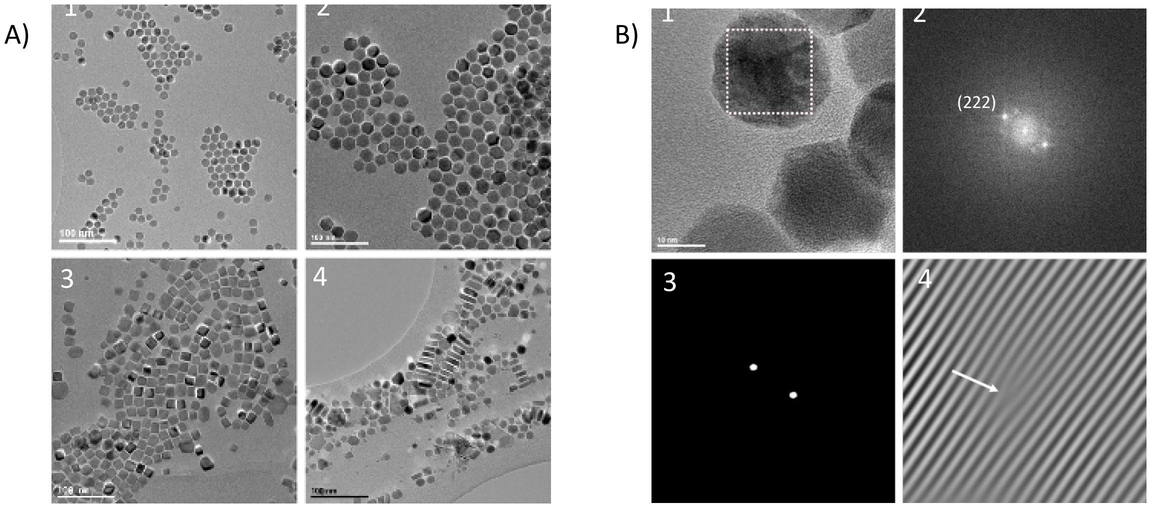
In nanomedicine, the goal is to develop multimodal nanoparticles (NPs) to speed up targeted diagnosis, to increase its sensitivity, reliability and specificity for a better management of the disease. Besides being excellent T2 contrast agents for MRI, iron oxide NPs are promising as therapeutic agents by magnetic hyperthermia when correctly designed (high magneto-crystalline anisotropy) and they also have an interest for photothermal treatment[1]. Recently, it has been reported that the defects in nanoparticles may have a strong influence on therapeutic efficiency of both treatments [2][3]. So, defect evaluation on different sized and shaped NPs is a crucial point to find the best NPs design for ensuring multimodal therapies.

We have thus optimized the reproducible synthesis of iron oxides NPs with different sizes (10 and 20 nm) and shapes (nanocubes and nanoplates) by the thermal decomposition approach by tuning synthesis parameters such as the reaction temperature, the heating rate and the nature of surfactant. The synthesis conditions to obtain high yield in nanoplates have been optimized using artificial intelligence algorithms. Then, defects such as dislocation or antiphase boundaries were evaluated by XRD and FFT studies on HRTEM images and by calculating band gaps and Urbach energies. NPs behaviors towards the different kinds of therapies were investigated both in suspension in water and viscous media and in cancerous cells allowing to establish the key role of defects and NPs design for ensuring a multimodal therapy.



A) TEM images of various sized and shaped NPs: 1 - 12nm spherical NPs, 2 - 22nm spherical NPs, 3 - 15nm nanocubes, 4 - 30nm nanoplatelets. B) 1-HRTEM image of 22nm NPs. 2-FFT of the area of HRTEM image. 3-Mask of the FFT. 4- Zoom of inverse FFT showing defects in the plan (222)

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Theragnostic agents for breast cancer treatment: design of Iron Oxide Nanoparticles for multimodal therapies strategies

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One of the aims of nanomedicine is to develop multimodal nanoparticles (NPs) to enhance the treatment and diagnosis of cancer. Breast cancer is the most diagnosed cancer and the leading cause of cancer death in female population. Because of the resistance of cancer to typical chemotherapy and for the secondary effects these therapies present on patients, there is a strong need to develop precise medicine. The combination of therapies to target individual cancer-specific vulnerabilities is a way to increase the efficacy of anticancer treatment. Therefore, besides precision diagnosis, challenges for personalized nanomedicine are to develop multifunctional theragnostic nanoplatforms to be able to target specifically tumoral cells, to test quickly different treatments and to follow-up the effect(s) of the treatments by imaging.

The selective accumulation of NPs in diseased organs to enable precise diagnosis and targeted therapy is a relevant issue. Most of developed NPs accumulate, after intravenous injection, in eliminatory organs and usually low amounts achieve the tumor site. For a precise treatment, active targeting with affinity ligands to achieve tumor specificity is crucial. Among NPs developed for nanomedicine, superparamagnetic iron oxide nanoparticles (IONPs) are promising as they may be designed to display multimodal therapy. Indeed, besides being excellent T2 contrast agents for MRI, IONPs are promising as therapeutic agents by magnetic hyperthermia when suitably designed.

We developed dendronized IONPs (DNPs) coated with an original dendron molecule. Studies *in vivo* have demonstrated that they have antifouling properties, for example, they do not present a strong accumulation in the reticuloendothelial system. They present a favorable biodistribution and bioelimination profiles, and due to these characteristics, they are interesting nanoplatforms for the investigation of precise treatments. Through the dendron molecule we conjugated different TL (specific peptides) whose have affinity for certain molecules overexpressed in two types of breast cancer: MCF-7 and MDA-MB-231 cell lines. We saw a rise in the internalization amount of DNPs with TL compared with the same DNPs without TL. In this sense, the magnetic hyperthermia showed to be more efficient when working with the targeted DNPs. Additionally, we conjugated chelating agents (CA), with this approach a radioisotope was successfully loaded and we could follow the biodistribution *in vivo* by molecular imaging techniques like PET and SPECT. Figure 1 is a representation of our targeting approach therapy.

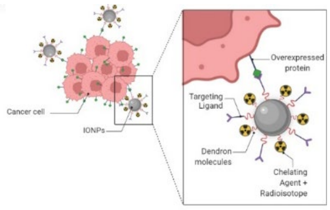

Figure 1 Overexpressed proteins on cancer cell membranes (green square). IONPs with dendron on the surface (red chains) functionalized with TL (purple) and CA (yellow).

Materials for electronic and magnetic applications

Multimodal neuromorphic transistors with metal oxide-chalcogenide heterostructure for artificial in-memory computing chip

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Sunchon City and Republic of Korea

ABSTRACT:

Towards the hardware realization of power-/space-efficient, more intelligent neuromorphic computing system, one of the key challenges is to develop artificial photo-neuromorphic device showing photo-sensitive neuromorphic responses and multi-spectral activation to photonic signals in a neuron-/synapse-like fashion[1].

Here, artificial neuromorphic device showing photosensitive neuromorphic response and broadband spectral photonic signal multi-gating functionality is designed using all solution-processed metal oxide/chalcogenide hybrid structure and defective hetero-interface. Compared to conventional photonic/electronic synapses mimicking simple synapse-level dynamics without neuronal function[2,3], our metal oxide/chalcogenide hybrid neuromorphic device could demonstrate major photonic-signal triggered overall neuromorphic dynamics (synaptic and neuronal functions) under remote/multiple gating condition of multi-spectral optical signals. Photonic synaptic weight change was embodied from photo-persistent current phenomena generated on defective hetero-interface of metal oxide/chalcogenide hybrid structure. Various photonic synaptic responses are optimized via hetero-synaptic optoelectronic signal condition. More significantly, high-order neuronal computation functions and association learning activities were sufficiently demonstrated from metal oxide/chalcogenide hybrid neuromorphic device via computational processing of multiple-photonic signal spikes.

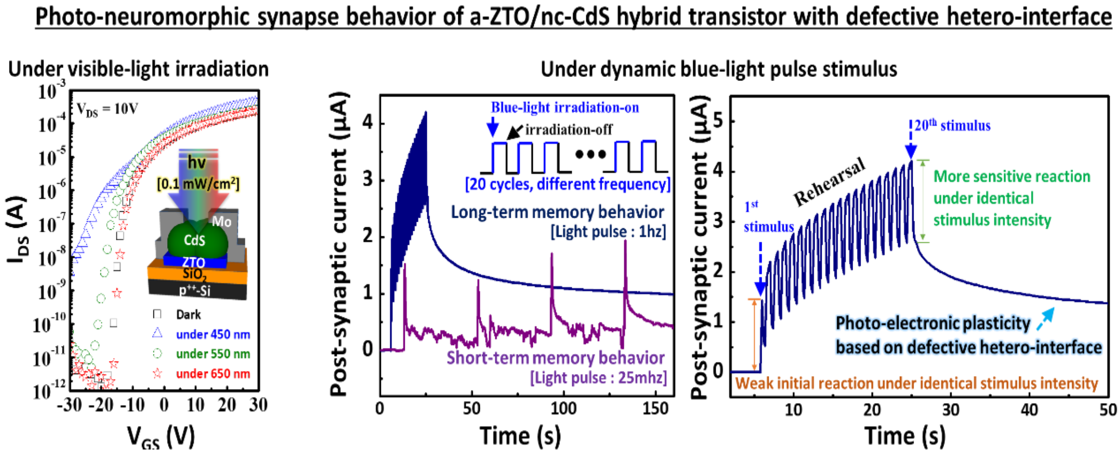
Photo-neuromorphic synapse behavior of a-ZTO/nc-CdS hybrid transistor with defective hetero-interface

