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Nanomaterials & Application

BOOK OF ABSTRACTS

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PLENNARY LECTURES

Biopolymers, their surface modifications and characterization and their potential application in biomedicine

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Polymer based biomaterials possess many advantages. Among others it is their flexible processability into various shapes employing a broad range of forming methods known for polymers. Understanding interactions of solid biomaterials with living systems or their constituents (proteins, nucleic acids, oligo- and polysaccharide, lipids) is prerequisite for applications in regenerative medicine, as vascular grafts, as biosensors or as low protein fouling layers. Studying the surface properties of these materials allows for a correlation of the physicochemical composition, morphology and wetting, with polysaccharide, protein or living cells' adhesion or growth on these materials. In that respect polymeric thin films and coatings are useful for basic investigations of interactions due to their defined character, reproducible preparation and accessibility to modern surface analytical techniques. Among these techniques are atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), quartz crystal microbalance (QCM-D), surface plasmon resonance (SPR) and fluorescence microscopy. Polymeric biomaterials can further be coated on specific substrates or shaped into 3D printed, nanofibrous or particulate objects useful for mentioned biomedical applications. This lecture will give examples on what kind of chemical reactions and surface modifications can be performed with biodegradable or bio-based polymers and how these materials can be processed into various shapes ranging from thin films to 3D printed objects. Besides processing, examples on detailed surface interaction studies will be given.

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Some Recent Developments on the Synthesis of Inorganic Functional Nanomaterials

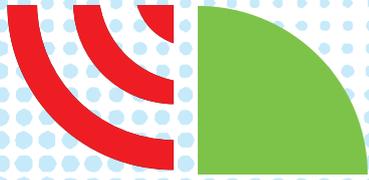
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Inorganic functional nanomaterials exhibit diverse fascinating functions arising from their size, dimension, composition, electronic structure, crystal structure, porosity, etc. The controllability of the composition, structure, and morphology of inorganic functional nanomaterials depends on the synthesis, and the development of synthetic methods is critical to greatly advance the field of functional nanomaterials. Studies on their chemical syntheses can contribute to create new materials and their applications because the designability of formed nanomaterials largely depends on synthetic methods. Silica- and siloxane-based porous materials have not yet been developed from the viewpoint of precise synthesis. In this presentation, some recent developments on the synthesis of inorganic functional nanomaterials and their potential precursors, that have been conducted in my group, will mainly be presented.

Various building blocks can be used for their ordered arrangements toward preparation of porous materials. Cage-type siloxane oligomers are attractive zero-dimensional (0D) compounds as building blocks for silica-based ordered materials. The dimensional conversion from 0D to 3D can be controlled by various ways, including the use of directional hydrogen bonding. Introduction of heteroatom among siloxane cages can also be possible, which will be useful for further precise design of silica-based porous materials. Among various inorganic layered materials layered silicates are unique 2D building blocks for the construction of 3D crystalline silica with confined nanospaces. Dimensional conversion from 2D to 3D has its own advantage to accommodate guest species between the layers. In particular, metal incorporated microporous crystals are expected to act as high performance catalysts. Layered metal hydroxides are also attractive materials because of their compositional varieties and layer surface modification. Silica nanoparticles can be regarded as building blocks for construction of mesoporous materials by preparing colloidal crystals. Their interstices are regarded as pores in the range of mesopore size if the size of silica nanoparticles are chosen appropriately. Au nanoparticles with carbon linkers, having nanospace among them can be created. This idea can be extended to the preparation of crystalline metal oxides.



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KEYNOTE LECTURES

Ultrafast switching in 1T-TaS₂ charge configuration memory (CCM) devices

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Frustrated charge density wave systems can minimize their energy by forming different domain configurations of commensurate phase separated by intricate patterns of fractionally charged domain walls. Switching between different domain configurations can be very fast, and the accompanying change of resistance may be fruitfully used for non-volatile memory devices. We show that in 1T-TaS₂, the prototype low-temperature memory material, switching occurs in less than 500fs, while the retention time is tunable by temperature. The switching energy is currently demonstrated to be < 70 fJ with 40 ps electrical pulses with a 4 μm device, and is shown to scale with device dimensions. Functional devices down to 40 nm feature size have been demonstrated with 4 ns electrical write pulses and endurance exceeding 10^7 cycles without degradation. The microscopic charge configurations in different resistive states can be imaged by scanning tunneling microscopy, showing a complex dual vortex structure. Non-trivial defects created during the quench appear to stabilize the non-volatile memory state. With projected switching energies in the atto-J range, THz speeds and low-temperature operation, such CCM are ideal for forthcoming cryogenic and quantum computing memories.

Molecular models of hybrid nanomaterials

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Metal oxide nanoparticles emerge via nucleation in sol-gel processes in organic media. Both hydrolytic and non-hydrolytic reactions produce in one-step nano-size molecular species, with apparent core-shell structure, resembling oxo-metallates formed on partial hydrolysis in both aqueous and organic media. In the present contribution, we will present a broad variety of model molecular species on the way from alkoxide precursors to oxide nanoparticles. In these species, we utilized ligands actively used in preparation of hybrid organic-inorganic materials such as substituted phenols ^[1, 2] and phosphonic acids ^[3]. Different ligand-to-metal ratios and acidity conditions were applied to reveal the principles in formation of the structures. It could be noticed that the core is always well-ordered and often can be identified as crystalline sometimes even by X-ray studies, and more securely by electron diffraction in TEM. It bears generally an imprint of the corresponding solid phase resulting from dense packing of metal cations and oxygen anions. The shell contains residual organic ligands inherited from the precursor molecules and is amorphous. This insight into reaction mechanisms permits to control the size and shape of resulting particles, their hydrophilicity/hydrophobicity and surface reactivity. Hydrolytic approach leaves most often some residual hydroxide groups and solvating water molecules on the surface of the particles contributing to the amorphous shell. Higher temperature solvothermal reaction offers generally much better crystallinity than the room temperature hydrolytic one. Elevated temperature helps to improve the diffusion of metal ions and removes the hydroxide and organic residues from the surface. The control of crystallinity and composition and structure of the shell define surface interactions of the produced particles and their both solution and chemical stability in biological systems and in the environment ^[4].

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An enhanced generation of singlet oxygen through the use of Au bipyramids/SiO₂ core-shell nanoparticles for application in photocatalysis

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Gold nanomaterials display interesting nanoplasmonic features with potential application in various fields depending on the size and shape of the metal nanoparticle (NP). Au bipyramids (AuBPs) exhibit intense and well-defined plasmon resonance, easily tunable with the aspect ratio and synergy between Au NPs and chromophores can enhance the photophysical properties of nearby molecules. In Rose Bengal (RB)-NPs systems for the production of singlet oxygen (¹O₂), it is now well established that the control of the dye-to-NP distance ranging from 10 to 20 nm is crucial to achieve the proper coupling between plasmon resonance and the dye^[1]. We have developed AuBPs@mesoporous SiO₂ core-shell nanostructures to control the distance between metallic surface and photosensitizers in order to increase the production of ¹O₂ through metal-enhanced fluorescence (MEF). An enhancement of ¹O₂ generation has been shown with the obtained anisotropic AuBPs and AuBPs@mSiO₂ in presence of RB using different methods of ¹O₂ quantification. They are of interest to the application in photooxygenation reactions *e.g.* α-terpinene to ascaridole, an anthelmintic drug.

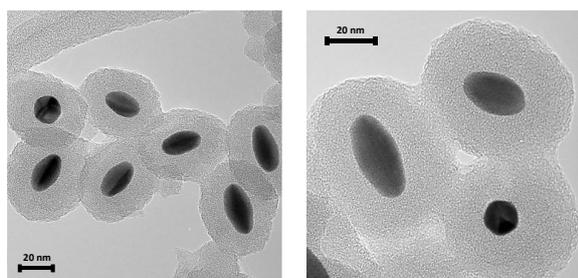


Fig. 1. TEM images of AuBPs@mSiO₂ at 280kX and 490kX

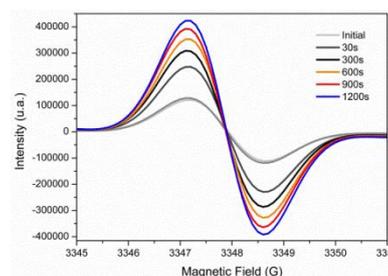


Fig. 2. EPR/TEMP spectra of AuBPs@mSiO₂ in presence of RB under visible irradiation as a function of time

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Plasmonic affinity biosensors and their medical applications

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The need for rapid and sensitive detection of biomolecules and investigation of their interactions exists in numerous fields, such as molecular biology, medical diagnosis, food safety and security. Optical affinity biosensors based on surface plasmons (sometimes referred to as surface plasmon resonance (SPR) or plasmonic biosensors) represent the most advanced optical label-free biosensor technology and hold potential to meet this need ^[1, 2].

We shall discuss selected recent advances on multiple fronts of plasmonic biosensor research. These will include advances in the design of plasmonic nanostructures and the development of optical platforms for high-performance plasmonic sensors as well as functional coatings. In addition, transport of target molecules in microfluidic systems of plasmonic biosensors will be also discussed and routes to improving performance of nanoplasmonic biosensors will be outlined ^[3].

Examples of medical applications of plasmonic biosensors will be also given. We shall describe the use of plasmonic biosensors to investigate biomolecular interactions related to Alzheimer's disease. In particular, we demonstrate the binding of mitochondrial matrix protein 17 β -hydroxysteroid dehydrogenase type 10 to cyclophilin D (cypD) which can affect the opening of the mitochondrial permeability transition pore mediated by cypD. We shall also report on plasmonic biosensors for diagnosis of myelodysplastic syndromes (MDS). MDS is group of hematological malignancies with a risk of evolution into acute myeloid leukemia. We use a plasmonic imaging biosensor and an array of proteins immobilized on the surface of the sensor to quantify interactions between the immobilized proteins and blood plasma samples, and demonstrate that this approach allows for discrimination among different MDS subgroups and healthy donors.

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Optical sensors based on micro- and nanocellulose materials

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Functional textiles and non-wovens are presented that combine micro- and nanostructured cellulose with indicator chemistry. Thus, sensor materials are obtained that can be used in wound dressings to detect the onset of infections, or that are deposited onto polymer foils to measure amines during food spoilage.

In detail, bacterial nanocellulose is functionalized with pH sensitive indicator dyes to yield materials that detect pH in wounds via colour changes from yellow to red. Since the indicator dyes are covalently linked to the fibrous nanocellulose, no leaching or contamination is observed, which is mandatory for use in practical applications.

In another approach, crystalline nanocellulose is modified with fluorescent dyes and deposited via aerosoljet printing onto various substrates, i.e. textiles. The generated materials can be used to measure e.g. vaporous acids or bases in the work environment.

Furthermore, cellulose microparticles are functionalized with indicator dyes which show a colour change from green to red when brought into contact with amines that are formed e.g. during spoilage of meat. These coloured microparticles are embedded into silicone and, consequently, are no longer cross-sensitive to pH changes [1].

The sensor materials are characterised in terms of response performance. Also, the generic synthetic approach of the dyes is pointed out, allowing a whole range of new ion-sensitive dyes and fluororeactants to become available [2].

The vinylsulfonyl group used for covalent linkage of the indicator dyes to cellulose is particularly attractive because the ether bonding guarantees exceptionally long lifetime. In contrast to e.g. the amide linkage, it can withstand washing cycles in alkaline medium at temperatures up to 95° Celsius, steam-heat ironing and sterilisation [3,4]. The materials have been shown to be non-cytotoxic and, when immobilised onto textiles, to be OekoTex® class 1 approved. The same indicator chemistry has also been linked to biomaterials such as wool or collagen.

