NANOAPP
Nanomaterials & Application
22. - 26. September, Portorož, Slovenia

BOOK OF ABSTRACTS

Portorož – Slovenija

September 22-26. 2013

IOS
Institute for Environmental Protection and Sensors

University of Maribor

ICG Montpellier
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UNIVERSITÉ DE LYON

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АКАДЕМІЯ НАУК УКРАЇНИ
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Aleksandra Lobnik
Andreja Gutmaher

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1. International Scientific Conference | 1. Mednarodna znanstvena konferenca

NANOAPP International Scientific Conference on Nanomaterials & Applications
NANOAPP Mednarodna znanstvena konferenca Nanomateriali & aplikacije

Venue | Prizorišče
GH Bernardin, Portorož, Slovenija

Dates | Datum
22nd - 26th of September 2013 | 22. – 26. september 2013

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Prof. Dr. Stephane Parola, ENS Lyon, University of Lyon, CNRS, France
Prof. Dr. Michel Wong Chi Man, Institute Charles Gerhardt Montpellier, France

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FOREWORD

Welcome to the NANOAPP 2013 Conference in Portorož, Slovenia

We are delighted to have you participate in the **NANOAPP 2013** (www.nanoapp.org) which celebrates the “First Year of many to come” at Grand Hotel Bernardin, Portorož, Slovenia.

Scientists and industry will be offered a forum for the presentation of the latest research and discoveries in the field of advanced nanomaterials and their applications at a global level. World-renowned scientists in the field of ***synthesis and applications of novel nanomaterials for medicine, biotechnology, energy, environment, sensors, and textiles*** will be present at the meeting. Great emphasis will also be placed on delivering information about the impact of nanomaterials and nanotechnology on the environment and human health.

The Conference will be held four days, starting on Monday, September 23rd and concluding on Thursday, September, 26th. The meeting will consist of both oral and poster contributions.

We offer special thanks to the Co-chairs, Organizing Committee, The International Scientific Committee, and the many on-site assistants for their tireless efforts in producing this world-class event. We hope you enjoy your stay in Portorž, and that you experience a truly valuable and memorable meeting.

Chair of the NANOAPP 2013 Conference

Prof. Dr. Aleksandra Lobnik

NANOAPP
Nanomaterials & Application
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Day 1: Sunday, 22nd September 2013	
16:00 - 19:00	**Registration -** Congress Centre Foyer Grand Hotel Bernardin
19:00 – 21:00	**Welcome Reception and Posters -** Foyer Terace Grand Hotel Bernardin
End of the Day 1	
Day 2: Monday, 23th September 2013	
9:00 - 9:10	**Emerald Room: Welcome Remarks - Prof.Dr. A. Lobnik, Slovenia and Prof.Dr. M. Wong Chi Man, France**
Chair	**Prof.Dr. A. Lobnik, Slovenia**
9:10 - 9:25	**Minister of Economic Development and Technology - M.Sc. S. Stepišnik, Slovenia**
9:25 - 9:35	**Rector of the University of Maribor - Prof.Dr. D. Rebolj, Slovenia**
9:35 - 10:30	**Special invited talk of Nobel Prize Winner Prof.Dr. L. Kajfež Bogataj, Slovenia: Climate change: Could Nanotechnology be the Environmental Saviour?**
10:30 – 11:00	**Coffee Break and Posters**
Chair	**Prof.Dr. A. Lobnik, Slovenia**
11:00 - 11:10	**Minister of Education, Science and Sport - Dr. J. Pikalo, Slovenia**
Chair	**Prof.Dr. M. Wong Chi Man, France**
11:10 – 12:10	**Plenary Lecture K1: Prof.Dr. K. Kuroda, Japan - Silicate-based building blocks for nanomaterials and nanocomposites**
12:10 – 13:10	**Plenary Lecture K2: Prof.Dr. C. Sanchez, France - Integrative Chemistry based approaches to Inorganic and Hybrid Nanostructured Solids**
13:10 - 14:40	**Lunch**
Chair	**Prof.Dr. S. Parola, France**
14:40 – 15:40	**Plenary Lecture K3: Prof.Dr. D. Avnir, Izrael - Molecularly doped metals: A new family of functional nanohybrid materials**
15:40 – 16:30	**Coffee Break and Posters**