Under visible-light irradiation

Under dynamic blue-light pulse stimulus

Figure 1 : Artificial photonic neuromorphic transistors with metal oxide/chalcogenide hybrid structure; device configuration and neuromorphic dynamics

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IMPACT OF DIFFERENT SOLUTIONS ON THE QUALITY OF COPPER-OXIDE-BASED TRANSISTORS PREPARED BY SOL-GEL TECHNIQUE

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ABSTRACT:

Metal oxides are very promising group of electronic materials for their wide range of applications such as solar cell, gas sensors, or field-effect transistors. Even though the sputtering is the most common way of their deposition, for commercial use is this technology not an option due to the high-cost. For this reason, alternative technique, such as sol-gel technology, is required. Recently, the copper oxides have been envisioned as a candidate for low-cost advanced semiconductor suitable for field-effect transistors. An optimized technology would allow to reach charge mobility comparable with polycrystalline and amorphous silicon. However, due to the complex parameters of sol-gel technique is this level difficult to reach and fine tuning of technology is needed. Here we will focus on optimization of copper-oxide-based transistors fabrication technology. The detailed analysis of mixed solvents application revealed their impact on structural and electronic properties. It was shown that isopropyl alcohol and 2-methoxyethanol in weight ratio 1:3 provides the most crystalline film with highest effective mobility.

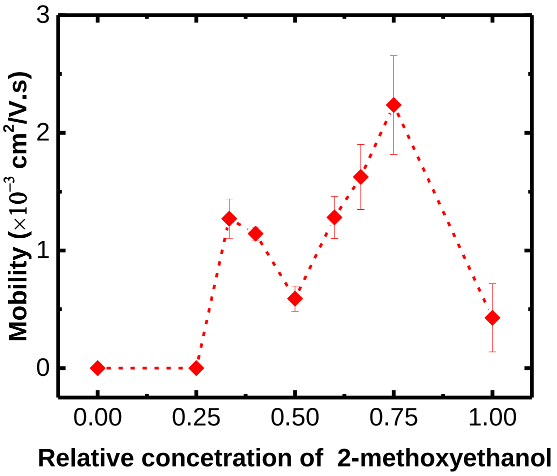

Figure 1 : The effective mobility as a function of relative concentration of 2-methoxyethanol

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CHARACTERIZATION OF GAOOH FILMS PREPARED BY TWO-DIMENSIONAL GELATION PROCESSES

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ABSTRACT:

Gallium oxide hydroxide (GaOOH) is a ultrawide bandgap semiconductor and holds great promise for photocatalysis materials in the clean energy conversion.[1] GaOOH nanoparticles were synthesized through hydrothermal method.[2] However, the growth of GaOOH films has not been reported. In this work, we demonstrate the growth method of GaOOH films using two-dimensional (2D) gelation processes at room temperature in the atmosphere. The sol solution was prepared by the stirring at 60ºC for 1 h using tris(acetylacetonato)gallium (0.4 mol/l), monoethanolamine (2.0 mol/l), and 2-propanol. After aging the sol solution at room temperature, it was spin coated onto quartz substrates. The spin of 3000 rpm for 30 s was repeated 5 times. 2D gelation processes of the sol films generated from the substrate edge were evaluated. The gel point and gelation velocity of the films depended on the aging time, which may be caused by the gradually precipitation of neutral molecules in the sol solution. The sol/gel reaction boundary proceeded in the in-plane direction, and belt-like structures with a width of several micrometers were formed perpendicular to the boundary. Since anisotropic growth of GaOOH microplates also occurred on the belt-like structures, it is considered that the orientation of GaOOH occurs during the gelation reaction. In the as-grown films, an absorption peak due to impurities was observed at a wavelength of 310 nm, but it disappeared by the annealing at 250ºC. The bandgap energy of the sol-gel derived GaOOH films was estimated to be 5.6 eV.

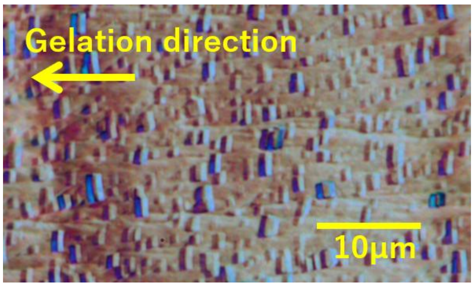

Figure 1 : Typical optical microscope image on the GaOOH film after 1 h from the 2D gelation reaction. The sol solution used was aged for 6 days. The gelation velocity was 1.2 μm/h. Anisotropic growth process of microplate structures was observed on the surface perpendicular to the gelation direction.

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Electron Responsive Viologen-Based Supramolecular Gels

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ABSTRACT:

In a nutshell, a gel is a material in which a large amount of solvent is trapped in a molecular network. In supramolecular gels, self-assembly of the network is achieved by non-covalent interactions (π-π stacking, H-bonding, ion pairing, solvophobic forces…) between low molecular weight gelators (LMWGs). Unlike polymeric gelators LMWGs have a well-defined chemical structure, offering the possibility to tune the material properties at the molecular level [1]. Stimuli responsive self-assembled molecular materials are capable of changing their organization in response to various stimuli (pH, T, P, magnetic field, light…). Such responsiveness has been proved useful in numerous fields such as catalysis, smart materials, pollutant removal, drug delivery system, development of sensors and memory devices [2]. However little examples of electro-responsive supramolecular materials are to be found in the literature [3]. The potential of such materials has recently been demonstrated through the development of a gel-based memristor exploiting conductivity changes associated to a sol/gel transition triggered by heating or DC bias [4]. Viologens carry much interest for the development of new functional materials and have already shown promising results for applications in molecular electronics [5]. We have recently reported a supramolecular metallogel able to undergo a gel-sol transition triggered by photo-reduction of its viologen moiety [6][7]. In the wake of this promising result a previously described viologen based gelator [8] has been synthesized and its gelation conditions have been investigated (Figure 1). Rheological and conductivity measurements have shown that gels of tunable strength and conductivity could be obtained. First photoreduction trials have shown that the viologen based gelator could be photoreduced in its gel state, giving a blue coloration to the material.

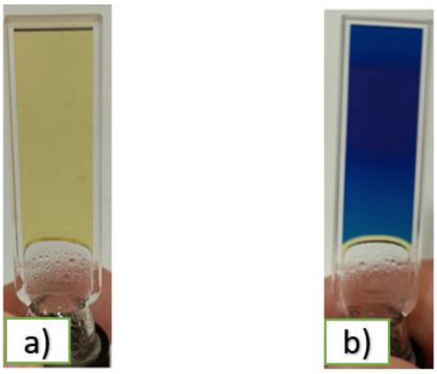

Figure 1 : Viologen based organogel: Before (a) and after irradiation at 455nm (b)

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DISCOVERING THE ROOM TEMPERATURE FREQUENCY-DEPENDENT DIELECTRIC PROPERTIES OF $LaFeO_3$ NANOPARTICLES

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ABSTRACT:

This is work reports the structural, and frequency-dependent dielectric properties of $LaFeO_3$ nanoparticles (NPs) synthesized by the reverse micelle technique. Powder X-ray diffraction data analyzed with a Rietveld refinement technique revealed the single-phase and orthorhombic distorted perovskite crystal structure of the $LaFeO_3$ NPs having Pbnm space group. crystallite sizes and lattice strain on the peak broadening of $LaFeO_3$ NPs were studied by using Williamson-Hall (W-H) analysis. The scanning electron microscopy images show the crystalline nature and formation of nanostructures with a uniform distribution of particles throughout the sample. Frequency-dependent dielectric properties of $LaFeO_3$ NPs have been explored in detail such as dielectric constant (ε',ε"), dielectric loss (tanδ), and a.c. conductivity (σac).

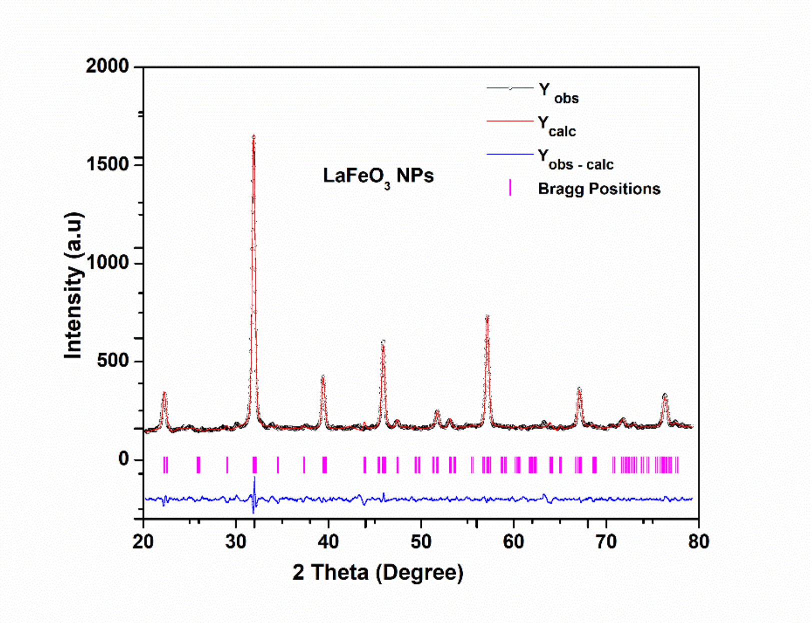

Figure 1: XRD pattern of $LaFeO_3$ NPs fitted with the Rietveld refinement program. The vertical bars indicate expected Bragg's reflection positions for an orthorhombic structure.