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Autonomous nanomaterials for the controlled delivery of biologically active molecules

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The development of materials for the controlled delivery and release of biologically active molecules, such as pharmaceuticals, is currently an area of intense research interest. A variety of strategies have been described in the literature, ranging from simple approaches that exploit physical characteristics of the delivery vehicle such as size, pore tortuosity, etc to control the delivery of a drug payload, through to sophisticated autonomous systems that respond to environmental parameters such as pH to trigger release of the payload. Key prerequisites for such systems include biocompatibility, control of release rates, high loadings and protection of payloads, enhanced shelf lives, efficient targeting, minimal premature release and efficient cellular uptake.

This talk will discuss a range of such strategies, beginning with the synthesis of simple nanoparticle systems with controlled porosity (exploiting control of delivery via parameters such as particle size) through to sophisticated autonomous systems that are capable of delivering two or more drug payloads in response to an environmental trigger such as pH. Two key examples of the latter approach will be described:

- Beginning with silica-based materials with engineered porosity (MCM-41), a functional molecule capable of molecular recognition (stalk) is grafted onto the external surface of the material. The pores are then filled with an oncology drug (such as camptothecin). The pore apertures are subsequently “closed” by addition of a second molecule that is complexed by the stalk, and which serves as a cap. The stalk and cap can be tailored to respond to external stimuli such as pH, with the cap being released by the stalk within a target pH range, thus releasing the drug payload. The cap itself can also serve as a drug, opening up the possibility of designing sophisticated combination therapy systems.
- A limitation of this first approach is that the pores are relatively small, limiting the range of biologically active species which can be incorporated. The use of polyionic complex (PIC) micelles, which are complexes formed between opposite-charged polyelectrolytes, enables materials with pore sizes of around 8 nm to be prepared, thus providing opportunities for encapsulating and releasing a wider range of biologicals. An important characteristic of such systems is that the formation of the micelles occurs within a well-defined pH window, enabling their aggregation and disaggregation to be controlled via the external pH. The use of a drug molecule, such as neomycin B, as one component of the PIC micelle thus enables biologically active species to be directly incorporated into the evolving structure with relatively high loadings and subsequently released in response to changes in pH.

In-vitro tests demonstrating the efficacy of such autonomous nano-systems against cell lines such as breast cancers (first case) and bacteria such as *E. coli* (second case) will be described.

Functionalization of porous silicon nanoparticles for controlled nucleic acid delivery.

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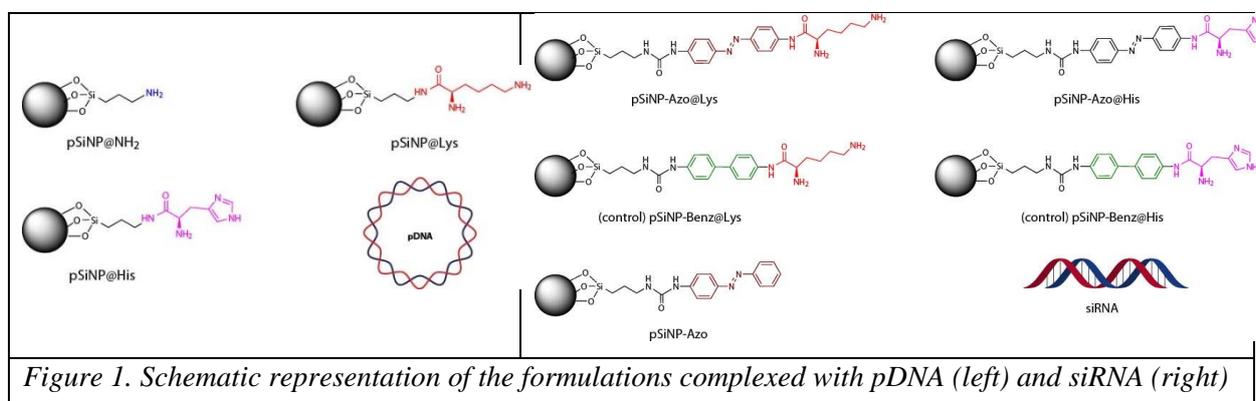
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Mesoporous pSiNp (50-150 nm) with narrow size distribution and a high surface area were prepared by electrochemical etching of single-crystal silicon wafers in an ethanolic hydrofluoric solution, removal of the porous layer, ultrasonic fracture and centrifugation according to established procedure.[1] The pSiNp were chemically functionalized for the complexation of nucleic acids. Several formulations were prepared by functionalizing the fresh pSiNp using silanisation chemistry to anchor functional aminated ligands for further grafting of amino-acids (histidine, lysine). Positive charges beared by the amino-acids allow electrostatic interactions with nucleic acids. The grafting of the organic moieties on pSiNp were characterized with different techniques: zeta potential, FTIR, solid-state NMR and gel retardation assay.



Furthermore, *in vitro* experiments confirmed two important issues, 1) The influence of the *azo* groups in siRNA delivery in MCF-7 *luc* cells upon two photon irradiation. 2) Expression of luciferase in HEK-293 cells upon incubation of functionalized pSiNp complexed with pDNA.

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Designing the microstructure of solution-derived ferroelectric-oxide thin films

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Ferroelectric-oxide thin films can serve as flexible and reconfigurable components that enable miniaturization of electronic devices and systems. For example, barium strontium titanate, $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ $x=0-1$, or shortly $(\text{Ba,Sr})\text{TiO}_3$ is one of the most studied microwave ferroelectric materials. In paraelectric phase but still close above its composition-dependent Curie temperature $(\text{Ba,Sr})\text{TiO}_3$ exhibits high dielectric permittivity, high voltage tunability and low dielectric losses at microwave frequencies. $(\text{Ba,Sr})\text{TiO}_3$ thin films have been used as active parts of frequency-agile components suitable for earth and space communications, contributing also to compactness with reduced dimensions.

In barium titanate the relation between the grain size and dielectric properties – the dielectric grain size effect – has been extensively studied; and in general, the permittivity increases with increasing grain size. In thin films (thickness range typically from a few 10 nm to a few 100 nm) not only the composition but also presence of residual stresses, electrodes and microstructure of the films, i.e. size and shape of the grains strongly influence their functional properties. In Chemical Solution Deposition of thin films, the microstructure develops in the process of crystallization from the as-deposited amorphous film. Control of nucleation – homogeneous or heterogeneous – and growth processes is thus critical in the design of the microstructure. In the contribution we discuss the evolution of microstructure in $(\text{Ba,Sr})\text{TiO}_3$ thin films. Controlling the processing parameters, mainly the thickness of individual deposited layers in relation to the total film thickness, and the heating regime enables the design of the microstructure, and consequently of functional properties of the studied films.

Structure and magnetic properties of hexaferrite and bi-magnetic hexaferrite/maghemite nanoplatelets

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Barium hexaferrite (HF) nanoplatelets display a high uniaxial magnetocrystalline anisotropy with an easy axis that is perpendicular to the platelet. This unique property gives them tremendous potential in innovative applications, for example, in the magneto-mechanical eradication of cancer cells. As the nanoplatelets adopt a distinct structure and composition, which are significantly different to the bulk, they can be considered as novel structural variations of hexaferrite stabilized on the nanoscale. For example, the structure of the normally used nanoplatelets (~ 50 nm wide and 3 nm thick) can be represented by a SRSRS stacking sequence, where S and R represent a hexagonal $(\text{BaFe}_6\text{O}_{11})^{2-}$ and a cubic $(\text{Fe}_6\text{O}_8)^{2+}$ structural block, respectively. The weak point of the HF nanoplatelets is their modest saturation magnetization, M_s . The M_s can be effectively increased by coating them with a shell of soft-magnetic maghemite ($\gamma\text{-Fe}_2\text{O}_3$ - M). Given the cubic S block termination of the platelets, layers of M, with a cubic spinel structure, can be easily grown epitaxially, forming a sandwiched M/BHF/M platelet structure (Figure 1). As the two phases are magnetically exchange-coupled the formed composite nanoplatelet homogeneously magnetizes like a single-phase particle.

In the lecture the evolution of the structure and the magnetic properties with the growth of the HF nanoplatelets, as well as the synthesis and the magnetic properties of the composite nanoplatelets, will be presented.

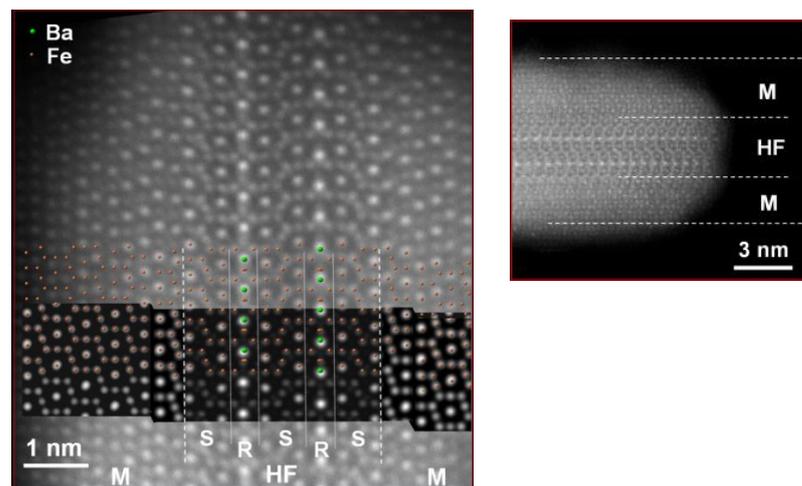


Figure 1: HAADF STEM images of composite nanoplatelet composed of a hexaferrite (HF) core in between of two maghemite (M) layers with the calculated images for HF ($\langle 10\text{-}10 \rangle_{\text{HF}}$) and M ($\langle 101 \rangle_{\text{M}}$).

The role of surface chemistry on physico-chemical properties of nanoparticles

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A high surface-to-volume ratio of nanoparticles with the related high chemical reactivity allows us to tune their surface chemistry for a variety of applications. However, the high surface reactivity also lowers the chemical stability of nanoparticles in comparison to bulk materials of the same composition and structure. We will discuss beneficial and harmful effects of surface ligands on the physico-chemical properties of nanoparticles. A more in depth presentation will include two examples from our studies.

First, we will focus on lanthanide-doped NaYF₄ nanoparticles. NaYF₄ nanoparticle co-doped with Yb³⁺ and Er³⁺, Tm³⁺ or Ho³⁺, i.e., upconverting nanoparticles (UCNPs), emit visible or near infrared light after an excitation with a lower-energy near infrared light. They have been studied as alternative multimodal biomarkers but their usage is being questioned due to surface quenching of the luminescence and chemical instability in aqueous media. The effect of surface chemistry on the luminescence surface quenching and dissolution of UCNPs in aqueous media will be discussed. Some surface ligands even show the opposite effects. Although, they increase the brightness of UCNPs due to the reduction of surface quenching they also promote their dissolution [1]. We will propose the optimum surface chemistry for keeping the UCNPs bright and chemically stable.

Second, we will present a surface chemistry optimization of magnetic nanoplatelets (NPLs) that led to the development of the first ferromagnetic (FM) liquid [2] and a room-temperature liquid magnet. The magnetic NPLs are based on barium hexaferrite (BHF) with the magnetization aligned perpendicular to the basal plane. The physisorption of dodecylbenzenesulfonic acid (DBSa) on the NPLs surfaces allows for their dispersion in alcohols or nematic liquid crystals. In the latter case, a FM liquid is formed since the magnetic NPLs are FM coupled a liquid-crystalline medium [2]. Furthermore, FM ferrofluids are formed in highly concentrated suspensions of magnetic NPLs in alcohols. They are liquid magnets with a spontaneous magnetization and form magnetic domains even in the absence of an applied magnetic field. In contrast to the DBSa, phosphonic ligands induce a surface dissolution of the BHF NPLs, dispersed in water. We will show the first evidence of the dissolution of BHF NPLs since BHF is considered as practically insoluble in water. A possible dissolution mechanism will be proposed.