SYMPOSIUM A		**SYMPOSIUM B**		**SYMPOSIUM C**	
Nanomaterials/Hybrid Nanomaterials		**Magnetic Nanomaterials**		**Nanomaterials and Applications**	
Room	**Emerald I**	**Room**	**Emerald II**	**Room**	**Mediteranea I**
Session Chair	**Prof.Dr. K. Kuroda, Japan**	**Session Chair**	**Prof.Dr. R. Zboril, Czech Republic**	**Session Chair**	**Prof.Dr. A. Majcen Le Marechal, Slovenia**
16:30 – 17:00	**Invited Lecture I1: Prof.Dr. M. Osada, Japan** Two-Dimensional Oxide Nanomaterials and Their Applications	**16:30 – 17:00**	**Invited Lecture I4: Prof.Dr. S. Kobe, Slovenia** Magnetic nanostructures towards elimination of heavy rare earth in Nd-Fe-B magnets	**16:30 – 17:00**	**Invited Lecture I7: Prof.Dr. F. Romanato, Italy** Nanofabrication of composite materials for plasmonic sensing applications
17:00 - 17:30	**Invited Lecture I2: Prof.Dr. A. Shimojima, Japan** Porous Hybrid Networks Assembled from Cage-type Siloxanes and Organic Linkers	**17:00 - 17:30**	**Invited Lecture I5: Prof.Dr. B. Pichon, France** Assemblies of Magnetic Iron Oxide Nanoparticles with tuneable Nanostructures and Magnetic properties	**17:00 - 17:30**	**Invited Lecture I8: Prof.Dr. L. D. Carlos, Portugal** Luminescent thermometry at the nanoscale
17:30 - 18:00	**Invited Lecture I3: Prof.Dr. C. Gerardin, France** Polymer-functionalized mesoporous silica: preparation using dynamic polymer micelles as structuring and functionalizing agents	**17:30 - 18:00**	**Invited Lecture I6: Prof.Dr. D. Makovec, Slovenia** Synthesis of Nanocomposite Particles by Coating Magnetic Spinel Ferrite onto Different Core Nanoparticles: Nanocomposite Particles Based on a Hexaferrite ($BaFe_{12}O_{19}$) Core and a Maghemite (γ-Fe_2O_3) Shell	**17:30 - 17:50**	**Oral Presentation O1: Prof.Dr. F. Romanato, Italy** The nano technological Venetian district. An approach to technological transfer.

19:00 –	**Departure to Piran - 20 minutes easy walk**
20.00 - 21.30	**Concert: Anton and Nina Merkoci in THE CONVENT OF ST. FRANCIS IN PIRAN**
End of the Day 2	