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Main Menu

Materials for sensors, optics, nonlinear optics, photonics and optoelectronics

NIR laser curing of InZnO precursors involving thermoplasmonic effects for gold nanoparticle/semi-conductor thin films preparation

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ABSTRACT:

Over past few decades, thin-film oxide semiconductor materials have attracted huge interests[1], such as the applications of biomedical, nanogenerators, gas sensors, photomemories or photodetectors. Among kinds of device fabrication processes, sol-gel method has been commonly used as a solution process for its interest as versatility and lowering down the cost. However, a high temperature annealing is required which limits the application of this process for integration on flexible substrates. We demonstrate in this work that thermoplasmonic effects can be used to cure, at room temperature sol-gel thin film in order to obtain a material with interesting semi-conductive properties. The design of the structures is given in Fig 1.a. Laser-dewetted Au nanoparticles (NPs) arrays which work as nanoheaters were firstly synthesized. After IZO solution coating, the 2nd NIR laser annealing effectively worked for thin film IZO curing, which could be confirmed by the decrease of vacancies from O(1s) peak analysis (Fig.1 (b)) of x-ray photoelectron spectroscopy (XPS). Additionally, thanks to localized surface plasmon resonance (LSPR) absorption given from Au NPs, photoresistance effect can be obtained. Thanks to the wide excitation spectrum of Au NP and hot electron transfer[3], the photosensitivity of the photodetectors could be obtained in visible range (515-630 nm), and extended NIR (780 nm), (Fig.1 (c)).

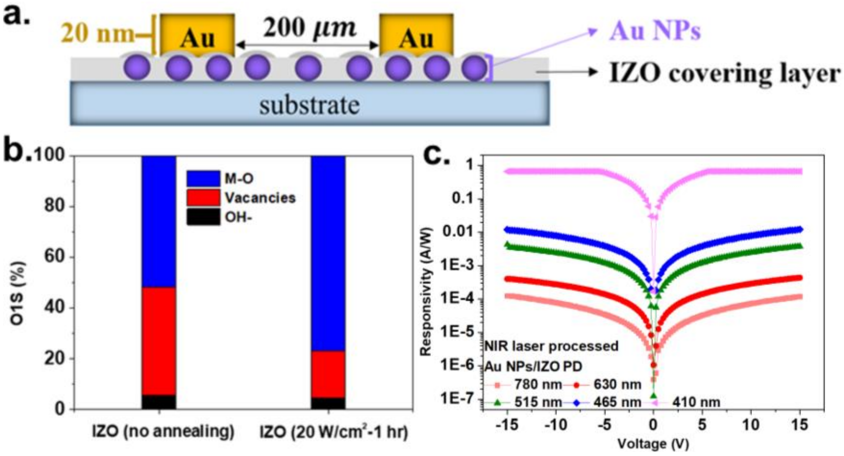

Figure 1: NIR laser processed Au NPs/IZO PD (a) the device structure (b) the analysis of XPS after IZO curing (c) light detection performance

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ADVANCED SOL-GEL IV-VI-DOPED INORGANIC THIN FILMS FOR TEMPERATURE SENSING INSTRUMENTATION

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ABSTRACT:

IV-VI quantum dots-doped SiO_2 and SiO_2-P_2O_5 thin films were prepared by sol-gel method, spin coating technique [1, 2, 3]. Different substrates were used for deposition such as glass, ITO (indium tin oxide) layered on glass and silicon, respectively [3]. Precursor composition, gelation time, substrate rotation speed, number of deposited layers and pH of the precursor sols were changed in order to regulate the hydrolysis and condensation mechanisms to accomplish uniform and homogeneous thin films [3]. H_3PO_4 and diethyl phosphate were used as precursors for P_2O_5 to explore their influence on the gelation time and deposition parameters [4]. Nanostructured materials were obtained by drying and subsequent annealing of the deposited films. The nanostructured network forming role of silicon dioxide and phosphorous pentoxide were evidenced by structural and morphological characterization of the deposited thin films [1, 4]. The optical band gap was graphically resolved in correlation with the size dependent quantum confinement effect, the latter being liable for the optical absorption cut-off and luminescence characteristics [2]. UV-VIS-NIR transmission spectroscopy, photoluminescence, luminescence decay and related measurements were also performed [2, 4]. Various excitation wavelengths were used aiming to choose the performing materials regarding the photoluminescence characteristics, showing the potential application of these nanostructured materials for temperature detection.

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Au decorated WO3/$La_{0.8}Pb_{0.2}FeO_3$ (LPFO) heterostructure materials for H_2S gas sensing application

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ABSTRACT:

In this study, a H_2S sensor with Au decorated $WO_3/La_{0.8}Pb_{0.2}FeO_3$ (LPFO) heterostructure has been successfully prepared. We used sol-gel technology combine electrospinning process to fabricate WO_3 nanofibers and dip into the $La_{0.8}Pb_{0.2}FeO_3$ sol solution then evaporated the gold particles. The WO_3 nanofiber was jointed with $La_{0.8}Pb_{0.2}FeO_3$ perovskite film to form a PN-junction heterostructure sensor and the evaporated Au particles time is 15 seconds. The results show the best H_2S gas sensitivities were 82% for 10 ppm H_2S, while the operating temperature was 175 °C. The heterostructure binding of H_2S gas sensor can effectively increase the response and has good recovery and stability. Finally, the gas sensing mechanism for the WO3/$La_{0.8}Pb_{0.2}FeO_3$ is also discussed.

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Improved response of a ratiometric fluorescent pH sensor by sol-gel materials

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ABSTRACT:

A fuorescent pH sensor is one of the most useful tools for practical applications as in environment, industry, biomedicine, etc. Therefore, in this study, 8-hydroxypyrene-1,3,6-trisulfonic acid trisodium salt (HPTS) – a fluorescent pH-sensitive dye - was doped into silica particles which synthesized from precursor tetraethyl orthosilicate (TEOS) or commercial fumed silica and then incorporated with D4 polyurethane hydrogel for fabrication of the fluorescent pH-sensor. The pH detection range of this pH-sensor was improved by adding several kinds of sol-gels containing functional groups to the supporting polymer. The presence of functioned groups of sol-gels seems to influence the interaction of HPTS as well as of the pH-sensing membrane with the charged species upon protonation or deprotonation and lead to changes in the linear pH detection range. For correction of a variety of analyte-independent factors in fluorescent sensors and providing a precisely quantitative analysis, a referent dye was combined in this pH-sensing membrane to make a ratiometric fluorescent pH-sensor.

Keywords: HPTS, TEOS, ratiometric pH-sensing membrane, functional groups of sol-gel

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NON-LINEAR SOLID-STATE OPTICAL FILTERS BASED ON SOL-GEL MATRIX DOPED WITH PLATINUM ACETYLIDE CHROMOPHORES

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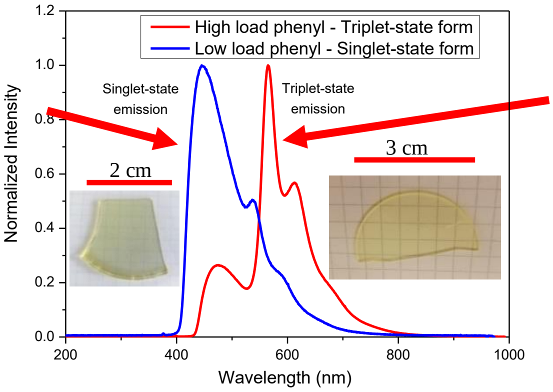
ABSTRACT:

Sol-gel materials are commonly used as a solid matrix to host organic chromophores. Previously, we introduced a photochrome and 2-photon absorber into a hybrid organic-inorganic sol-gel synthesized via a fast sol–gel process [1]. In that case a solid-state non-linear material was demonstrated based on a mechanism of initiation of nonlinear response by 2-photon absorption in the UV-range wavelengths, which triggered photo-chromic absorption in the visible range wavelengths through resonant energy transfer (RET).

In this work we present a fast sol-gel matrix doped with platinum acetylide chromophores [2,3], which are designed to undergo efficient intersystem crossing from a singlet-state to a triplet-state, resulting in an enhanced nonlinear optical response. The intensity of phosphorescence relative to fluorescence is a measure of triplet state quenching due to dissolved oxygen in the host. The fluorescence and phosphorescence emission of a platinum acetylide chromophore, molecule 1 in ref [2], dissolved in an aromatic nonpolar sol-gel matrix [4] is presented in Figure 1. Fluorescence is observed in the low aromatic load material, suggesting the material contains significant amounts of dissolved oxygen. Phosphorescence is observed in the high aromatic load material, suggesting the material excludes dissolved oxygen [5]. The effect of a platinum acetylide chromophore [3] in polar and non-polar sol-gel matrices was also investigated and will be discussed in more details.