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Towards Programmable and Intelligent Nanosystems based in Mesoporous Materials

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In the last decade, a significant advance took place in materials chemistry. Two key factors of this progress are the development of reproducible nanomaterials synthesis, and the control of self-assembly processes. The combination of these powerful concepts leads to produce multiscale materials with hierarchical architectures, which mimic the complexity of those found in Nature.

Mesoporous materials (MM) with high surface area and controlled mesopore diameter (2-50 nm) are an example of these complex nanosystems. The pore architectures can be finely tuned and “decorated” with organic, biological or nanoscale functions. This field evolved from the mere production of high surface area matrices to programmable nanosystems, in which confinement effects, responsivity, or collaborative functionality can be imparted into the structure through the control of positional chemistry of a variety of tunable chemical or nanostructured building blocks.

The richness of this emergent field will be presented by discussing the design pathways to MM with finely tuned pore size, connectivity, surface or wall nature. Mesopores can be then modified by molecular species, biomolecules, polymers or nanospecies, leading to hybrid MM with an amazing variety of chemical behaviors. An exquisite tuning of the properties can be achieved by combining synthetic and characterization tools with theoretical models and simulations, essential to understand the complexity of the synthesis paths and the final properties. This in-depth basic knowledge is key to ultimate nanosystems design.

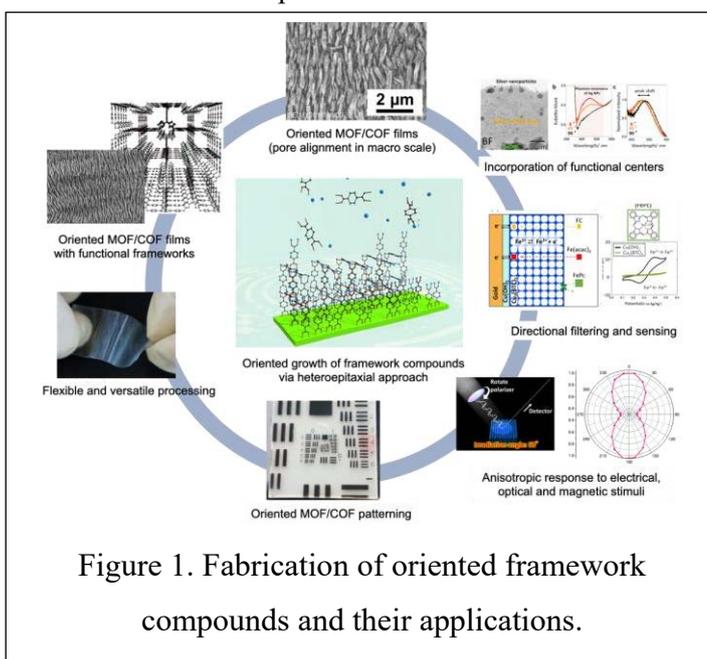
The combination and feedback of synthesis, characterization and modeling leads to pre-designed nanosystems with complex structures and well-defined functional location. Confinement, interactions and localized reactivity can be used as topological tools for building nanosystems able to host different chemical or biochemical groups with highly controlled positioning and interactions. These concepts permit to build tunable catalysts, enzyme cascade hosts, intelligent bioscaffolds, remotely activated nanoparticles, chemical-to-optical transducers or perm-selective membranes. A potentially infinite variety of nanosystems with externally controllable behavior is at our disposal, opening the path to design intelligent matter with wide applicability in wearable sensing, prosthetics or theranostics.

Aligning pores in framework compounds via sol-gel approach

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Framework compounds such as metal-organic frameworks (MOF) and covalent organic frameworks (COF) are characterized by their micro pores which offer a huge accessible surface for applications in gas storage, catalyst and others. Additional functionalities for electronics, photonics and magnetics applications can be attained by an accommodation of functional guests (molecules, ions, or nano objects) into such pores[1]. An achievement of device scale MOF/COF thin films with controlled crystallographic orientations has been required to enhance these sophisticated functionalities for real applications. Recently, the authors have reported the heteroepitaxial growth of MOF via solution processing of the precursor metal hydroxide oriented films[2]. The resultant MOF film exhibited crystallographic orientation along all three axes, which can be used as quasi-single crystal because pores are aligned to the specific directions in the macroscopic scales. In this presentation, recent advances on the fabrication and application of the oriented MOF/COF films will be reviewed. Topics include (see Figure 1)[2-7]: fabrication of oriented MOF/COF films via solution processing, versatility of the epitaxial growth approach, impregnation of functional molecules and nano particles, and others.



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Tailoring properties of nanoporous materials for efficient CO₂-capture

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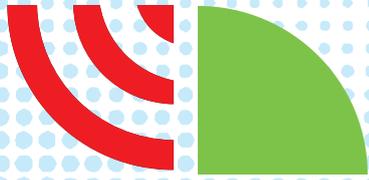
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Intensive research on technologies for efficient CO₂ capture has been recently dominated by investigations on porous materials with tailored properties for sorption-based CO₂ capture with reduced recovery-energy-penalties. Studies revealed three most promising groups of porous materials: (1) zeolites and porous silicas; (2) metal-organic framework materials (MOFs); and (3) porous carbon materials. Each group has their particular advantages and disadvantages, depending also on the specifications of the gas mixture, temperature and pressure during adsorption, the contact time and diffusion issues in dynamic processes.¹ Zeolites in general show very high CO₂ uptake at low CO₂ partial pressures and high selectivity against N₂. The limitations of zeolites for CO₂ capture are mainly due to narrow pores, which cause slow capture process and consequently slow diffusion of gases, and strong affinity of zeolites to adsorb water, which is regularly present in the flue gasses. Recent optimisations of MOFs for CO₂ capture applications revealed some new materials that show superior capture capacities and selectivity with respect to zeolites. Disadvantages of MOFs for large scale CO₂ capture applications are mainly sensitivity to moisture, causing degradation of crystalline structure and severe reduction of performance in multiple cyclic adsorptions, less mature shaping procedures and process engineering comparing to zeolites. On the other hand the CO₂ capture performances of more hydrophobic carbons are less sensitive to the presence of water but their chemical inertness provides typically lower CO₂ uptakes and selectivity against N₂ compared to the zeolites and MOFs. In the light of searching for an adsorbent, which would fulfil the requirements for efficient post-combustion CO₂ capture even in the presence of water, we developed some new approaches of materials preparation and optimisation. Innovative methods, which will be presented in the lecture, include functionalization of MOF with different amine groups and/or immobilization of zeolite- and MOF-nanoparticles within mesoporous matrices, including mesoporous silicas and polyHIPEs (polymerized high internal phase emulsions).

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INVITED LECTURES

Catalytic water cleaning using nanoporous materials

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Organic compounds are one of the most important groups of pollutants present in wastewater. Advanced oxidation processes (AOPs) have recently been intensively investigated because they can generate highly reactive free hydroxyl radicals, which decompose organic pollutants to inorganic compounds such as H₂O, CO₂ and inorganic species. Fenton AOP is one of the AOPs with an advantage. It does not require costly reactors, which is important for industrial application. The currently used Fenton AOP in commercial applications is an iron based Fenton catalytic system based on iron salts as catalysts dissolved in the system (homogeneous catalytic system) and hydrogen peroxide as an oxidant working at pH = 3. However, this catalytic system has two of environmentally important drawbacks such as 1) the operation of the system in acid conditions (pH=3) and 2) the presence of iron ions after the reaction in the effluents. In our previous work, we designed a manganese based Fenton-type catalyst on porous silica support working in heterogeneous catalytic system and at neutral pH as a highly promising alternative.^[1-3] However, only one drawback of iron based Fenton catalytic system was solved in this way. The solution of second drawback of iron based Fenton catalytic system, which means to prevent a presence of metal ions in the effluents after the reaction, is the focus of this lecture. We will present a design of bimetal catalyst on porous silica support working at neutral pH and Fenton or photo-Fenton conditions.^[4]

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Mesoporous metal oxide anodes for Li-ion batteries

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Lithium-ion batteries are today most attractive rechargeable batteries due to high energy storage per unit volume and weight. However, their performance still needs further development for use in high energy density applications, e.g., cars and large scale energy storage. Thus an important direction is improvement of anode materials. Tin oxide is a material that attracted a lot of interest because of its high theoretical capacity. It was demonstrated that mesoporous anodes composed of nano sized SnO₂ particles (NP) show substantially higher specific capacities, rate performance, coulombic efficiency, and cycling stabilities compared to available commercial tin oxide. A discharge capacity of 778 mAh g⁻¹, close to the theoretical limit of 781 mAh g⁻¹, was achieved ^[1].

Investigation of NP tin oxide at different cycling conditions and higher temperature could extract more than the theoretical capacity. All initial capacities in this case show values above 1600 mAh/g, due to formation of soluble electrolyte reduction products and partial dissolution of solid electrolyte interphase species. The most stable behavior over 120 cycles was obtained at room temperature or at cycling with a fast rate at elevated temperature.

To make batteries cheaper and more environmentally friendly, materials with low toxicity, abundant in the nature, and low in cost are required. In this sense iron oxide is ideal for next generation anode materials. NP of γ -Fe₂O₃ are successfully prepared via facile hydrolysis of iron iodide complex precursor with following oxidation under mild conditions. Electrodes of γ -Fe₂O₃ NPs initially deliver capacities of 1100 mAh g⁻¹ and increase by up to 300 mAh g⁻¹ by following an activation step of the electrodes ^[2].

The electrodes produced from obtained in reducing media MnO₂-nanostructures were tested as electrodes of lithium ion batteries delivering initial discharge capacities of 968 mAh/g for anode (0 to 2.0 V) and 317 mAh/g for cathode (1.5 to 3.5 V) at 20 mA/g current density. At constant current of 100 mA/g, stable cycling of anode achieving 660 mAh/g and 145 mAh/g for cathode after 200 cycles is recorded. Post diagnostic analysis of cycled electrodes confirmed the electrode materials stability and structural properties ^[3].

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One-pot synthesis of advanced aminosilicas for environmental remediation

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The ecological crisis is a global problem of the 21st century. The development of effective technologies and new smart materials could provide efficient solutions for the overall strategy of cleaning up and minimization the generated pollution. Currently, various aqua environments require drastic improvement in the extraction of metals, organic compounds (e.g. dyes) and water disinfection. Recently, silica materials with amonipropyl groups (spherical particles, xerogels etc.) have become commercial products produced to adsorb some heavy metals, dyes, lipids, mycotoxins, or pesticides^[1]. The next step is to change the chemical structure of the surface and porosity of spherical silicas with amino groups to improve the sorption characteristics of such materials and introduce additional adsorption centres into the surface layer. Therefore, we synthesized (using one-pot technique) and studied various silica microspheres containing primary and secondary amino groups, as well as combinations of amino groups with methyl or phenyl groups on the surface and ethylene or phenylene bridges in the structure of silica network^[2]. These samples were used to carry out adsorption of metal ions (copper(II), europium(III)), and organic dyes (methylene blue, acid red 88, fluorescein). It can be concluded that the sorption capacity for metal ions depends on the content of functional groups and their availability, whereas the adsorption of dyes relates to the hydrophobic groups on the particles surface. The analysis of antibacterial properties also showed that additional hydrophobic groups on the surface of silica particles may increase the number of contact sites between the bacterial cells and the surface of the particles, slowing down the bacterial reproduction.

The research is financed from Swedish Research Council grant DNr.2018-04841 and the project VEGA 2/0156/19.