Day 3: Tuesday, 24th September 2013

SYMPOSIUM A		**SYMPOSIUM B**		**SYMPOSIUM C**	
Nanomaterials/Hybrid Nanomaterials		**Magnetic Nanomaterials**		**Nanomaterials and Applications**	
Room	**Emerald I**	**Room**	**Emerald II**	**Room**	**Mediteranea I**
Session Chair	**Prof.Dr. M. Osada, Japan**	**Session Chair**	**Prof.Dr. S. Kobe, Slovenia**	**Session Chair**	**Prof.Dr. B. Simončič, Slovenia**
9:00 - 9:30	**Invited Lecture I9: Prof.Dr. M. Ogawa, Japan** Morphosynthese of nanoporous silicas from well defined particles to homogeneous coating	**9:00 - 9:30**	**Invited Lecture I11: Prof.Dr. S. Bégin-Colin, France** Dendronized magnetic nano-objects for MRI and hyperthermia	**9:00 - 9:30**	**Invited Lecture I14: Dr. L. Scherer, Switzerland** Controlled caffeine transfer through light-responsive membrane
9:30 - 10:00	**Invited Lecture I10: Prof.Dr. M. Wong Chi Man, France** New functional bridged silsesquioxanes	**9:30 - 10:00**	**Invited Lecture I12: Prof.Dr. R. Zboril, Czech Republic** Iron-bearing materials in advanced environmental and biomedical nanotechnologies	**9:30 - 10:00**	**Invited Presentation I15: Dr. M. Likon, Slovenia** Poplar seed fibers – Examples of the use of natural nano / micro materials in practice
10:00 - 10:20	**Oral Presentation O2: Dr. D. Lisjak, Slovenia** Tailoring the size and morphology of nanoparticles by chemical substitution for specific applications	**10:00 - 10:30**	**Invited Lecture I13: Prof.Dr. N. TK Thanh, United Kingdom** Next Generation of Magnetic nanoparticle for Biomedical Application	**10:00 - 10:30**	**Invited Lecture I16: Prof.Dr. B. Vončina, Slovenia** Preparation, characterization and application of photochromic nanocapsules
10:20 - 10:40	**Oral Presentation O3: Prof. Dr. Y. Zub, Ukraine** Features of the Formation of Functional Polysiloxane Nanolayer on the Surface of Ceramic Membranes	**10:30 - 10:50**	**Oral Presentation O6: Dr. S. Gyergyek, Switzerland** Synthesis of iron oxide magnetic nanoparticles and their heating properties	**10:30 - 11:00**	**Invited Lecture I31: Dr. M. Čajlaković, Austria** Hybrid organic–inorganic nanocomposites and their applications in optical sensing
		10:50 - 11:10	**Oral Presentation O7: Dr. P. Jenuš, Slovenia** Influence of an applied magnetic field on the magnetic nanoparticles assembly	**11:00 - 11:20**	**Oral Presentation O9: Prof. Dr. L. Scherer, Switzerland** Textiles meet Light
11:40 - 12:00	**Poster Session**				
12:00 - 13:30	**Lunch**				
Chair	**Prof.Dr. C. Sanchez, France**				
Room	**Emerald I**				
13:30 - 14:30	**Plenary Lecture K4: Prof.Dr. J. Wang, USA - Catalytic Nanomachines: Design and Applications**				
14:30 - 15:30	**Plenary Lecture K5: Prof.Dr. D. Mihailovič, Slovenia - Bistable control of electronic order on the femtosecond timescale in transition metal chalcogenide non-volatile memory devices**				
16:00 - 19:00	**Departure for Excursion to Sečovlje Salina Nature Park**				
End of the Day 3					

Day 4: Wednesday, 25th September 2013

SYMPOSIUM A		SYMPOSIUM B	
Nanomaterials and Energy		Nanomaterials and Environment	
Room	**Emerald I**	**Room**	**Mediteranea**
Session Chair	**Prof. Dr. D.Mihailović, Slovenia**	**Session Chair**	**Prof.Dr. Y. Zub, Ukraine**
9:30 - 10:00	**Invited Lecture I17: Prof.Dr. M. Gaberšček, Slovenia** Nanomaterials for batteries and fuel cells	**9:30 - 10:00**	**Invited Lecture I21: Prof.Dr. O. Solcova, Czech Republic** Nanomaterials for Photocatalytic Reactions
10:00 - 10:30	**Invited Lecture I18: Prof.Dr. N. Zabukovec Logar, Slovenia** The Potential of Nanoporous Materials in Heat Storage Applications	**10:00 - 10:30**	**Invited Lecture I22: Prof.Dr. M.-J. Menu, France** Bifunctional silica nanoparticles as new nanoprobes for biofilms exploration
10:30 - 11:00	**Invited Lecture I19: Prof.Dr. D. Boyer, France** Smart lighting devices based on the combination of luminescent nanocomposites with UV or blue emitting LEDs	**10:30 - 11:00**	**Invited Lecture I23: Prof.Dr. B. Heinrichs, Belgium** Nanostructured Catalysts with enhanced properties for pollutant and waste treatment
11:00 - 11:20	**Oral Lecture O11: Dr. M. Lira-Cantu, Spain** Application of V2O5 Xerogel as Hole-Transport Layer in Organic Solar Cells: Towards Low Cost Printed Optoelectronic Devices	**11:00 - 11:20**	**Oral Lecture O13: Dr. M. Bauman, Slovenia** Adsorption of heavy metal ions by highly functionalized SiO2 particles
11:20 - 11:40	**Oral Lecture O12: Dr. N. Francolon, France** Surface modification of core-shell NaYF4:Yb,Tm@SiO2 nanoparticles for the early prostate cancer diagnosis in the NIR range	**11:20 - 11:40**	**Oral Lecture O18: M. Morozova, Czech Republic** Thin Sol-gel TiO2 Layers as the Simple Chemical Sensor
11:40 - 12:30	**Scientific Committee Meeting**		
12:10 - 13:30	**Lunch**		
Chair	**Prof. Dr. D. Avnir, Israel**		
Room	**Emerald I**		
13:30 - 14:30	**Plenary Lecture K6: Prof.Dr. H. Hofmann, Switzerland - Inorganic Nanoparticles for medical applications**		
14:30 - 15:30	**Plenary Lecture K7: Prof.Dr. S. Parola, France - Metal nanoparticles as a tool for controlling the properties of dyes. Applications in bioimaging and optics.**		
Chair	**Prof.Dr. L. Blum, France**		
15:30 - 16:30	**Plenary Lecture K8: Prof.Dr. J. Homola, Czech Republic - Biosensors Based on Surface Plasmons: Advances and Applications**		
18:00	**Conference Dinner on the Terace nearby St. Bernardin Church**		
End of the Day 4			