Figure 1 : Fluorescence and phosphorescence emission of polar platinum acetylide chromophore in solid-state sol-gel materials



Low aromatic load FSG – Chromophore in Singlet-state form presents fluorescence emission

High aromatic load FSG – Chromophore in Triplet-state form presents mostly phosphorescence emission

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HYBRID SOL-GEL WAVEGUIDE SENSOR FOR DAMAGE DETECTION IN AEROSPACE DOMAIN

Maxime Royon [1], Damien Jamon [1], Thomas Blanchet [1], François Royer [1], Francis Vocanson [1], Emmanuel Marin [1], Adriana Morana [1], Aziz Boukenter [1], Youcef Ouerdane [1], Yves Jourlin [1], Sylvain Girard [1]

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ABSTRACT:

Based on hydrolysis and condensation reactions, the sol-gel chemistry route is a powerful process involving the synthesis of glassy-like materials [1] where applications can be observed in many fields. In the framework of the Cleansky2 (Horizon 2020) ADD-ON (Advanced Damage Detection through Optical sensor Network) project, we demonstrate the feasibility of using a non-intrusive sol-gel approach for damage sensing over large surfaces (aircraft wings) [2]. Figure 1a represents the targeted structure manufactured by the direct UV-laser writing technique. This latter is a TiO_2-SiO_2 sol-gel waveguide matrix architecture on a large surface (40 x 40 cm^2) obtained by a direct-laser writing approach. After the light injection into all the waveguides, the detection and impact localization can be deduced through the 2D mapping grid, where the output light distribution indicates the presence of damages. The characterization of TiO_2-SiO_2 guides will be discussed, namely their optical properties (refractive index, mode confinement) revealing that important guiding properties can be achieved from the visible to infra-red range. As for instance, Figure1b shows an overview of a 2D waveguide grid on large surfaces deposited by the spin coating approach on a soda-lime glass while a zoom is given in Figure 1c, clearly evidencing that such architecture can be created using the direct writing technique. Finally, after being impacted (Figure 1d), the light extinction occurs evidencing that the sol-gel photonic device based on the light transport can act as an on/off sensor since the output light distribution is totally lost.

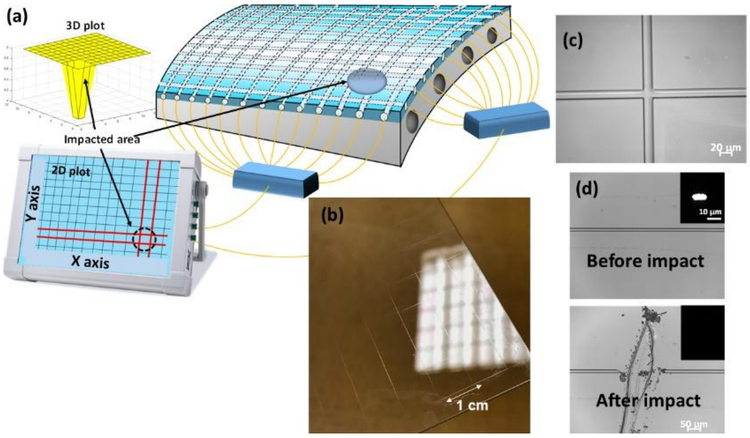

Figure 1 : (a) Overview of the sensor principle where a damage leads to the rupture of one or several TiO_2-SiO_2 guides. (b) Example of a 2D waveguide grid (40 x 40 cm^2) obtained a soda-lime glass substrate. (c) Grid observed with an optical microscope. (d) Example of impact detection.

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Nd^{3+}:YAG MICROSPHERE POWDERS AND ITS RANDOM LASER EMISSION

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ABSTRACT:

Nd^{3+}:YAG crystals have been used to develop photonic devices since the 1960s. Its unique properties, which stem from the combination of the YAG structure with lanthanide ions, have made it the most widely employed material in commercial solid-state lasers[1]. This work reports the synthesis of dense Nd^{3+}:YAG particles prepared by Spray Pyrolysis (SP) using boehmite doped with Ln^{3+} ions, as a precursor[2], prepared by sol-gel methodology. During the synthesis, no clusters emerged, and the particles did not coalesce even after thermal treatment at 1100 °C. All characterization confirmed that the YAG phase was obtained as a spherical micro- and sub-micrometric material. In addition, the photoluminescence spectra showed the expected spectroscopic profile of Nd^{3+} replacing Y^{3+} at the dodecahedral sites. The obtained materials were produced with different lanthanide contents (exploited as a simultaneous gain and scatter medium for random laser (RL) application), and the RL emission gain was affected, with threshold of 0.10 mJ/mm^2 (5% Nd^{3+}), 0.21 mJ/mm^2 (4.5% Nd^{3+}), 0.30 mJ/mm^2 (4% Nd^{3+}), 0.36 mJ/mm^2 (3.5% Nd^{3+}), 0.40 mJ/mm^2 (3% Nd^{3+}), 0.57 mJ/mm^2 (2.5% Nd^{3+}), and these values are lower than that observed for other Nd^{3+} ion based RL studies. The SP methodology described offers the advantage of not introducing impurities in the final product because there is no external contact with the precursors, and each drop constitutes a homogeneous mini reactor that has the same chemical composition as the initial solution[3,4], and could be easily scaled up for a pilot setup or industrial production.

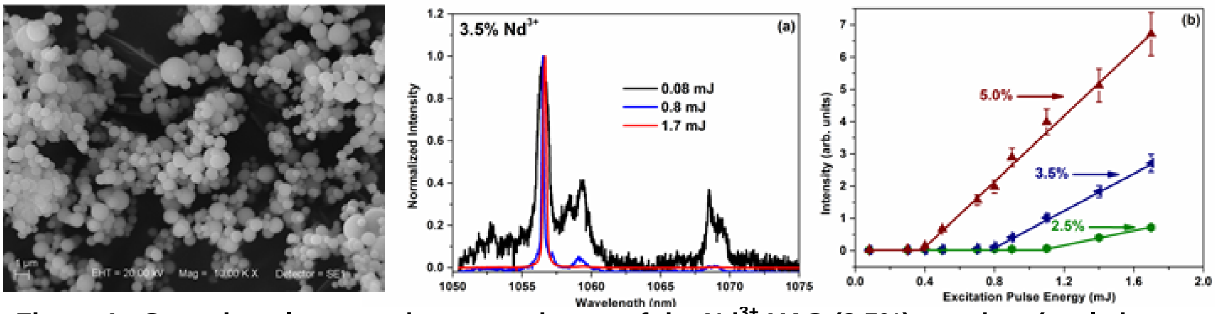

Figure 1 : Scanning electron microscopy image of the Nd^{3+}:YAG (3.5%) powders (scale bar = 1μm), (a) Spectral narrowing of the Nd^{3+} photoluminescence band (transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$) in the 3.5% Nd^{3+} doped sample and (b) corresponding output peak intensity versus the EPE for powders.

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SOLUTION PROCESSED PEROVSKITE WHISPERING GALLERY MODE MICROLASERS BY INKJET PRINTING

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ABSTRACT:

Perovskite-based photonics is an intensively growing field of studies related with photoactive materials known as perovskites. All-inorganic perovskites have great optical properties that determine its application in photonics as a gain medium in lasers [1]. Whispering Gallery Mode (WGM) lasers are types of lasers that have resonators with two axis symmetry, typically toroids, microdisks, spherical caps etc. Light can move around the internal boundary of such structures due to total internal reflection effect and continuously saturate gain medium causing lasing.

Solution processing of WGM microlasers is of great interest [2]. Inkjet printing is great for this purpose [3], due to the possibility of accurate dosing of the solution drop and its positioning. Using a solution of perovskite precursors and a polymer as ink, inkjet printing makes it possible to create a resonator of the desired shape once and crystallize gain media in it in situ. Dimatix Material Printer - 2800 with 10 pL cartridge was used for printing. The size of the resulting spherical caps was 25 μm on the PDMS substrate. Completely dried dots are composite microstructures of perovskite nanocrystals with a polymer. Thus, it is possible to create arrays of microlasers of any shape.

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Elaboration of photoluminescent thermometric nanoprobes by soft-chemistry synthesis: application in tribological contacts

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ABSTRACT:

Reduction of friction and heat dissipation in mechanical contacts is a major concern. Experimental techniques to measure temperature at the surface of solids in contact are then a great interest [1]. Considered as an efficient, non-destructive, and high-accuracy sensor, photoluminescent upconversion (UC) probes have a great potential. Pressure is also a major parameter varying in the contact, photoluminescence's independence to pressure is also important. In this study, the nano-probe has been chosen as the nanoparticles (NPs) gadolinium orthovanadate ($GdVO_4$), doped 10% Yb and 2% Er [2]. These photoluminescent probes are synthesized by soft chemistry method and TEM analysis shows their morphology of homogenous ellipsoids with size smaller than 50 nm. Thanks to the UC energy transformation from Yb to Er, they emit strongly green lights under λ_{exc} =970 nm. The thermometry calibrations are performed at 25 – 205°C, at ambient pressure (Fig. 1a & b). Then, their independence of the pressure (up to 1 GPa) is verified at 4 temperatures, using a diamond anvil cells (DAC) encircled by a heating ring for an isotherm environment under pressure (Fig. 1c). The luminescence intensity ratio (LIR) of the thermally coupled emission peaks is shown to be independent to pressure and to range linearly with temperature, and this variation is reversible. According to these analytical results, the {$GdVO_4$, Yb; Er} NPs can be applied as thermometer probes in tribological friction for future in situ measurements.