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

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The ink-jet printing of biocompatible silica sols has gained popularity, both for biosensor production and development of holographic devices. However, there still remain significant issues related to premature clogging of ink-jet printheads when printing aqueous silica sols. To better understand the causes of clogging of piezoelectric ink-jet nozzles, printing studies were coupled with studies of colloidal stability along with silica deposition on surfaces, both under normal flow and piezoelectrically-driven oscillating flow through an inkjet cartridge. Our studies show that clogging most likely results from deposition of silica colloids onto the internal surfaces of the printhead, followed by displacement of micron-sized pieces of the deposited material upon piezoelectric deformation of the printhead surface, which then block the nozzles of the printhead. Based on this result, we formulated a low pH sol derived from sodium silicate and evaluated its colloidal stability, binding to silica surfaces and resistance to clogging of inkjet nozzles under normal and voltage driven oscillating flow (Figure 1). We show that silica sols with a pH of 3.1 provide optimal printing behaviour while allowing reproducible printing of spatially controlled silica patterns on paper to produce enzyme-based biosensing devices.

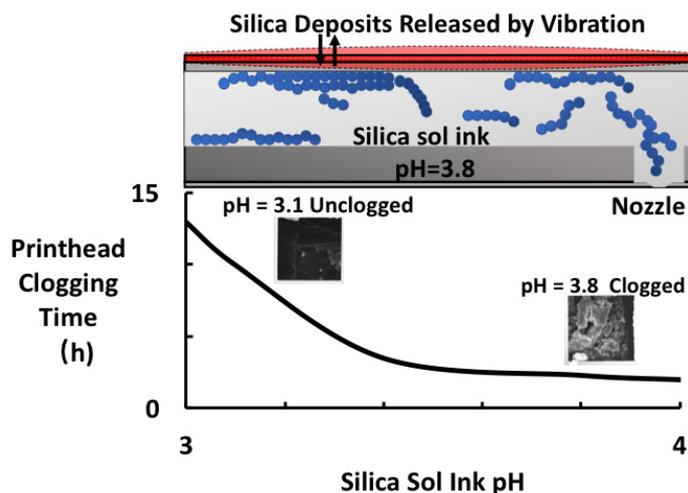


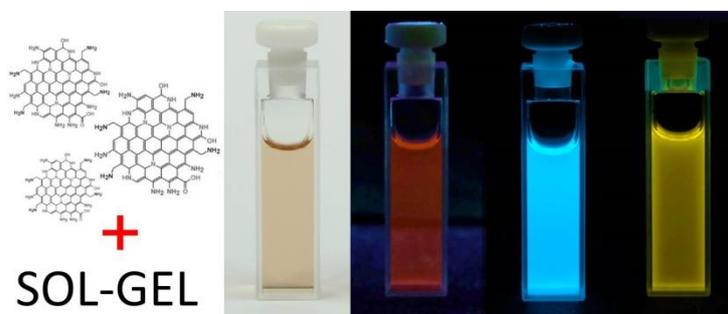
Figure 1. Mechanism of nozzle clogging during ink-jet printing of silica sols.

Integration of C-dots in hybrid nanocomposite films

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

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Multiscale computational approaches to photo-induced processes in nanosystems

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Advanced molecular simulations can provide fundamental insights into the atomistic structures, dynamics and photophysical properties of complex nanosystems, yielding sound interpretation of experimental spectroscopic data and allowing *in silico* design of new materials with tailored optical properties. Achieving good accuracy for such simulations is challenged by the multiscale nature of molecular nanosystems, requiring combination of various advanced computational techniques that can provide reliable structures, dynamics, and electronic properties in complex environments. In this talk, I will present our computational studies on photo-induced processes in nanosystems, including organic nanocrystals composed of push-pull dyes^[1] and hybrid organic-inorganic nano-objects involving gold nano-bipyramids (see Figure 1).^[2]

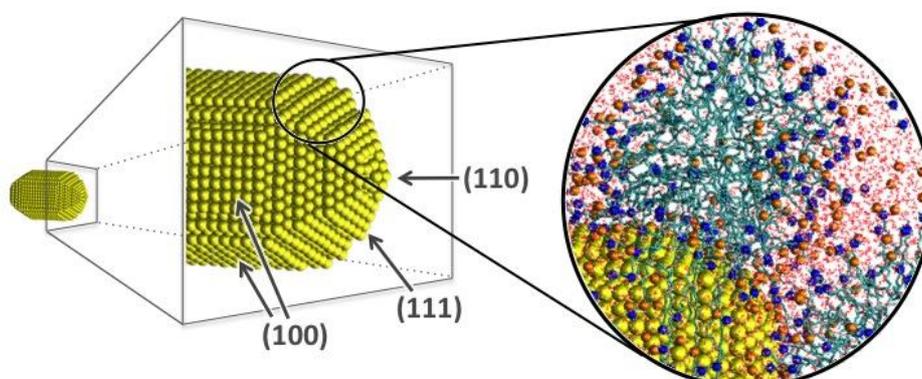


Figure 1. Model of a gold nanograin in realistic environment.

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Towards more industrially attracting NIR-to-VIS up-converting materials

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Nanomaterials with spectral up-conversion (UC) properties have aroused an enormous interest among the scientific community for its ability to transform infrared radiation into visible emissions. This unique feature allows their application fields as diverse as in photonics, sensors, security, photocatalysis, photovoltaic technologies and biomedicine.^[1-3] However, the low efficiencies of the conversion process and the lack of easy methods of synthesis and application of these nanostructures have limited their industrial exploitation.

This talk will present the recent developments of our research group trying to overcome some of these limitations. Firstly, a simple, ultrafast, low-cost and scalable method of synthesis and functionalization of the most efficient lanthanide-doped NaYF₄ UC nanoparticles based on microwave radiation will be presented. Afterwards, the incorporation of these UC nanoparticles into solid matrices compatible with the current production technologies, such as in PDMS polymers, will be also described. A detailed study of the optical properties by hyperspectral microscopy reveals the enhancement of some emissions depending on the nature of the matrix and also on the degree of dispersion/aggregation of the active nanoparticles.

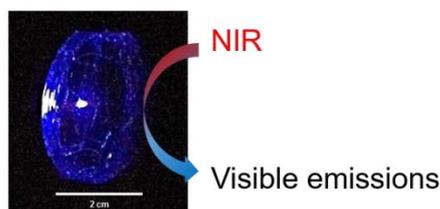


Figure 1. Picture of a siloxane-based hybrid material with blue emission upon NIR excitation.

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Design of NIR chromophores and nanoparticles for two-photon fluorescence and photo-acoustic imaging

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Two-photon excitation fluorescence (TPEF) and near infrared photo-acoustic microscopy (PA) are two complementary microscopy techniques particularly suitable for imaging of the vascular system. In depth *in-vivo* TPEF requires long wavelength fluorophores absorbing and emitting in the far-red/NIR (650 – 1300 nm), which corresponds to the optical transparency window of tissues, but efficient fluorophores are still rare. PA imaging on the other hand uses non fluorescent chromophores able to generate an acoustic signal following excitation at a given wavelength. We will try to show in this presentation how chemists tackle this issue by designing new fluorophores structures and exploring new approaches based in particular on nanoparticle formulation.

In the ENS chemistry laboratory, various series of push-pull chromophores (i.e. dipole molecules in which an electron donor group is connected to an electron-acceptor group via a conjugated bridge) have recently been designed, which emit in far red and can be excited by excitation with two photons in the first and even the second NIR window (except up to 1200 nm). Careful molecular engineering around the dipole structure has allowed us not only to fine-tune the emission wavelength, but also to significantly improve the quantum fluorescence efficiency in solution or in the solid-state. Encapsulation in polymer and silica nanoparticles in a core-shell mixture or preparation of fluorescent NPs obtained by reprecipitation by solvent shifting allowed deep vascular imaging by two-photon excited fluorescence microscopy.

Finally, the design of dyes suitable for PA imaging at 660 and 810 nm and their formulation in NPs will be presented.

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Poly- and oligosaccharide based biomedical materials

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Poly-, oligo- and monosaccharides are ubiquitously found in the living world where they execute functions ranging from energy storage to biochemical recognition. Materials derived from these natural building blocks are therefore of special interest in the areas of sustainability and biomedicine. In this presentation several examples are given on how poly- and oligosaccharides can be chemically modified by ether, ester and amidation reactions yielding products useful for biomedical applications. Derivatives are obtained that have different chemical (solubility, stability, reactivity) and physical (optical, magnetic) properties. Processing of the materials into coatings, patterns, nano-fibers or porous substrates allows for an exploitation as biomaterials in contact with living systems. Such applications can be biosensing ^[1], anti-fouling coatings ^[2] or tissue engineering scaffolds ^[3].

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Modulation of the liposomal membrane fluidity for targeted drug delivery to cancer cells

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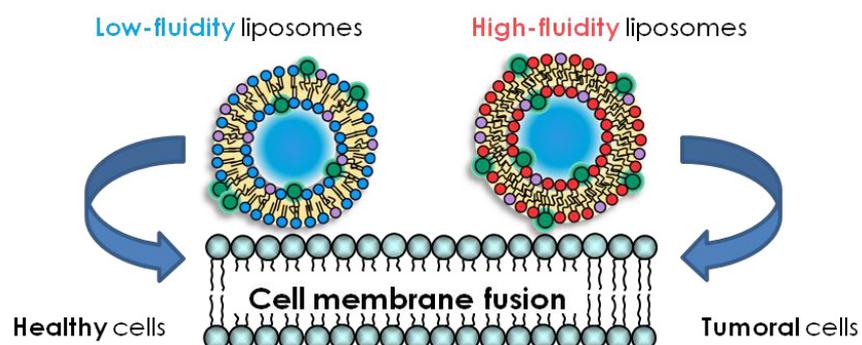
Drug vectorization with liposomes is focused on the coupling of liposomes with a small ligand-like molecule to target a specific cell type. However, these carriers lose their possibility to fuse with the target's membrane, and instead rely on an endocytosis mechanism for delivering their encapsulated drug, a process that can damage the active molecule and then compromise its efficiency.

Although physicochemical changes between the membrane of tumoral and healthy cells have been widely reported, these properties have not yet been exploited for drug delivery purposes. Our aim was then to design a liposomal carrier that can achieve specific targeting using membrane physicochemical properties instead of a ligand-receptor interaction.

To assess the role of membrane physicochemical properties on the carrier-cell interaction, we used liposomes containing phosphatidylcholines (PC) of different melting point depending on their acyl chain composition to create a wide range of membrane fluidity. As models, we used 4 human prostate cancer cell lines with varying aggressivity. The liposome-cell interaction was visualized on plates by epifluorescence microscopy, and the mechanism was characterized by using two types of fluorophores, namely NBD-DOPE and calcein.

We found that low phase transition temperature (T_m) liposomes targeted preferentially tumoral cells rather than control cells. Conversely, while high T_m liposomes showed no interaction with tumoral cells, they interacted strongly with the control cells. The signal obtained with the two fluorescent probes showed that the liposome-cell interaction is probably a membrane fusion.

The specific targeting of either tumoral or non-tumoral cells was obtained by adjusting the composition of the liposomal membrane: low T_m liposomes fuse with the membrane of tumoral cells while high T_m liposomes fuse with the membrane of control cells. These results demonstrate that liposomal membrane properties are a key parameter when designing a liposome drug carrier to achieve specific targeting.



Influence of composition and size of the soft and the hard-magnetic phase on magnetic properties of ferrite-based hybrid magnets

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In the last years, much effort has again been devoted to the research of ferrite-based permanent magnets, due to the so-called rare-earth crisis.¹ In particular, a quest to enhance ferrites' BH_{\max} , is still underway. Large BH_{\max} values are found in magnets combining substantial magnetization at remanence (M_R) with high coercivity. Both parameters are influenced by materials properties, such as crystalline and shape anisotropy and particle' size. Here, the influence of composition, particle size, sintering conditions on the microstructure and magnetic properties of strontium ferrite (SFO)-based composites will be presented.

Powders' mixtures consisted of commercial SFO powder consisting of micron-sized, isotropic particles, or hydrothermally (HT) synthesized SFO with hexagonally-shaped platelets with a diameter of 1 μm and thickness up to 90 nm, and a soft magnetic phase in various ratios. Powders were sintered with spark plasma sintering (SPS) furnace. Starting powders and hybrid magnets were examined by means of phase composition (XRD) and microstructure (TEM, SEM). Their magnetic properties were evaluated with vibrating sample magnetometer (VSM), permeameter and by single-point-detection (SPD) measurements.