Day 5: Thursday, 26th September 2013

SYMPOSIUM A		SYMPOSIUM B	
Nanomaterials in Bio/Medical Applications		Nanomaterials in Sensors	
Room	**Mediteranea I**	**Room**	**Adria**
Session Chair	**Prof.Dr. H. Hofmann, Switzerland**	**Session Chair**	**Prof.Dr. J. Homola, Czech Republic**
9:00 - 9:30	**Invited Lecture I24: Prof.Dr. J. O. Durand, France** Porous silicon nanoparticles functionalized for 2-photon photodynamic therapy of cancer cells	**9:00 - 9:30**	**Invited Lecture I29: Prof.Dr. L. Blum, France** Nano- and micro-structuration of the sensing layers for chemiluminescence-based biosensors and electrochemical sensors.
9:30 - 10:00	**Invited Lecture I25: Prof.Dr. G. Goglio, France** Glycine Nitrate Process: a suitable route to elaborate complex oxide nanoparticles for biomedical applications	**9:30 - 10:00**	**Invited Lecture I30: Prof. Dr. M. Es-Souni, Germany** Template synthesis of Nanomaterials for energy and sensing applications
10:00 - 10:30	**Invited Lecture I28: Prof.Dr. M. H. Delville, France** Correlative qualitative and quantitative aspects of titanium oxide nanoparticles fate and toxicity in skin cells and multicellular living specimens	**10:00 - 10:30**	**Invited Lecture I27: Prof.Dr. L. Vellutini, France** A nanodesigned silica surface for biotechnology applications
10:30 - 10:50	**Oral Lecture O16: Dr. D. Warther, Switzerland** Sub 25nm mesoporous silica nanoparticles for retinoblastoma cells labeling and two-photon photodynamic therapy	**10:30 - 10:50**	**Oral Lecture O17: Dr. Š. Korent Urek, Slovenia** Benefits of Using Mesoporous Materials for Heavy Metal Optical Detection
10:50	**Closing Remarks - Prof.Dr. A. Lobnik, Slovenia and Prof.Dr. M. Wong Chi Man, France**		
Room	**Mediteranea I**		
	End of the Conference		

Climate change: could nanotechnology be the environmental saviour?

Lučka Kajfež Bogataj
University of Ljubljana

Wasteful and inequitable consumption and production especially during last decades have had a devastating environmental impact resulting in climate change, desertification and huge losses to biodiversity. Effects that scientists had predicted in the past would result from global greenhouse gas emissions causing climate change are now occurring: loss of sea ice, longer, more intense heat waves, more extreme weather events, crop failures and rising ocean levels.

There has been considerable debate on the role of innovation in responding to climate change. Essential fields of innovation are how to reduce energy consumption by employing more efficient technologies that minimize use of fossil fuels, adopting technologies that utilize renewable energy and energy storage technologies including carbon separation, capture, sequestration and conversion. Some of the technological solutions offer solutions to climate change but they may also have unintended environmental, economic and social consequences. High tech 'drop-in' techno-fixes might not be enough to save us from climate change; we may need system level change. In many instances the cheapest and most effective energy savings will be achieved through demand reduction and policy to support it.

Nanotechnology may have a major role to play in responding to climate change. It is a powerful technology that has the potential to deliver novel approaches to the methods by which we harness, use, and store energy. Incorporation of nanotechnology into larger systems, such as the hydrogen based economy, solar power technology or next generation batteries and supercapacitors, improved insulation of buildings; fuel additives that could enhance the energy efficiency of motor vehicles potentially could have a profound impact on energy consumption and hence greenhouse gas emissions. However, detailed analysis of the benefits to be gained from the development of nanotechnology in the context of climate change are still missing.