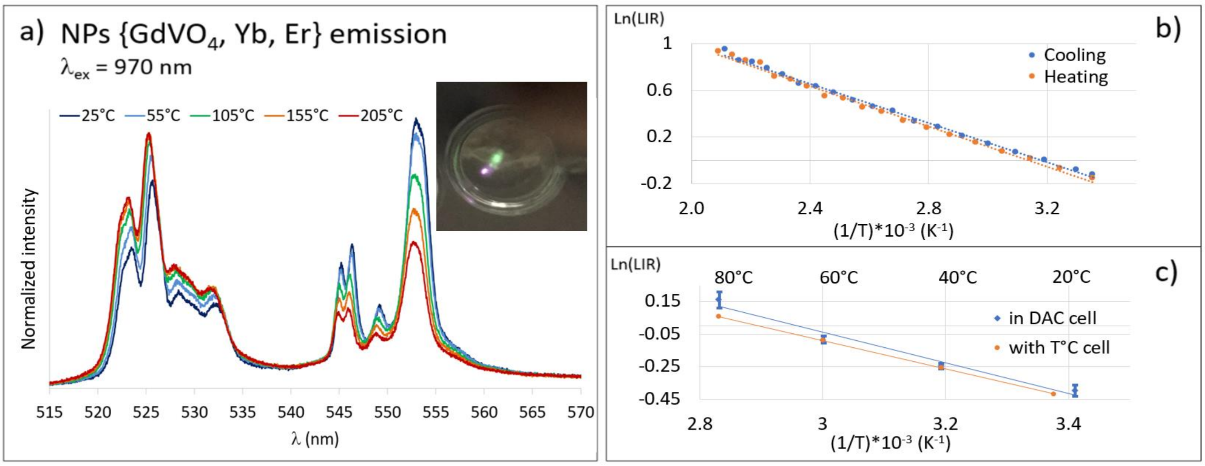

Figure 1 : (a) Normalized emission spectra of the synthesized $GdVO_4$, Yb; Er NPs. Inset: photograph of $GdVO_4$, Yb; Er NPs with a 980 nm laser pen; (b) Calibration of the $GdVO_4$, Yb; Er NPs powder in temperature under atmospheric pressure; (c) Calibration of the $GdVO_4$, Yb; Er NPs suspension of 0.5% wt concentration in pressure at different temperatures.

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SILICA SOL-GEL MATERIAL FOR THE SUPRAMOLECIULAR FLUORESCENT SENORS

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ABSTRACT:

One of the biggest problems of the fluorescent sensors made based on the sol-gel materials is the diversity of the surrounding of the sensor molecules. This results in different response of the receptor centers on the analyte thus lowering the overall sensitivity. A possible solution for this problem is using of supramolecular fluorescent receptor centers, e.g. complexes of the fluorescent molecules with organic cavitands [1]. This approach imposes a number of limitation on the conditions of sol-gel process such as reaction mixture composition, pH, etc. as the supramolecular complexes can exist in a limited set of conditions.

In this work, we develop a simple method of the synthesis of sensor materials based on the direct introduction of the predorganized into the reaction media followed by low temperature drying. The solid phase formation of the water soluble precursor tetrakis-(2-hydroxyethyl)-orthosilicate was carefully studied by means of fluorescent probing, SAXS and EPR measurements. The results of the solid phase formation study allowed to state the processes undergoing during the sol-gel synthesis of silica gel from the water soluble precursor and to describe the impurities molecules behavior [2].

The fluorescent sensor materials made by the developed method showed a huge difference in sensitivity comparing to the previously obtained ones [3], allowing the fine-tuning of sensor properties by rather simple technique.

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DEVELOPMENT OF SOL-GEL DERIVED PHOSPHORS FOR OPTICAL APPLICATIONS

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The Luminescent Materials (LM) group has been working for more than 20 years in the development of phosphors using alkoxide-based sol-gel process.[1] This synthesis way appears as the most convenient route since it leads at low temperature to versatile shapes like powders of controlled grain size, coatings or monoliths. It has also been proved that sol-gel route has a significant impact on the optical performance of phosphors since it allows a highly homogeneous dispersion of light emitting centres at molecular level. Efforts have been made both on the development of new matrices and on the improvement of existing phosphors, generally obtained by traditional solid-state way. This talk will be devoted to the presentation of several studies led on inorganic phosphors elaborated by the sol-gel process. These materials have been selected for their specific optical properties and their ability to be used in optical applications: lighting devices, scintillators or even displays.

Hence, the elaboration and characterization of three families of sol-gel derived phosphors will be presented and discussed: aluminates with the case of the well-known $Y_3Al_5O_{12}$:Ce^{3+} yellow phosphor, used in LED-based devices, fluorides with the example of $LiYF_4$:Eu^{3+}, for which LM group has implemented the first sol-gel synthesis process[2] and rare-earth doped orthoborates[3] $LnBO_3$ that can be used as efficient phosphors for displays or as scintillators. For each case, structural, morphological, and optical features will be briefly described, with a focus on the added value of the sol-gel process. The usefulness of specific characterization techniques such as SAXS or XAS to understand the underlying mechanism involved in the sol-gel process will also be discussed[4-5].

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A lead-free sol-gel substitute for PZT with high performance piezoelectric properties

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ABSTRACT:

As they present high electromechanical properties and low cost, lead containing PZT-based materials are the dominant piezoceramics for a wide range of applications. However, the RoHS Directive aims to prevent the risks posed to human health and the environment related to the management of electronic and electrical waste by restricting the use of ten substances: among them minerals like lead, cadmium, mercury or organics like polybrominated biphenyls (PBB) or dibutyl phthalate (DBP).

As a consequence, the need for lead-free solutions in electronic components and systems is receiving increasing attention within the semiconductor and electronics industries. In this work, main efforts were focused on the preparation of hafnium doped barium titanate (BaHfxTi1-xO3; BHT) sol-gel materials and compared to ones prepared by the solid-state synthesis (cosintering of inorganic powders). An original process to prepare homogeneous BHT sols, concentrations up to 1 M, free from strong organic complexing agents, was first developed. Dilution in ethylene glycol allows controlling parameters such as viscosity and colloids sizes in solution, which ensure a time-stable sol for several months at room temperature. From this sol, either thin films, or homogeneous BHT powder can be processed. A densified bulk material obtained from these powders shows really good electromechanical properties (typically a thickness coupling factor k_t close to 50%, equivalent to standard PZT materials) for applications such as ultrasonic transducers or vibrational energy harvesters. Their integration into energy harvesting prototypes such as cantilever beams for the recovery of ambient vibratory energy is underway in collaboration with an industrial partner.

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Efficient wrapping polymer by salt addition for carbon nanotubes in organic solvent.

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Nanotechnological applications of carbon nanotubes (CNTs) related to the selective separation of CNTs chiralities, remains greatly challenging and hampers suggested nanotechnological applications. Single-walled carbon nanotubes (SWNTs) dispersion in N-methyl-2-Pyrrolidone (NMP) solutions with addition of the Polyvinylpyrrolidone (PVP) polymer has been presented [1]. NMP has been demonstrated as an efficient organic solvent for dispersion of SWNTs by surfactant or polymer assisted ultrasonication [2]. To enhance photoluminescence (PL) properties, we have developed dispersions of SWCNTs in organic solvents-stabilised by addition of NaI salt at different concentrations [3]. The intensity of the PL bands increased through the additions of the salt.

In this work we study the salt (NaI) effects on CNT–NMP-PVP dispersions. The effect of salt addition increases with an increase of the salt concentration. The CNT–NMP dispersions become thermodynamically less stable at higher concentrations of salts, the PL intensities tend to increase with increasing the concentrations of salt until the threshold, which can be related to the unique process which makes these SWNT-NMP-PVP solutions thermodynamically unstable. The results show significant enhancement of SWNTs photoluminescence for solution containing samples when compared with the initial SWNTs samples. The result shows excellent stability with respect to reduced re-aggregation of the nanotubes. Figure 1 shows the strong absorption properties in the near IR spectral range. Figure 2 shows PL intensity measurements for a stability study taken at 570 nm excitation. It can be clearly seen that the intensities of PL increased for samples 1, 2 and 3 but for sample 4 the intensity was reduced with increased salt concentration. Moreover, PVP polymer wrapped around the carbon tubes making the solution more thermodynamically stable. That means might be same interaction energy between the salt and polymer transfer to the carbon tubes that lead to increase the photoluminescence (PL) intensity in samples as shown in figure 1. In this study we show that the SWNTs-NMP-PVP solution with addition of sodium iodide can show very promising properties, comparable with the results in case of SWNTs-NMP with sodium iodide but without PVP. Small salt concentrations of sodium iodide salts are capable of salting out carbon nanotubes from their dispersions. These findings provide new access for CNT bundles engineering in nano-science.