Depending on the concentration and composition of soft phase the M_R of the composite can be altered. Application of external magnetic field before the consolidation induces the anisotropy in commercial, and HT synthesized SFO, leading to an increase in the M_R of hybrid magnets. Moreover, sintering with SPS promotes the alignment of HT synthesized SFO particles in the direction of the applied pressure, which is also the direction of SFOs' easy axis and thus the enhancement in M_R is perceived leading to the M_R/M_S higher than 0.8. Besides, after SPS almost no grain growth was observed, which is beneficial for exploiting advantages of nanosized-induced phenomena also in bulk sintered samples.

Acknowledgement:

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Crafting properties of domain walls in bismuth ferrite ferroelectric material

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BiFeO₃ (BFO) is a lead-free ferroelectric material with superior Curie temperature (T_c) and as such relevant for high-temperature applications. However, the use of BFO is hindered by its conductivity mainly coming from nm-sized local features known as domain walls (DWs). DWs are created spontaneously at the T_c and separate two regions of uniform polarization in ferroelectric materials. Recently, we explained that higher DW electrical conductivity is due to the segregation of charged defects at the DWs [1].

In this presentation we will show that DWs conductivity in bulk BFO can be tailored by controlling the type and concentration of point defects using different processing conditions (temperature, atmosphere, cooling rates). With the support of different microscopy methods down to the atomic level (Figure 1) we will explain how different processing conditions affect DW thickness, shape, local unit-cell distortion and the type and concentration of the defects at DW. We will correlate these structural features with local DW conductivity and finally with a macroscopic electro-mechanical response of bulk BFO.

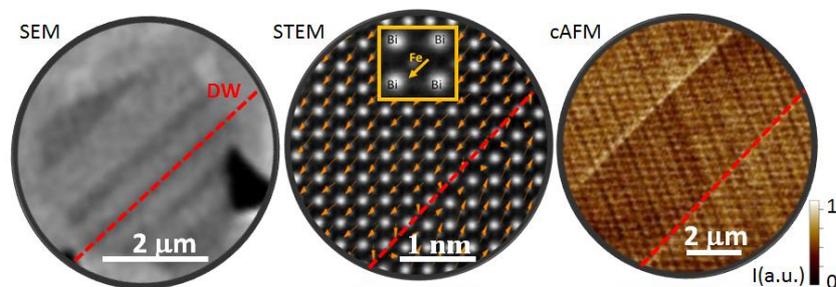


Figure 1: Domain wall (DW – marked with dashed line) in BiFeO₃ at different length scale. DW as imaged by scanning (SEM), scanning transmission (STEM) electron microscope and conductive atomic force microscope (cAFM) where enhanced current signal at DW is seen. In the inset of STEM image, with overlaid Fe displacement directions, Bi and Fe atom columns are marked.

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Nanohybrid silica: investigation of self-assembling properties and physical properties using multiscale approach and DFT calculations.

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Over the past two decades significant efforts have been directed towards the elucidation of synthesis/structure/function correlations to guide the development of synthetic strategies for controlling the composition, size and shape of nanomaterials. In this context, organic–inorganic nanohybrids incorporating bridged silsesquioxanes have been of particular interest, due to their versatility and the structural control that can be achieved through independent modulation of the properties of the organic bridge and inorganic moieties. Such strategies have also been applied to the production of thin films on a variety of substrates, driven by the continuous need to develop new and enhanced materials with nanostructures engineered over multiple length scales for applications in electronics, optics, sensing, ferromagnetic, shape-selective membranes, etc.

In this talk, I will first present a fundamental study of the nanostructuring mechanisms of model hybrid silica. Our experimental investigation was performed using an *in operando* approach (vibrational spectroscopies under pressure, light diffusion, microscopy) coupled with DFT calculations. Parameters controlling the evolution of the system during sol–gel processing: supramolecular interactions, hydrolysis, polycondensation, and nucleation and growth of the hybrid solid in solution were investigated. The relation between structural properties and applications will be then highlighted¹⁻⁴.

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Controlled polymer-inorganic assembly process for the preparation of functional mesoporous hybrid nanomaterials

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Ordered mesoporous materials resulting from the synergy between supramolecular templating and sol-gel processes exhibit unique porosity and surface properties, which make them highly attractive as drug delivery systems, sensors, adsorbents or catalysts, and more generally for applications in fields as diverse as human health, environment protection and sustainable energy. Functionalization of their mesopores by organic, organometallic or biologically active functional groups can be achieved by well-controlled processes. Bringing polymer functionalities in those systems could confer new physical and chemical properties to these hybrid materials, but that remains a quite challenging task: post-functionalization routes applied on template-free porous materials hardly succeed in providing homogeneously distributed polymer chains of controlled chemical function, polymer block length and density of function. The use of polyion complex micelles as structure-directing agents can allow overcoming the different issues related to the preparation of polymer-functionalized mesoporous materials. Polyion complex micelles are dynamic assemblies obtained by electrostatic complexation between a double-hydrophilic block copolymer and an oppositely charged polyelectrolyte, their formation is reversible in water as a function of pH and ionic strength. Their use for structuring silica is highly beneficial since (1) they allow the preparation of ordered materials whose structure (2D hexagonal, lamellar, 3D spherical cubic) and pore size can be easily controlled, (2) they allow recovering and recycling the pore-generating polymers and (3) they enable the direct preparation of polymer-functionalized mesoporous structures. Another great benefit of the use of PIC micelles is that the ability to finely tune the affinity for silica of the corona polymer blocks allows the preparation of nanoparticles of controlled colloidal size. Finally this synthesis route could be extended to the preparation of periodic mesoporous organosilicas whose interest in biomedical applications was evidenced ^[1,2].

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Prussian Blue Analogues for the adsorption of humid organic vapours

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Porous coordination polymers are exciting molecule-based materials, made of metal ion nodes and molecular building blocks, which have attracted a great deal of attention for several decades not only from the fundamental point of view, but also due to potential technological applications in several fields including catalysis, gas storage, separation and purification.¹ The most explored families of porous coordination polymers belong to Metal Organic Frameworks (MOFs) and Prussian Blue Analogues (PBA). They have been investigated as promising alternatives for activated carbon or zeolite materials usually used in industry for gas storage or separation/purification processes. In the frame of a wider project on the physicochemical properties of Prussian Blue Analogues,² we have demonstrated for the first time that the hydrophilic/hydrophobic character of the lipophilic PBA material can be tuned by a simple control of the coordinated water to the metal centres. While the completely dehydrated material shows a hydrophobic feature, a switch to an hydrophilic character is actuated by overcoming the water relative pressure threshold at $p/p^\circ \sim 0.03$. The advantage of this unusual phenomenon has been demonstrated by optimized sorption of polar ethanol, able to engage hydrogen bonding and van der Waals interactions. Remarkably, the hydrophobic – hydrophilic character of the PBA does not alter its lipophilic balance and the material maintains its capacity to efficiently adsorb non polar species like n-hexane in humid or in dry atmosphere.³ This behaviour will permit to optimize the affinity of the host materials as a function of the nature of adsorbed molecules, which is of great interest for different applications such as humid streams purification.

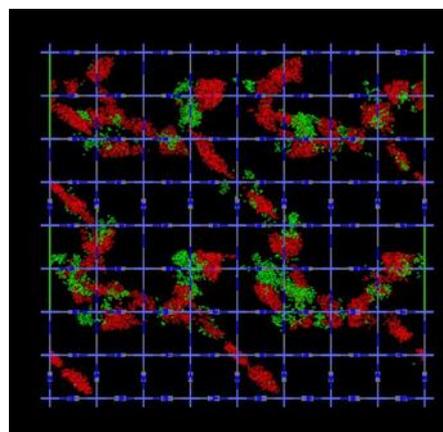


Figure 1. Modeled structure with the co-adsorption of water and n-hexane vapors for completely dehydrated $\text{Co}[\text{Co}^{\text{III}}(\text{CN})_6]_{0.66}$.² Red zones represent n-hexane molecules and green zones show water

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Assessment of Advanced Photocatalytic Oxidation process for Micropollutant Elimination in Municipal and Industrial Waste Water Treatment Plants

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1. Introduction

Pharmaceuticals, personal care products, pesticides and other chemicals used for domestic purpose or industrial or agro-food production are continuously discharged into wastewater and lead to global contamination of the aquatic environment all over Europe^[1]. Removal during conventional wastewater treatment is unsatisfactory knowing that only 20 to 50% of micropollutants are removed in current waste water treatment plants^[2].

The objective of the AOPTi project is to develop and validate an innovative technology to ensure efficient elimination of different types of micropollutants and toxic effects in waste water. The process is a tertiary treatment process, which can be easily integrated into municipal and industrial WWTPs. It is an economical physico-chemical treatment step after the conventional biological treatment^[3]. The process is based on oxidation by ozone and a subsequent photocatalytic treatment. The technology is developed for companies involved in the water purification sector and for companies with toxic effluents loaded with micropollutants. Process parameters have to be determined depending on the type of waste water in order to lead to almost total degradation of all micropollutants and to ensure absence of toxicity of the resulting water. Treated water will be characterized in term of chemical transformation products (TPs) and toxicity.

2. Methods

At the pilot scale (flow rate = 150 L/h), 24 major micropollutants have been chosen to model waste water like pesticides (simazine, diuron, isoproturon, DTT, atrazine, lindane), plasticizers (DEHP, tributyl phosphate), brominated compounds (PBDE), pharmaceuticals (metoprolol, diclofenac, carbamazepine...), industrial chemicals (PFOS), contrast agent (iohexol, iopromide). Their degradations are quantified by GC-MS/MS and UHPLC-MS.

Photocatalysts have been synthesized by organic sol-gel methods^[4] and deposited as thin transparent films by spray-coating inside the long alkaline-free tube for a pilot test: pure TiO₂ and doped titanium dioxide (with Ag and/or commercial Evonik P25 nanoparticles). Samples were characterized by profilometry, GIRXD, UV-Vis transmission. The absence of leaching was characterized by ICP-AES and MS.

3. Results and discussion

The best photocatalyst for the degradation of the 22 micropollutants is TiO₂ doped with 2 wt.% of Ag and 10 wt.% P25. The results are presented in Figure 1, in which the percentage of each micropollutant present in water is shown after different treatments (ozonation, adsorption and photocatalysis). In Figure 1 (on the left):

(i) Chlortoluron and isoproturon are totally degraded by ozonation for 30 min; (ii) atrazine, DDT and BDE are totally disrupted thanks to photocatalysis; (iii) for the other micropollutants, their percentage of degradation evolves from 10% to 90% after a photocatalytic treatment for 6 h.

In Figure 1 (on the right):

(i) Carmabazepine, diclofenac, sulfamethoxazole, clarithromycin and terbutryn are totally degraded by ozonation for 30 min; (ii) metoprolol is partially degraded after a photocatalytic treatment of 6 h (about 12% remains); (iii) the other pollutants are totally disrupted thanks to the photocatalytic treatment and sol-gel coating.