There are also emerging concerns about the potential risks that nanotechnologies present to the environment and the ability of current regulatory regimes to sustainably manage those risks. As nanotechnologies are an emergent field of science and technology, it is not yet clear precisely how big is the environmental footprint of nanomanufacturing. The energy demands of nanomaterials manufacture, the global warming potential of manufacturing, the chemical burden of manufacturing, the water demands of production, the impact of manufacturing on resource depletion and land use are still unknown. On the other hand nanotechnology might play an important role in adaptation to new climate conditions by providing effective adaptation solutions for the built environment, agriculture etc. Very little systematic research exists in that direction.

Many important questions still do not have answers. Should there be a prohibition on the intentional release of nanomaterials into the environment until the climate change benefits can be demonstrated to outweigh the risks? Do we need a rigorous assessment of nanoproducts inspite of complex, time consuming, and expensive detailed scientific analysis? Should nanoproducts only be undertaken for technologies with the utmost of potential and where a simpler substitution is not available? Is nanotechnology just another rapidly growing industry more focused on maximizing production and technological development than on environmental efficiency or sustainability? Are some areas of nanotechnology research a dangerous distraction from the real emissions mitigation we need to be undertaking – and represent a substantial opportunity cost for mitigation measures that could instead be receiving funding? Only after all above questions are properly addressed, we can judge if nanotechnology is an unqualified environmental saviour that will enable us to pursue ‘business as usual’ while substantively reducing our environmental footprint.


Nanotechnology to Combat Global Warming
Reduced Energy Consumption and Improving Efficiency
• Use of High Strength Materials
• Nanocatalysts to Improve Fuel Efficiency
• Reducing Friction in Engines
• Improved Insulation for Buildings
• Advanced Lighting Technology
Carbon Management
• Separation
• Capture
• Sequestration
• Conversion
Renewable Energy and Storage Technologies
• Solar Cells
• Fuel Cells
• Hydrogen Economy
• Energy Storage
- Batteries
- Supercapacitors

Silicate-based building blocks for nanomaterials and nanocomposites

Kazuyuki KURODA

Department of Applied Chemistry & Kagami Memorial Research Institute for Materials Science and Technology, Waseda University, Shinjuku-ku, Tokyo 169-8555, JAPAN

kuroda@waseda.jp

The possibilities of silica-, silicate-, and siloxane-based building blocks for the design of nanomaterials and nanocomposites will be presented. Layered alkali silicates, such as layered sodium octosilicate, have $SiOH/SiO^-$ groups on the interlayer surfaces which can be modified chemically with various silylating agents. The properties of modified silicate sheets are controlled by the introduction of functional groups. Organic modification of interlayer surfaces by silylation provides various possibilities including exfoliation to nanosheets. Tubular silicate imogolite is a unique inorganic component for materials design. Nanosized silica- and siloxane-based components, such as mesoporous silica nanoparticles (MSN) and dendritic siloxane oligomers should also have high potentiality because the surfaces can be modified in various ways to adapt the conditions required for various applications. Layered silicates can also be regarded as 2D building blocks which can be converted to three dimensional networks by interlayer condensation or by using cross-linking agents. KSW-2 type mesoporous silica is prepared by the interactions between layered silicate kanemite with surfactants. Because mesoporous materials are compositionally, structurally, and morphologically tuned, there are many potential applications in various fields including separation, catalysis, nanocomposite formation, medicine, electronics, optics, etc.

"Integrative Chemistry based approaches to Inorganic and Hybrid Nanostructured Solids"

Clément Sanchez

Collège de France, Laboratoire de Chimie de la Matière Condensée de Paris, CNRS, Université Pierre et Marie Curie. Collège de France, 11 Place Marcelin Berthelot, Bâtiment D. 75231, Paris, France.