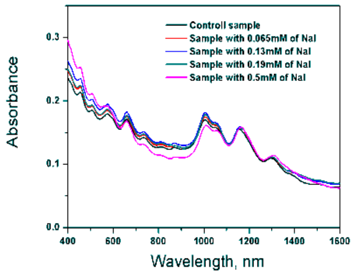

Fig.1 Absorption spectra of SWNT-NMP-PVP different sample with and without salts

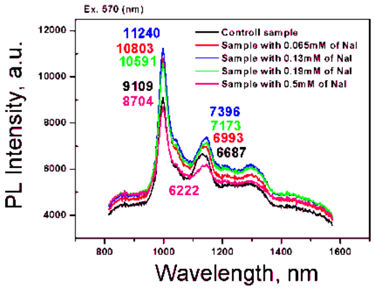

Fig.2 Spectra at the excitation at 570 nm for for different sample with and without salts.

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Synthesis and improvement of the transmission coefficient of Bragg reflectors

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Distributed Bragg reflectors (DBRs) are multilayer structures with alternating layers of high and low refractive indices, providing tailorable reflection spectra. DBRs have received considerable interest in photonic and optoelectrical applications as wavelength filters, polarization splitters, and high-reflection mirrors due to the ease of fabrication as well as controllable optical properties. This talk will address the production and development of Bragg reflectors; SiO_2/TiO_2 was investigated. SiO_2 and TiO_2 are the materials of choice for this study because of their big refractive index contrast among the existing transparent metal oxides. The films of various thicknesses have been deposited via a multilayer sol-gel route combined with the dip-coating deposition of thin films followed by thermal treatment at 550°C. The SiO_2 and TiO_2 Synthesized from Tetraethylorthosilicate (TEOS; $Si(OC_2H_5)_4$; 98.0% GC), Fluka-Chemika), Tetra Butyl Ortho Titanate (TBOT; $(C_4H_9O)_4Ti$; Fluka-Chemika) as a precursor respectively. In this work, we studied the effect of doping TiO_2 with copper acetate hydrate on the stop-band position of SiO_2/TiO_2 Bragg reflectors was investigated. In UV/visible spectrometry measurements, Fig.1 shows the evolution of the DBR's transmittance spectra with the increasing number of Bragg's pairs, we notice summarizes the transmittance minimum of the Bragg's band at 415 nm rapidly fall reaching a minimum of 0.63% and Fig.2 In this situation, we doped the titanium oxide by copper acetate hydrate (2at. %) we observed a shift in the center of the forbidden band from 415 nm to 506 nm, which corresponds to the visible spectral range(redshift), as well as the broadness of this band and a decrease in the transmittance of the DBR at 506 nm and the transmission coefficient at 1.81%. Which is to say, we've arrived at a good Bragg reflector. These results can be used in optical microcavities, solar chains, waveguides, and lasers. That is to say, responding to specific needs and issues. The study is in progress to improve its characteristics and reach high-performance Bragg reflectors, which allows considering new applications.

Keywords: SiO_2/TiO_2 Bragg Reflector; multilayer; sol-gel; transmission coefficient; red-shift

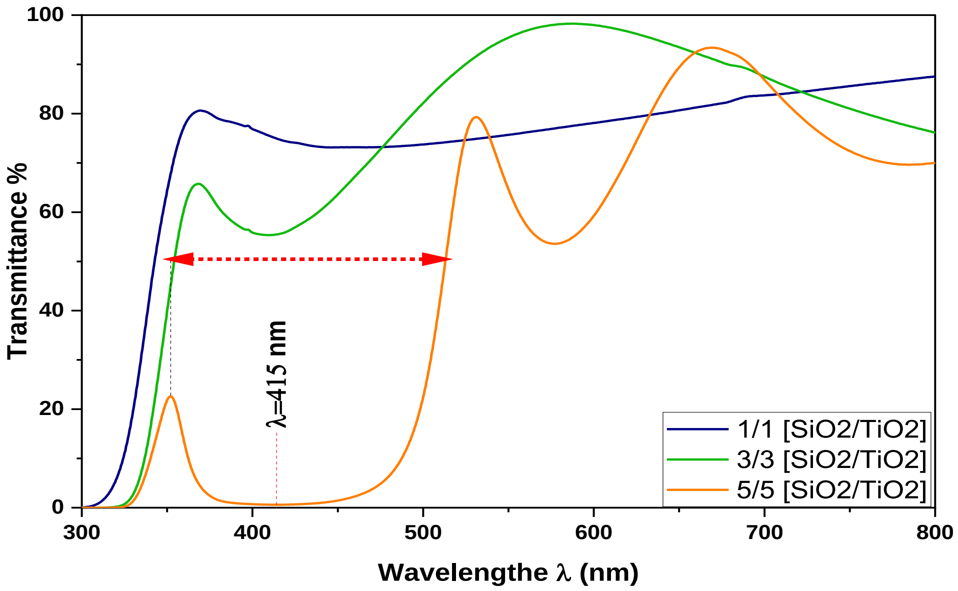

Fig. 1 Evolution of the transmittance spectra DBR as the number of multilayers.

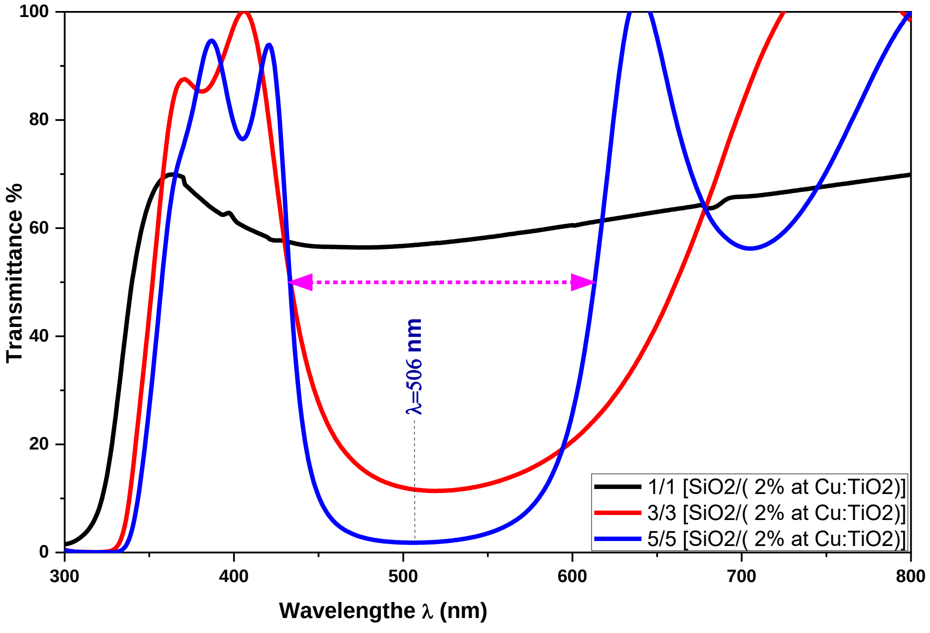

Fig. 2 The transmittance spectra DBR as 2 at.% Cu:TiO_2 and the number of multilayers.

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COLOR MULTIPLEXED IMAGES PRINTED ON PLASMONIC TiO_2:Ag NANOCOMPOSITE FILMS.

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ABSTRACT:

Authentication of goods, storage and displaying of time limited information are parts of hot topics in current societies. To respond to these needs, hiding several images in a single printing, which appear selectively under different angles of observation, could be of great interest. Several techniques have been developed based on holography , moiré methods, specular effects or on the use of dichroic plasmonic colors. An other way is the new technology developed at Laboratory Hubert Curien combining plasmonic nanocomposite films and laser scanning techniques, that leads to the concept of color image multiplexing to multiple dimensions defined by polarization, angle of view or illumination conditions [1,2].

Here, we present the process from the nanocomposite film to the color image. For this, a mesoporous TiO_2 film is synthesized by a sol-gel method before coating on a transparent substrate. Its porosity is filled with silver precursors by soaking the film in a silver salt solution, rinsing, drying and illuminating under UV light. In a second time, the colors are produced by laser processing of these random metasurfaces and they result from a combination of absorption, interference, and diffraction phenomena enabled by laser-controlled shaping and self-organization of metallic nanoparticles, in the TiO_2:Ag nanocomposite thin film. The formed nanostructures and their colors differ depending on the scanning speed, laser power, polarization, focusing, repetition rate or density of the drawn lines. Some examples of printed multiplexed image will be given to show the interest of this path.

Figure 1: Laser printed multiplexed image.

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ADVANCED SOL-GEL IV-VI-DOPED INORGANIC THIN FILMS FOR TEMPERATURE SENSING INSTRUMENTATION

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ABSTRACT:

IV-VI quantum dots-doped SiO_2 and SiO_2-P_2O_5 thin films were prepared by sol-gel method, spin coating technique [1, 2, 3]. Different substrates were used for deposition such as glass, ITO (indium tin oxide) layered on glass and silicon, respectively [3]. Precursor composition, gelation time, substrate rotation speed, number of deposited layers and pH of the precursor sols were changed in order to regulate the hydrolysis and condensation mechanisms to accomplish uniform and homogeneous thin films [3]. H_3PO_4 and diethyl phosphate were used as precursors for P_2O_5 to explore their influence on the gelation time and deposition parameters [4]. Nanostructured materials were obtained by drying and subsequent annealing of the deposited films. The nanostructured network forming role of silicon dioxide and phosphorous pentoxide were evidenced by structural and morphological characterization of the deposited thin films [1, 4]. The optical band gap was graphically resolved in correlation with the size dependent quantum confinement effect, the latter being liable for the optical absorption cut-off and luminescence characteristics [2]. UV-VIS-NIR transmission spectroscopy, photoluminescence, luminescence decay and related measurements were also performed [2, 4]. Various excitation wavelengths were used aiming to choose the performing materials regarding the photoluminescence characteristics, showing the potential application of these nanostructured materials for temperature detection.