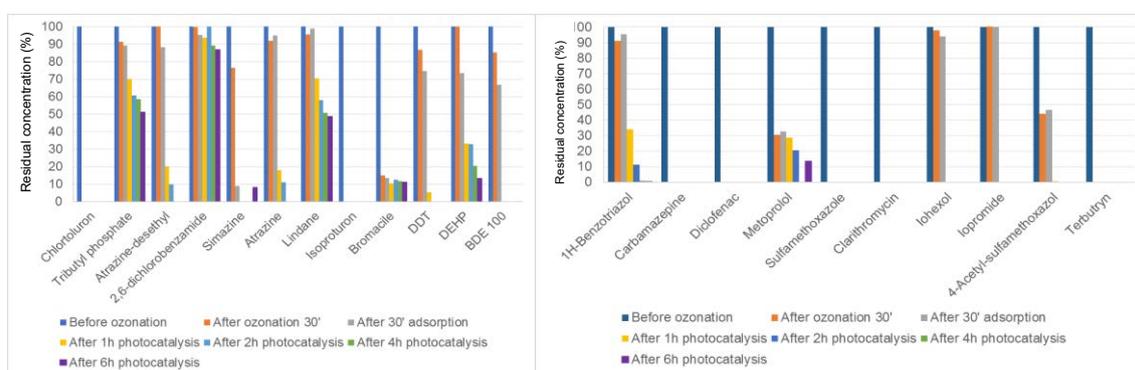


Figure 1. Evolution of 22 micropollutants concentrations during the ozonation and photocatalytic tests.

4. Conclusions

It is concluded that the use of an ozonation treatment followed by a photocatalytic treatment allow disrupting different micropollutants present in waste waters. And the toxicity of waters very strongly decrease during the AOP treatments.

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Ferroelectric oxides and halide perovskites: application in solar cells and solar transistors

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State-of-the-art halide perovskite solar cells employ semiconductor oxides as electron transport materials. Defects in these oxides, such as oxygen vacancies (Ovac), act as recombination centres and, in air and UV light, reduce the stability of the solar cell. Under the same conditions, the PbZrTiO₃ ferroelectric oxide employs Ovac for the creation of defect-dipoles responsible for photo-carrier separation and current transport, evading device degradation. We report the application of PbZrTiO₃ as the electron extraction material in triple cation halide perovskite solar cells. The application of a bias voltage (poling) up to 2 V, under UV light, is a critical step to induce charge transport in the ferroelectric oxide. Champion cells result in power conversion efficiencies of ~11% after poling. Stability analysis, carried out at 1-sun AM 1.5 G, including UV light in air for unencapsulated devices, shows negligible degradation for hours. Our experiments indicate the effect of ferroelectricity, however alternative conducting mechanisms affected by the accumulation of charges or the migration of ions (or the combination of them) cannot be ruled out. Our results demonstrate, for the first time, the application of a ferroelectric oxide as an electron extraction material in efficient and stable PSCs. These findings are also a step forward in the development of next generation ferroelectric oxide-based electronic and optoelectronic devices.

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New cross-linked chitosan-graphene oxide anion exchange membranes for fuel cell applications

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Search for technical advances and optimal solutions in the field of energy, ranging from designing new power sources to securing its financial viability and environmental conformability, has been at the forefront of scientific and applied endeavors for several of years now. Anion exchange membrane fuel cells have recently received increasing attention since in principle they enable a reduced fuel crossover, improved water management, and the use of a wide range of fuels. Present work describes a novel polymer based nanocomposite anionic exchange membranes (AEMs) with improved features for direct alkaline fuel cell applications. AEMs based on chitosan (CS), magnesium hydroxide (Mg(OH)₂ and graphene oxide (GO) with benzyltrimethylammonium chloride (BTMAC), as the hydroxyl conductor, were fabricated by a solvent casting method. To impart better mechanical properties and suppressed swelling, the enzymatic cross-linking with dodecyl 3,4,5 – trihydroxybenzoate (DTHB) having C-10 alkyl chain was employed. Structure and surface morphology, KOH uptake and swelling ratio, ethanol permeability, mechanical property, ionic conductivity, cell performance and stability of AEMs were investigated.

The highest peak power density value of 72.7 mW cm⁻² was obtained at 209 mA cm⁻² when the pristine CS+Mg(OH)₂ AEM was used as polymer electrolyte membrane in the direct alkaline ethanol fuel cell at 80 °C. This is the highest reported power density value for chitosan based membranes.

Acknowledgements

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Geo-inspired approaches for extending the range of inorganic nanoparticles

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The range of solids reported as nanoparticles is strikingly narrow compared to the library of bulk solids reported from conventional solid-state chemistry^[1]. Many of these solids unreported at the nanoscale show properties without equivalent among more common solids studied as nanoparticles, including ultrahardness, (electro)catalysis, and magnetism. Because nanoscaling can deeply modify such properties, efforts to reach still unreported nanoparticles are of high importance. Yet, researchers face a synthetic challenge: how to produce nanoparticles of solids typically obtained by solid-state reactions at high temperature?

We will present our recent efforts to reach such challenging nano-objects, by focusing on syntheses inspired from geological processes, namely in inorganic molten salts and under very high pressures^[1-5]. Molten salts are thermally stable, possess large solvating ability, and fasten reactions compared to solid-state reactions, thus leading to original nanostructures under kinetic control. High pressures provide specific conditions of crystallization, as shown by diamond. We will discuss cases of nanoparticles showing properties different than those of bulk phases. Perovskite oxide nanocrystals (Figure)^[3] with original spin transport properties will be addressed, then we will move to metal borides^[2,5] for electrocatalysis and energy conversion.

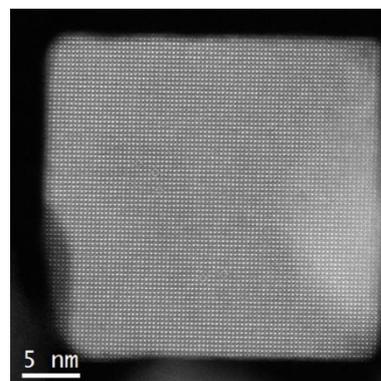


Figure. STEM-HAADF image of a $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ nanocrystal synthesized in molten salts at 600 °C and showing surface-driven

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Hybrid fluoride nanoparticles for bioimaging

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Rare earth fluoride nanoparticles present extremely interesting properties which make them potential contrast media for in vivo imaging. Original synthesis routes allowing large scale production have been developed. Surface modification towards biomedical developments have been assessed. In particular we focused on brain pathologies (neurodegenerative diseases and Stokes). We report here the design of a multimodal hybrid nanoprobe suited for enhancing contrast in three different medical imaging modalities (Fig.1). Contrast enhancement in MRI and in a recently developed spectral photon counting scanner computed tomography (SPCCT) is intrinsic to its inorganic GdF_3 core.^{1,2} The third modality, two photon imaging, is provided by suitable organic moieties^{3,4} grafted on the core via different strategies. Pre-clinical experiments showed that this versatile nanoparticle platform successfully enhance MRI contrast in the brain of small animal and provide high intensity two-photon signal for in- vivo microscopy.

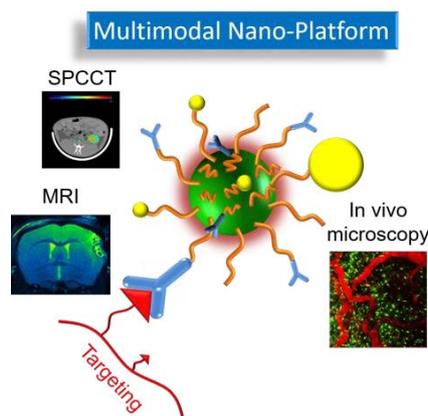


Figure 1. Hybrid nanoprobe for medical imaging applications.

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Modern solutions with nano-size features in wound care with emphasis on advanced preparation techniques

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Early and late complications connected with wound healing are still common causes for patient disability and even mortality. These not only significantly lower the patient's quality of life, but also present a huge financial burden for the healthcare systems around the world. Treatment of larger wounds often requires the use of more complex materials, which can ensure a successful renewal or replacement of damaged or destroyed tissues. The domain of wound healing is vast and growing rapidly. Firstly, the possibility to anticipate macro-scale wound dressing properties by modulating the materials on 2D thin films will be discussed. Through such studies, significant cost reduction can be achieved, especially, when expensive ingredients such as growth factors and drugs are explored. One of the most commonly used technique in the development of wound care materials is electrospinning, by which nanofibers that simulate the extracellular matrix (ECM) are fabricated. Natural ECM is a dynamic structure based on hierarchical nanostructures, with a crucial role in promotion and regulation of important cellular functions, such as adhesion, proliferation, migration, differentiation and morphogenesis. Through these features, the ECM is indirectly responsible for the skin's mechanical support, and, simultaneously, for its appropriate flexibility. By using electrospinning and developing a formulation based on biodegradable polymers, structures with crucial resemblance to the morphological characteristics of the skins ECM can be produced. Nanofibers have high-surface area, which makes them suitable for loading with drugs or other active biomolecules. Further, the benefits of such complex nanofibrillated structures with included analgesic drugs on skin cells will be presented. The more recent emphasis of our studies is on the development and fabrication of scaffolds by utilizing 3D bioprinting, which enables the reproducible production of complex geometric structures, with high spatial resolution using a broad range of biocompatible polymeric materials. Finally, the studies concerning the improvement of mechanical properties 3D printed scaffolds by adding nanofibrillated cellulose, the influence of added growth factors and analgesic drugs on skin cell proliferation, as well the development of a bioink with *in situ* incorporated skin cells suitable for 3D printing will be reviewed.

Acknowledgment

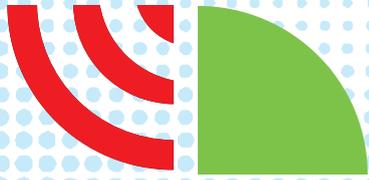
The authors acknowledge the financial support from the Slovenian Research Agency for Research (grant numbers: P2-0118, P3-0036 and Z2-8168), Ministry for Education, Science and Sport (grant number: 5442-1/2018/57) and through the Young Researcher Programme.

Nanoencapsulation of polyphenolic compounds

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Bioactive compounds (e.g. polyphenols) are valuable compounds due to their positive effect on health. Polyphenols are often concentrated in leaf tissue, bark layers, flowers and other plant materials. These natural sources of actives became attractive in last decade and the extraction of polyphenols from different plants is still interesting due to many factors that affect final extract composition and phenolic content. These compounds are mainly chemical instable and they are also poorly administrated upon oral consummation. Micro and nanocapsules have shown to be effective protection systems for bioactive substances. For encapsulation, different natural materials (polysaccharides, lipids, proteins) are used. Polysaccharides show biocompatibility and biodegradability and have other beneficial properties, such as antiviral, antibacterial and anticancer activity. We will present proliposomal and polysaccharides encapsulation of various polyphenols (e.g. resveratrol, catechines) prepared by emulsification followed by external gelation. The size distribution and morphology of micro- and nanocapsules was determined by using dynamic light scattering (DLS) and scanning electron microscope (SEM), respectively. The interactions between the encapsulated polyphenols and lipids were further characterised by fluorescence polarisation measurements, electronic paramagnetic spectrometry and differential scanning calorimetry.



NANOAPP 2019

Nanomaterials & Application

ORAL LECTURES

Functionalization of iron oxide core – mesoporous silica shell nanoparticles for removal of heavy rare earth elements.

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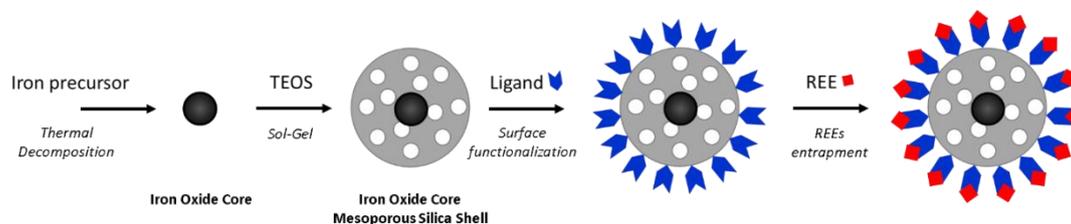
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Nowadays, contamination of water by heavy metals such as lanthanides has become a worldwide environmental concern with worrying impact on human health. In that context, we propose in this work the design of “magnetic nano-traps” made of an iron oxide core and a functionalized mesoporous silica shell in order to collect heavy rare earth elements from waste water. The magnetic iron oxide cores were synthesized by thermal decomposition of hydrated iron oxide in docosane. The resulting iron oxide nanoparticles stabilized in chloroform with oleic acid were then coated with a mesoporous silica shell through a sol-gel procedure. The resulting core-shell nanoparticles were characterized in terms of morphology, size and stability by TEM imaging and DLS. In order to trap heavy rare earth elements, the surface of the mesoporous silica shell needs then to be functionalized with entities able to chelate lanthanides such as diethylene triamine pentaacetic acid (DTPA). The efficiency of the grafting of silica surface with DTPA^[1] was assessed by FTIR, elemental analysis and EDX. Finally, their efficacy to entrap lanthanides was tested on different elements by soaking the nanoparticles with contaminated water for few hours and then collecting them simply with a magnet.

A



B

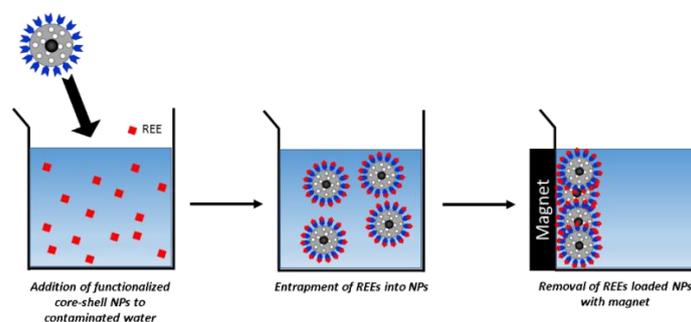


Figure 1: A) Synthesis route of functionalized core-shell nanoparticles for REEs removal B) Principle of REEs removal by magnetic core-shell nanoparticles

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Protein-repellent polysaccharide multilayers: Influence of charge and hydrophilicity

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The biofilm formation triggered by uncontrolled protein adsorption, on small-diameter vascular graft implants is one of the leading cause of infections during implantation. Herein, we report of polysaccharide based nano-coatings as protein-repellent coatings to tackle this challenge. A simple layer-by-layer strategy to functionalize surfaces of poly(caprolactone) (PCL) with antifouling multilayers manufactured from the positively charged aminocellulose and the negatively charged cellulose sulphate was employed successfully. The influence of net charge of the coatings as well as the hydrophilicity of the coatings on interactions with blood proteins was evaluated. The absorption kinetics of proteins on solid surfaces were looked into detail.

The multilayers formed coatings of up-to 20 $\mu\text{g}/\text{cm}^2$. The zwitterionic nature of the coatings has shown to repel bovine serum albumin (BSA), γ -globulin, and fibrinogen proteins, as shown by means of a quartz crystal microbalance.

Given the multiple functionalities and different physiochemical properties of polysaccharide-based multilayer coatings, this system showed to be easily extended to various material surfaces, thereby broadening its potential applicability also in microfluidics, diagnostic biosensors and others.

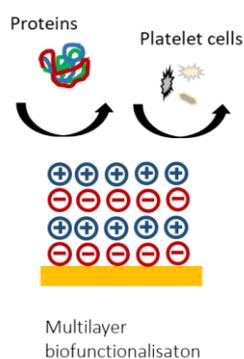


Figure 1: A scheme of protein-repellent charged-polysaccharide multilayers on a PCL surface.

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Safety of food contact material containing nanoparticles

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The materials in contact with foodstuffs are various materials which come into contact with foodstuffs during production, processing, preparation and storage of foodstuffs. Novel food contact materials containing nanoparticles have been developed recently and some already reached the market [1, 2]. These novel materials have improved properties in comparison to classical food contact materials. They may have antibacterial properties, absorb various gases, release aromas, detect presence of oxygen, carbon dioxide and bacteria, detect changes in temperature. Novel materials may also have improved mechanical and gas barrier properties, temperature/moisture stability, resistance to fire, UV resistance, optical and rheological properties and biodegradability [3]. The main risk of consumer exposure to nanoparticles present in novel food contact materials is through potential migration of nanoparticles into food. The first step in evaluating the safety of novel food contact material is characterisation of the material, followed by release testing and exposure assessment [4].

In the presentation, safety evaluation of food contact non-stick quasi-ceramic coating containing micro and nano TiO₂ is described. For characterisation of material, FTIR, electron and optical microscopy, EDXS and XRD were used. Possible migration of TiO₂ nanoparticles was studied by migration tests into simulants as well as by thermal and mechanical degradation of the matrix [5]. Exposure assessment was performed using migration testing results and EFSA Comprehensive Food Consumption Database.

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Nanotechnology in the Context of Slovenian Smart Specialisation Strategy

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Slovenian Smart Specialization Strategy (S4) is an operational plan and one of the key documents serving as a basis for European Cohesion Policy implementation in Slovenia. The mission of S4 is to facilitate Slovenia's transformation from a follower to a co-creator of global trends in three identified priority areas (1. Digital, 2. Circular, 3. (S)Industry 4.0) and nine areas of application (1.1. Smart Cities and Communities, 1.2. Smart Buildings and Home, 2.1. Networks for the transition to a Circular Economy, 2.2. Sustainable Food, 2.3 Sustainable Tourism, 3.1. Factories of the Future, 3.2. Health-Medicine, 3.3. Mobility, 3.4. Materials as Products). The partnership, so called Strategic Research Innovation Partnership (SRIP), were established for each of the nine areas of application. Each SRIP has established value chains (vertical activities) as a group of stakeholders who form a vertically integrated chain with complementarity in research, development and innovation. Identified key enabling technologies (KETs) such as nanotechnologies, modern production technologies for materials, photonics, plasma technologies, robotics, control technologies and ICT relate to several areas of applications and are therefore identified as horizontal activities.

Nanotechnologies are organized as horizontal network within SRIP Factories of the Future. The aim of this horizontal network is closed development of stakeholders working in the framework of nanotechnology and to integrate nanotechnology into vertical chains within all other SRIPs. Nanotechnologies are one of the most cross-cutting horizontal activity since it relates to all areas of application. Newly developed microscopic methods allow determining the impact of deformation in the wear of materials, which is important for the development of finished products from all areas of application. Nanotechnology is crucial in the process of miniaturization of products and intelligent automatization of production processes. Technology of sensors has an extremely wide range of applications from smart devices to bio-nano-sensors. In the field of health and medical diagnostics nanomaterials can be used for controlled delivery of drugs. On the base of existing competences and capabilities which emerged in Slovenia in recent years we have identified four priority areas to be addressed in the horizontal activity Nanotechnologies: (1) Smart sensors and nano-sensor structures for industrial, biomedical and environmental applications, (2) Smart surface coatings from

construction to the medicine, (3) Components for industry and medical applications, (4) Smart nanotech-based systems for sustainable environment and energy. As technologies depend on human resources and research equipment we strongly support and promote training activities and open access equipment.

We are aware that innovative potential of nanotechnology needs to be developed responsible, ensuring safe and environmentally sound use based on national and international standards, implementation of the internationalization liaison activities and open dialogue with the public. To learn more about Slovenian Smart Specialisation Strategy refer to Government Office for Development and European Cohesion Policy RS.

To learn more about Nanotechnology in the context of Slovenian Smart Specialisation Strategy refer to Strategic Research Innovation Partnership Factories of the Future (SRIP FoF).



NANOAPP 2019

Nanomaterials & Application

POSTERS

Synthesis of amino functionalized silica particles for binding rare earth metals

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Recycling and reuse of valuable materials (e.g. rare earth metals, REEs) is a growing trend since REEs are not used to their full extent as part of the circular economy ^[1]. REEs are more or less released from diverse industrial activities directly or indirectly into the environment via wastewater ^[2]. Due to the difficulties of collection, wastewater treatment and technological separation, the recycling rate for many of the elements (e.g. Nd, Y, Eu, Tb, Dy) is currently very low, less than 1% ^[3]. To support the move to a more circular economy, and to minimize the potential environmental impact, efficient recovery and reuse approaches are needed for the REE's recovery from wastewater. Adsorption process with the use of natural and synthesised silica based (nano)adsorbents is currently one of the most selective and economically and energetically appropriate methods for removing metal ions from water ^[4]. In the last period, silica dioxide (SiO₂) (nano)materials as adsorbent material are being developed in particular due to the non-toxicity, the high specific surface area, the distribution in controlled pore sizes, and the possibility of their surface functionalization with the corresponding organic substituents ^[5,6].

In this research, surface-functionalized sol-gel adsorbents were prepared by Stöber method and used as adsorbent material to bind REEs, more specifically terbium ions (Tb³⁺) ^[7]. Two alkoxysilanes were used for the preparation of amino (-NH₂) functionalized silica (SiO₂) particles; tetraethoxysilane (TEOS) and (3-aminopropyl) trimethoxysilane (APTMS) with potential to bind Tb³⁺. Prepared materials were characterized using various techniques; FT-IR spectroscopy, specific surface and porosity measurements with Brunauer-Emmett-Teller (BET) method, transmission electron microscopy (TEM), thermogravimetric analysis (TGA) and potential titration measurements. The binding efficiency and capacity of terbium ions by adsorbent particles from model salt solutions, adsorption isotherms, kinetics and thermodynamics behaviour of ions, were studied based on the analytics results of fluorescence spectroscopy ^[8].

The results showed high binding efficiency of Tb³⁺ ions (~94%) to amino (-NH₂) functionalized SiO₂ particles. The equilibrium concentration was achieved with 120 mg of adsorbent material after two hours of adsorption at room temperature (25 °C). Four adsorption isotherms models (Langmuir, Freundlich, Temkin and Halsey) were used to evaluate the adsorption process. The adsorption process was best described by the Langmuir adsorption model. Langmuir's isotherm refers to homogeneous adsorption, in which each molecule has constant enthalpy and activation energy (all sites have the same affinity to adsorbate). Adsorption of Tb³⁺ ions on the prepared materials followed the kinetics of pseudo-second

order, therefore promoting a chemical process involving valence forces by dividing or exchanging electrons. The calculated negative values of ΔG° illustrated the spontaneous adsorption properties or that the adsorption reaction system does not require energy from the environment. The enthalpy value (ΔH°) was positive due to the endothermic properties of the adsorption process, while the negative entropy value (ΔS°) suggested that there are no changes in the adsorbent internal structure in the adsorption system.

Acknowledgement:

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Silver-based nanocomposite materials for the multifunctional water treatment

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Clean drinking water is becoming a scarce resource and nanotechnology can improve the existing water treatment processes. Conventional membrane characteristics, such as antifouling, antimicrobial property, selectivity, flux increase and pore control can be improved with application of nanomaterials, consequently also decreasing energy demand, use of chemicals and thus the cost of membrane-based water treatment. Nano-silver shows increased antimicrobial properties that are becoming even more important with the emergence of resistant microorganisms. Silver nanoparticles (AgNWs), as well as released Ag⁺ ions are toxic for microorganisms and have strong biocidal effect even on multi-resistant bacteria, like *S. aureus*, *E. coli* and others [1, 2]. Additionally, silver is known as good electro-conductive material and providing minimal electrical current through a membrane has shown to greatly decrease the fouling, thus decreasing overall operational costs of water treatment [3].

AgNWs were synthesized with modified polyol process [4] and characterized by UV-Vis spectroscopy and transmission electron microscopy (TEM). Cytotoxicity of AgNWs was evaluated according to metabolic activity of human A549 cells after 24 h of exposure. Synthesized AgNWs were used for preparation of nanocomposites with simple dip coating or spraying technique of AgNWs on various polymer substrates. The objective was to obtain finely dispersed conductive network of AgNWs on suitable substrate, that would function as an electrical pathway for added electrical current as well as an antimicrobial surface. Prepared nanocomposites were characterized by scanning electron microscopy (SEM) and electrical conductivity testing. The most promising of the prepared nanocomposites were also evaluated for their antimicrobial efficiency and potential leaching of AgNWs. Such nanocomposites will be used for water sterilization with alternating current source decreasing the fouling as independent filters or additional filter layer for existing filter systems.