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NONLINEAR AND CHIRAL PLASMONIC GLASSES

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ABSTRACT:

Hybrid materials and in particular transparent monolithic materials (xerogels, aerogels) are intensively investigated for optical applications (sensors, filters, imaging, photocatalysis…) [1]. The preparation of 3D composite structures incorporating either molecular entities and/or functional nanoparticles represents a challenge on the way to optical devices. The preparation of monolithic transparent silica-based material using the sol-gel process and incorporation of functional nanostructures (plasmonic, luminescent) will be presented here.

The sol-gel process allows the design of transparent hybrid monolithic xerogels or aerogels. Plasmonic or luminescent nanostructures can be introduced during the process. Plasmonic nanostructures are functionalized in order to allow their homogeneous incorporation in the transparent hybrid silica matrices [2,3]. Co-dispersion of the metallic structures with dyes can be achieved [4,5]. The role of the concentration, shape and size of the metal nanoparticles on the nonlinear optical response is crucial, both in the visible and in the NIR. Similarly, chiral nanoparticles can be introduced to provide chiral properties to the final glass.

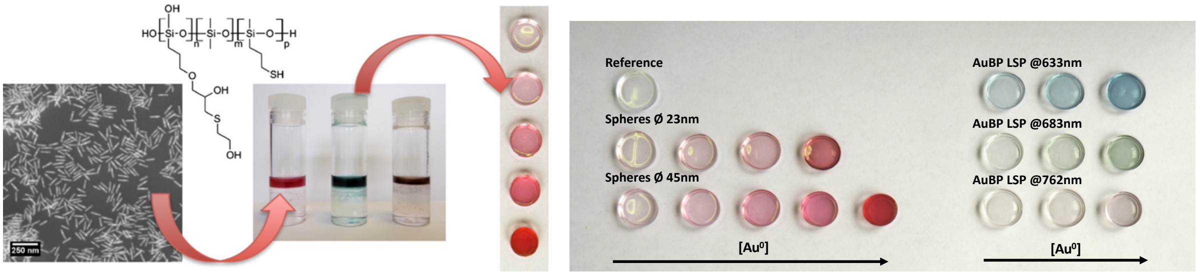

Figure 1 : Surface modification of the metal nanoparticles and transfer inside silica glasses.

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Crystallization kinetics and structural properties of pyrochlore phosphors emitting in short- and mid-infrared

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ABSTRACT:

Thorough scientific attention has been focused in increase the laser's power in short and mid-infrared. Significant advances in fields; such as LIDARs, chemical sensors, etc.; use such high-power lasers. For these laser applications to work, they require efficient luminophores operating in a spectral range safe for human eyes. The solution may be transparent ceramic based on lanthanide yttrium titanium oxides with the formula $(REE_xY_{1-x})_2Ti_2O_7$ where REE is a rare earth element with defined particle sizes and distribution. The homogeneity of prepared materials is dependent on the crystallization mechanism. This contribution clarifies the influence of crystallization mechanism and structure on luminescence properties.

We prepared ceramic luminophores with defined particles size, emitting above 2 um. We used the sol-gel approach for obtaining compounds with a nanocrystal structure of $(REE_{0,05}Y_{0,95})_2Ti_2O_7$, where REE=Yb, Er, Eu, Tm, Ho. We studied the nanocrystal structures and evaluated the effect of the nanocrystal size and phonon energy on the luminescence properties. The crystallization temperatures were found to be in the range of 1061 – 1068 K and they were dependent on the radius of REE ion. The nanocrystal growth for compounds doped by REE was driven by homogenous nucleation with a constant nucleation rate. For undoped compound $Y_2Ti_2O_7$ crystalization mechanisms corresponded to site-saturated nucleation. The obtained results provide key information about the crystallization properties and crystal structure of nanocrystalline luminophores and give necessary information for preparing pure nanocrystalline powders with tailored structural properties that are suitable for photonic applications.

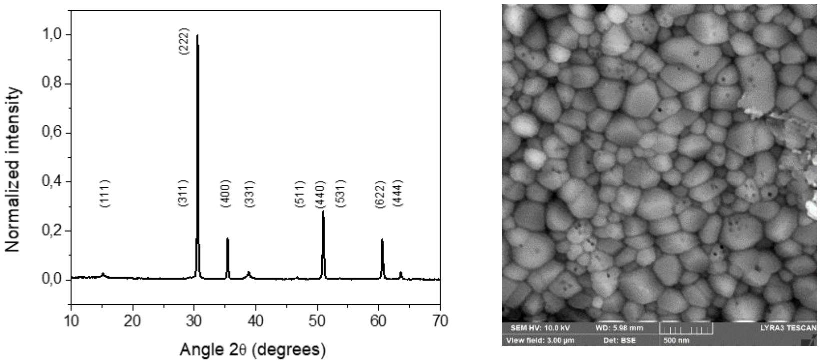

Fig. 1. Example of properties of nanocrystalline $(Ho_{0.05}Y_{0.95})_2Ti_2O_7$. Recorded diffractogram with denoted (hkl) indices on the left. SEM visualization of the sample nanocrystalline structure on the right.

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Understanding the microwave-synthesis of $CsPbBr_3$ perovskite nanocrystals for advanced optoelectronic devices.

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ABSTRACT:

Climate change and environmental degradation, mainly associated to the use of fossil fuels, are existential threats to the world. So, new and more advanced systems with reduced energy consumption have to be developed in order to allow a real energy savings. In this context, the fabrication of low-cost, environmentally-friendly and high-efficiency optoelectronic devices such as solar cells, LEDs, photodetectors, sensors or luminescent solar concentrators, is now more than ever a need to be addressed. The halide perovskites nanocrystals have been emerged as extremely appealing materials due to their promising properties such as high absorption coefficient, tunable absorption and emission ranges, and their high quantum efficiencies.

In this work, we present the microwave-assisted preparation of uniform $CsPbBr_3$ nanocrystals. A systematic analysis of different synthetic parameters was performed (temperature, time, reagents, solvent, etc.) allowed us to have a map of conditions to obtain crystals with controllable morphologies and crystalline phases in one step process. The versatility of microwave-assisted synthesis, not only in reaction time and temperature, but also in the nature of the salts and the solvents (or mixture of solvents), and additional complexing ligands and structure-directing agents, allow us to play with the nucleation and growth mechanisms and even making nano/microemulsions. This opens a land of possibilities for preparing nanostructured halide perovskite material, with a broad range of applications.

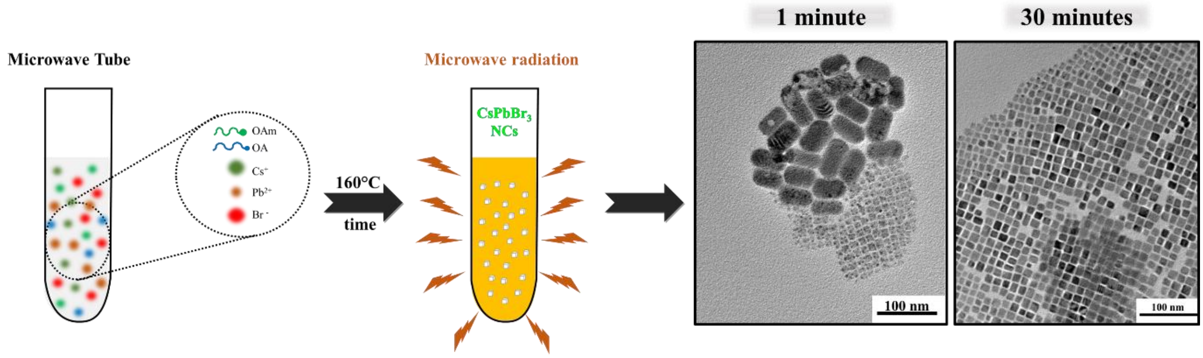

Figure 1: Proposed growth process of $CsPbBr_3$ NCs through the microwave-assisted synthesis approach and structural characteristics.

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Industrialization of sol-gel science and technology

AMMONIAC HARDENING WITHOUT CRAZING FOR SOL-GEL LAYERS

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ABSTRACT:

The Laser MégaJoule, operating in France near Bordeaux, for CEA's Simulation Program requires optical components in transmission working in NIR (1053nm) or UV-range (351nm). These windows, lenses and crystals are coated via sol gel processing with silica-based materials. Nevertheless, the layers made by this soft chemical process are brittle and hardly handleable without a post-treatment. Presently, the best industrial post-treatment is the ammoniac hardening. However, it is a very long process, (17 hours) which sometimes induces micro-crazing [1] in particular when layers are thick (Cf. Figure 1). In the present work, several characterizations, to analyze and control successfully the crazing effect, are described [2, 3]. In particular this study demonstrates that the processing time can be reduced by a factor of 2. Moreover we will present conditions that will lead to fully solve the stress-induced micro-crazing effect.