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Photochromic polyester fiber containing 1,3,3-Trimethylindolino-6'-nitrobenzopyrylospiran dye encapsulated into the silica particles

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Chromogenic material adapts to the changes of the external stimulus, such as temperature, light or pressure by color change. Among the family of chromogenic substances, photochromic materials undergo an ultraviolet (UV)-triggered transformation between two optical absorption states resulting in distinct color change [1].

When spiropyrans photochromic dyes are irradiated by UV light (Fig. 2) they isomerize from a ring-closed spiro species to its ring-opened species to form a corresponding metastable merocyanine structure. These structural changes are accompanied by visible color changes. The merocyanine isomers return to colorless species that have a ring-closed form by light blocking or thermal cyclization [2].

In this study, photochromic polyester (PES) fibers were extruded from the batch containing the mixture of polymer and silica particles (5% wt) with encapsulated photochromic dye 1,3,3-Trimethylindolino-6'-nitrobenzopyrylospiran. The dye was encapsulated into the silica particles via Stöber process by using tetraethoxysilane (TEOS) and trimethoxyphenylsilane (TMPS) as silica precursors.

Dry samples of silica particles with encapsulated dye were characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA). BET analysis was used for measurements of the specific surface area and UV lamp for the determination of silica and PES fiber photochromic properties.

Acknowledgment:

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Sensor membranes preparation with spray coating technique

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Spray coating is a promising technique for industrial application of the organic – inorganic thin films ^[1]. It is also appropriate for making sensor membranes on different type of foils, which can be used for production of intelligent packaging. With a single pass spray process, it is possible to produce different thin films with thicknesses ranging from 250 to 450 nm ^[2]. Spray coating have many advantages compared with other techniques (dip coating, spin coating...), such as: able to coat large and surfaces with different morphologies and roughnesses ^[3], no limitation in substrate size ^[4], versatile way to generate thin layers on different substrates ^[1], employs small amounts of material in a dilute solution ^[2], able to coat complex geometries at industrial scale ^{[1][3]}.

The sol–gel process provides a simple and easy route to obtain thin films with high purity, compositional homogeneity, and good properties, just in one step and at low cost. For this reason, thin films obtained by the sol–gel process are able to provide amazing properties at the nanoscale, compared with the bulk material ^[3].

In this research, we represent optical sensing system based on sol-gel sensor layers for determination of dissolved ammonia. Sol-gel based sensor layers in this research were made of combination of hydrophilic (tetraethoxysilane, TEOS) and hydrophobic (Phenyltrimethoxysilane, PhTriMOS) sol gel precursors. The preparation of a starting sol-gel solution, containing the indicator Bromophenol Blue, was carried out via the acid-catalysed sol-gel process. The sensing properties were evaluated according to spectral properties and dynamic range.

Results of this research shown that sensor membranes prepared with spray coating (with sprayed 3 layers of sol-gel solution) have very similar, almost identical, response to dissolved ammonia as sensor membranes made with spin coating, although for making of sensors with spin coating bigger mass of sol-gels was used. In case of spray-coated membranes with more layers (in this case 4) response at higher concentration of dissolved ammonia was detected.

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NiCu-silica-nanoparticles with incorporated anticancer drug for the potential treatment of skin cancer

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Silica coated magnetic NiCu nanoparticles are chemically stable, biocompatible and exhibit magnetic properties, suitable for biomedical applications. ^[1] The use of NiCu magnetic nanoparticles for such purpose is still a rather new field, but is attracting an increasing interest in the last decade. ^[1] A special field of the latest research present nanoparticles, which combined different therapeutic interventions (e.g. magnetic hyperthermia and active pharmacotherapy) to potentially improve the treatment efficiency. ^[2]

In the first study, we prepared Ni_xCu_{1-x} nanoparticles with a narrow size distribution by reducing a Ni and Cu oxide mixture in a silica matrix, using the sol-gel method. The silica coating ensured the nanoparticle non-toxicity and biocompatibility, and at the same time served as reservoir for drug incorporation. The developed nanoparticles it is possible to achieve the above mentioned dual therapy through, where the nanoparticles enable magnetic hyperthermia on their own, and at the same time, enable guidance (with the aid of an external magnetic field) of the drug-loaded nanoparticles to a targeted location and only there release the incorporated payload. As the drug of choice, 5-fluorouracil was used, whereas the synthesis procedures were optimized using another, model drug, paracetamol.

Based on the results of the performed *in vitro* drug release study (and the quantification of the released concentration with the help of an UV/Vis spectrophotometer), we can confirm the successful incorporation and desired release of the incorporated drugs, suitable for the targeted application.

The characterization of the Ni_xCu_{1-x} magnetic nanoparticles was performed using X-ray powder diffraction (XRD), thermogravimetric analysis (TGA), Fourier transform infrared spectra (FTIR), transmission electron microscopy (TEM), the surface morphology was characterized by atomic force microscopy (AFM). The suitable Curie temperature was determined using modified thermogravimetric analysis on a TGA/SDTA (Mettler Toledo). The release of the model drugs from the prepared formulation was studied directly in the UV/Vis Spectrophotometer (Cary 60 UV/Vis Spectrophotometer, Agilent, Germany). The cytotoxicity tests for the Ni_xCu_{1-x} anticancer drug-loaded nanoparticles were done using on human skin derived basal cell carcinoma cells.

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NiCu-silica composites as potential drug delivery systems

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Many groups have already investigated the use of NiCu nanoparticles as mediators for magnetic fluid hyperthermia ^[1], but we were the first who reported the potential of NiCu nanoparticles as bimodal therapeutic system, capable of simultaneous magnetic hyperthermia and targeted drug delivery. ^[2] The superparamagnetic nanoparticles have a magnetic core- we can manipulate them by an external magnetic field, a biocompatible layer- we can attach suitable receptors on them, and a therapeutic load- the drug can be incorporated inside the pores or hosted within internal cavities of the particles. ^[3]

In this study we incorporated three model drugs with different pharmacological activity into superparamagnetic Ni_xCu_{1-x} nanoparticles. The superparamagnetic Ni_xCu_{1-x} nanoparticles were prepared with a sol-gel method, the Curie temperature was in the therapeutic range for use in magnetic hyperthermia. The nanoparticles were prepared in a silica matrix to avoid the agglomeration during thermal treatment and to allow the adsorption of the drug inside the pores.

The release of the incorporated drugs was studied using an *in vitro* release system, whereas UV-Visible Spectrophotometry (UV/Vis) was used for quantification of the released amount of drug. The Ni_xCu_{1-x} nanoparticles were characterized using X-ray diffraction (XRD) analysis, thermogravimetric analysis (TGA/SDTA) and modified thermogravimetric analysis for determination of Curie temperature, Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and magnetic measurements (VSM). Surface area and pore size were determined by using BET analysis.

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Optical and sensing properties of N-(Rhodamine-B)-lactam-ethylenediamine (RhB-EDA) fluorescent sol-gel layers

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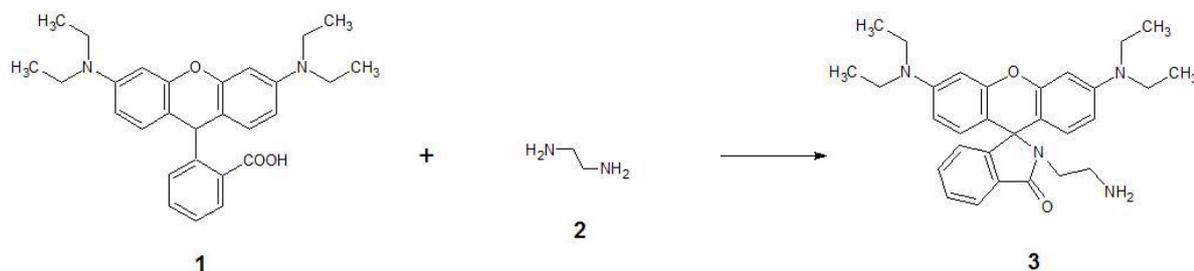
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This study presents chemical modification of a Rhodamine B (RhB) sensor probe by ethylenediamine (EDA), and investigation of its spectral, as well as sensor properties to the pH. Rhodamine-based sensor probe (RhB-EDA) was incorporated into various sol-gel materials using tetraethoxysilane (TEOS) and methyltrimethoxysilane (MeTriMOS) in various ratios for detection of pH in the range of pH 4.0 to 7.0, suggesting its utility for acid vesicle studies in cell biology, measuring the pH of lysosomes. The influence of varied micro-environment of RhB-EDA probe on pH response as well on optical properties were investigated.

RhB-EDA (3) was synthesised in our laboratory, by treating RhB (1) with EDA (2), which was followed by precipitation by water. After filtering the crude product and its drying in a vacuum dryer, RhB-EDA (3) was obtained in a 93 % yield (Scheme 1).



Scheme 1: Synthesis of RhB-EDA.

The probe was stored in the dark at Room Temperature (RT) and showed no changes in the structure, as well in the optical properties, after one year.

The nanotoxicity of RhB-EDA probe using MG63 and HUVEC cells was furthermore investigated, showing that RhB-EDA is toxic at high concentrations. For more accurate data on toxicity and its concentration dependence, the experiment on standard cytotoxic tests should be performed.

Sol – gel preparation of Ni_xCu_{1-x}/silica nanocomposites using different silica precursors

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The use of magnetic nanoparticles in biomedical applications has recently attracted considerable attention in fields like magnetic resonance imaging, drug delivery and magnetic hyperthermia. The early research in those areas focused mainly on iron oxide - based materials, due to their simple synthesis, high magnetization, and biocompatibility. However, they have also a significant drawback due to their high Curie temperature (T_C). Nickel – copper nanoparticles with the general formula Ni_xCu_{1-x} combine the above – mentioned advantages with a significantly lower T_C , making them a promising material for magnetic hyperthermia, as well as for targeted drug delivery ^[1].

To avoid agglomeration and/or oxidation of such nanoparticles, they usually have to be coated with silica, noble metals or polymers. The silica coating not only stabilizes the nanoparticles, but also improves their biocompatibility and allows further surface functionalization or drugs incorporation ^[2]. In this study, nanoparticles with the composition Ni_{67.5}Cu_{32.5} were prepared using the sol-gel method via an *in situ* application of the precursor tetraethyl orthosilicate (TEOS) or its combination with other silica precursors, e.g. (3-aminopropyl)triethoxysilane (APTES), phenyltriethoxysilane (FTES), vinyltriethoxysilane (VTES) and bis-1,2-(triethoxysilyl)ethane (BTSE).

The as-prepared coated nanoparticles were characterized using X-ray powder diffraction (PXRD), FTIR spectroscopy, thermogravimetric analysis (TGA), transmission electron spectroscopy (TEM), specific surface area and porosity (BET), and magnetization measurements (VSM). The results confirmed the absence of nonmagnetic oxides in samples, the presence of the silica coating formed from respective precursors, as well as a high potential for the use in magnetic hyperthermia. It can also be concluded that the basic characteristics of Ni_xCu_{1-x} nanoparticles can be varied to a certain extent with the preparation of functional coatings.

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Self-assembled Ge nanowire meshes grown with magnetron sputtering

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A simple method for achieving three-dimensional Ge nanowire mesh embedded in an amorphous alumina matrix, via magnetron sputtering deposition, was discovered. Structural properties of the meshes are governed by self-organized growth regime and depend on deposition speed and temperature. Possibilities for control of structure parameters were investigated, including nanowire width, distance between mesh knots, and angle between nanowires and film plane. A wide range of different meshes was deposited, with sizes less than 10 nm, and measured with Transmission Electron Microscopy (TEM) and Grazing Incidence Small Angle X-ray Scattering (GISAXS). Different charge transport regimes were found, including ohmic, space charge limited conduction and traps dominated ^[1].

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