Figure 1 : Title 1

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AN INNOVATIVE CONCEPT FOR INDUSTRAL SCALE PRODUCTION OF PEROVSKITE BASED PHOTOVOLTAIC CELLS

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ABSTRACT:

The project is about the development of an innovative deposition system, industrially scalable, to produce complex multilayer devices, whose diffusion is often held back by the production technologies adopted, which do not lend themselves to low-cost mass production. The problem is particularly felt in the case of new generation photovoltaic cells, and among these the perovskite-based cells, whose efficiencies are now comparable with those of commercial Si cells, but with estimated production costs greater than one if not two orders of magnitude, which holds back any hypothesis of industrial exploitation of the results obtained from research in the field.

The feasibility will be demonstrated through the construction of proof-of-concept cells, with dimensions equal to those of commercial Si cells, i.e., 150x150 mm.

To achieve the general objectives of the project, the intermediate objectives listed below will be pursued:

- Identification of the optimal materials and architecture for the construction of a 2-terminal perovskite/silicon tandem cell through continuous process technologies;
- Optimization of an innovative process for the deposition of layers using sol-gel.

Hybrid coatings for writing surfaces - whiteboards

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ABSTRACT:

Hybrid organic-inorganic materials based in the polydimethylsiloxane – silica (PDMS-SiO_2) system are known to be of great interest due to their wide range of possible applications, namely as biomaterials, anti-corrosion, anti-fouling, or anti-reflective coatings [1]. In the present work a new PDMS-SiO_2 hybrid coating was developed with the aim of eliminating the "ghosting" effect, which is characterized by the permanence of marker ink residues that remain on the writing surface of the whiteboard. To date, no whiteboard producer has also managed to eradicate the "ghosting" effect. In addition to the writing tests (which determine the degree of ghosting), the structural characterization results as well as the roughness, wettability and wear parameters will also be presented. The structures of the hybrid materials were analyzed by FTIR, ^{1}H MAS (magical angle spinning), ^{29}Si MAS and ^{29}Si-{^{1}H} CP-MAS (cross-polarization magical angle spinning).

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New Insights into the Growth Mechanism of WO_3 Gels by In-Situ Liquid-Phase TEM and Time-Resolved DLS.

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The electrochromic and photocatalytic properties of tungsten oxide (WO_3) find broad applications in display devices, smart windows or degradation of pollutants [1]. The synthesis of WO_3 does not require high temperatures, and soft methods fitting into “chimie douce” concept are well-established [2]. Following the sol-gel routes, it is possible to obtain WO_3 gels by acidification of tungsten salt solutions. The acidification leads to hydrolysis and consecutive condensation first to polyoxotungstate species and further to gel-like structure. Although the process has been studied by various techniques [3], we still lack the understanding on how the charged polyoxometallate species react with each other and form a gel.

Several models have been proposed, based on the condensation of a hypothetical “zero-charge complex” by hydroxylation and oxolation [4]. The recent developments in TEM, in particular the emergence of the in-situ Liquid Phase TEM (LP-TEM), may provide new insight into the nucleation and growth processes of WO_3-based nanostructures, with a particular focus on the early steps of gel formation.

Herein, using the ability of LP-TEM to monitor nanometric processes in real space, we report a first picture of the growth of WO_3 gels. This in situ analysis highlights several possible pathways for the growth mechanism, including the diffusion-limited cluster aggregation process. Indeed, a closer look into the reaction environment (Figure 1) reveals the presence of well-defined clusters, with a nanometric size, which apparently plays the role of elemental bricks for gel formation [5].

To further improve the comprehension of the first growth events, we have also carried out time-resolved DLS measurements for different tungsten salt concentration. As expected, a decrease in concentration (Figure 2b) lead to a decrease in intensity but, at the same time, we find similar sizes (Figure 2a), indicating the presence of precursors of few nm. In complement to these data, we also carried out ^{183}W NMR to show the presence of decatungstate polyanions in solution which seems to be the last existing species before gel formation and source of W during gel formation.

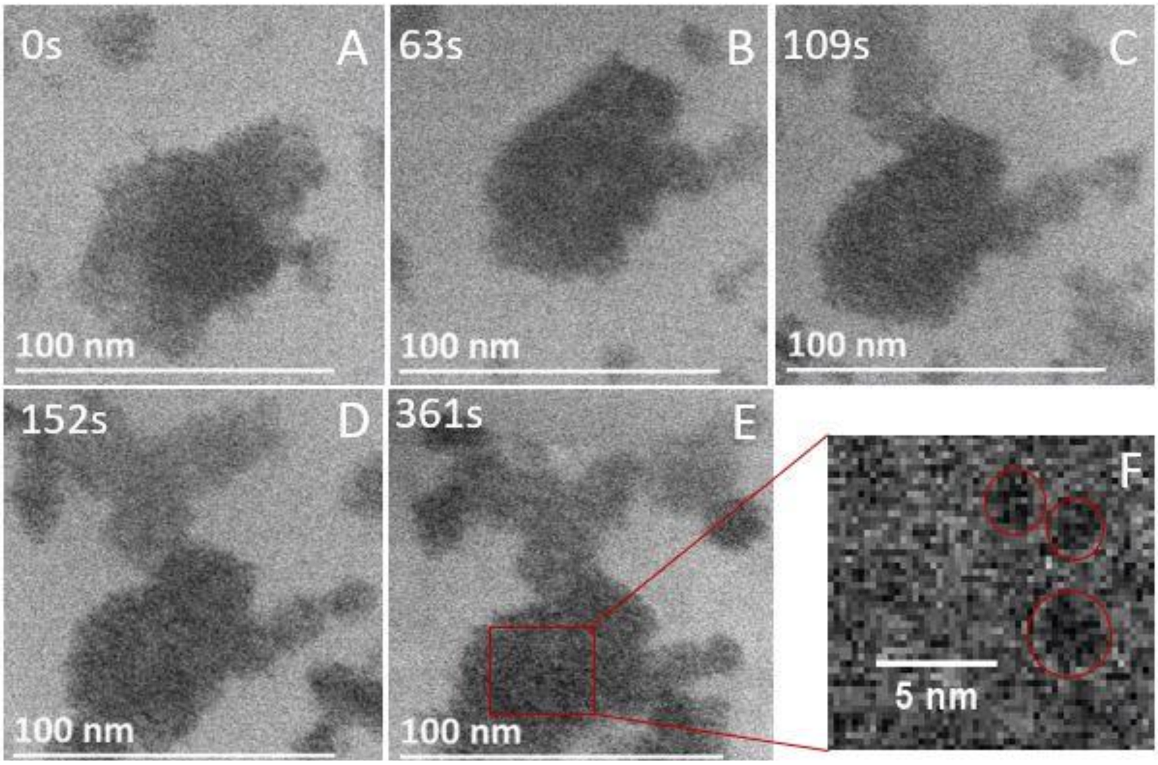

Figure 1: A-E: LP-TEM images of WO_3 gel growing by Diffusion-Limited Cluster Aggregation (DLCA). F: Zoom on the gel structure highlighting the presence of clusters with a few nm sizes.

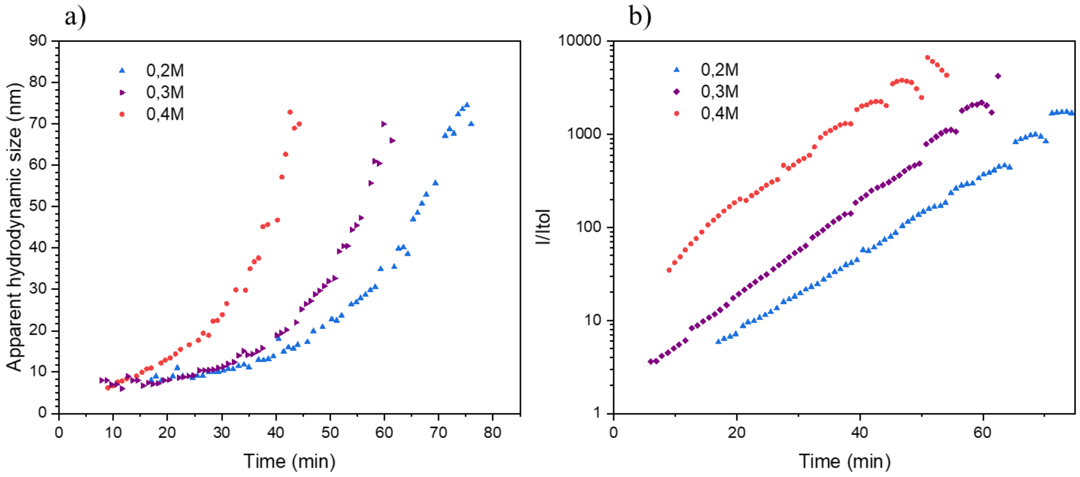

Figure 2: Time-resolved DLS measurements revealing the time evolutions of apparent hydrodynamic size (a) and of the absolute intensity (b) of tungsten gel precursors for different tungsten salt concentrations.

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