clement.sanchez@upmc.fr

Hybrid inorganic-organic materials can be broadly defined as synthetic materials with organic and inorganic components which are intimately mixed. They can be either homogeneous systems derived from monomers and miscible organic and inorganic components, or heterogeneous and phase-separated systems where at least one of the components' domains has a dimension ranging from a few Å to several nanometers. Hybrid phases can also be used to nanostructure or texture new inorganic nanomaterials (porous or non porous). The mild synthetic conditions provided by the sol-gel process such as metallo-organic precursors, low processing temperatures and the versatility of the colloidal state allow for the mixing of the organic and inorganic components at the nanometer scale in virtually any ratio. These features, and the advancement of organometallic chemistry and polymer and sol-gel processing, make possible a high degree of control over both composition and structure (including nanostructure) of these materials, which present tunable structure-property relationships. This, in turn, makes it possible to tailor and fine-tune properties (mechanical, optical, electronic, thermal, chemical…) in very broad ranges, and to design specific systems for applications. Hybrid materials can be processed as gels, monoliths, thin films, fibers, particles or powders or can be intermediates to design materials having complex shapes or hierarchical structures. The seemingly unlimited variety, unique structure-property control, and the compositional and shaping flexibility give these materials a high potential in catalysis, biocatalysis, photocatalysis, etc…. This lecture will describe some recent advances on the chemistry and processing of nanostructured and hierarchically structured functional inorganic and hybrid solids. Some of their properties will be discussed.

A few recent reviews :

Aerosol Route to Functional Nanostructured Inorganic and Hybrid Porous Materials , Boissiere, Cedric; Grosso, David; Chaumonnot, Alexandra; et al. ADVANCED MATERIALS Volume: 23 Issue: 5 Pages: 599-623 , 2011

Applications of advanced hybrid organic-inorganic nanomaterials: from laboratory to market Sanchez, Clement; Belleville, Philippe; Popall, Michael; et al. CHEMICAL SOCIETY REVIEWS Volume: 40 Issue: 2 Pages: 696-753, 2011

Molecular and supramolecular dynamics of hybrid organic-inorganic interfaces for the rational construction of advanced hybrid nanomatériaux, Grosso, David; Ribot, Francois; Boissiere, Cedric; et al.CHEMICAL SOCIETY REVIEWS Volume: 40 Issue: 2 Pages: 829-848 2011

Design and properties of functional hybrid organic-inorganic membranes for fuel cells , Laberty-Robert, C.; Valle, K.; Pereira, F.; et al. CHEMICAL SOCIETY REVIEWS Volume: 40 Issue: 2 Pages: 961-1005 2011

Titanium oxo-clusters: precursors for a Lego-like construction of nanostructured hybrid materials , Rozes, Laurence; Sanchez, Clement

CHEMICAL SOCIETY REVIEWS Volume: 40 Issue: 2 Pages: 1006-1030 2011

Bio-inspired synthetic pathways and beyond: integrative chemistry , Prouzet, Eric; Ravaine, Serge; Sanchez, Clement; et al. NEW JOURNAL OF CHEMISTRY Volume: 32 Issue: 8 Pages: 1284-1299 2008

Design, synthesis, and properties of inorganic and hybrid thin films having periodically organized nanoporosity , Sanchez, Clement; Boissiere, Cedric; Grosso, David; et al. CHEMISTRY OF MATERIALS Volume: 20 Issue: 3 Pages: 682-737 2008

Inorganic and hybrid nanofibrous materials templated with organogelators , Llusar, Mario; Sanchez, Clement CHEMISTRY OF MATERIALS Volume: 20 Issue: 3 Pages: 782-820 2008

Photonic and nanobiophotonic properties of luminescent lanthanide-doped hybrid organic-inorganic materials , Escribano, Purificacion; Julian-Lopez, Beatriz; Planelles-Arago, Jose; et al. JOURNAL OF MATERIALS CHEMISTRY Volume: 18 Issue: 1 Pages: 23-40 2008

Biomimetism and bioinspiration as tools for the design of innovative materials and systems , Sanchez, C; Arribart, H; Guille, MMG, NATURE MATERIALS Volume: 4 Issue: 4 Pages: 277-288 2005

Molecularly doped metals: A new family of functional nanohybrid materials

David Avnir

Institute of Chemistry and the Center for Nanoscience and Nanotechnology, the Hebrew
University of Jerusalem, Jerusalem 91904

We developed a nanomaterials technology, which enables, for the first time, the incorporation and entrapment of small organic molecules, polymers, biomolecules, and nanoparticles within metals; new materials, denoted dopant@metal, are formed. This type of materials has been unknown. The many millions of organic and bioorganic molecules, represent a very rich library of chemical, biological, and physical properties that the ~100 metals are devoid of. One can imagine the huge potential which can be opened by the ability to tailor metals with any of the properties of organic molecules. Metals will then have not only the traditional properties and applications, but also many new properties, which will merge their classical virtues (e.g., conductivity and catalytic activity) with the diverse properties of organic molecules. We have indeed found that the creation of dopant@metal yields new properties which are more, or different than the sum of the individual properties of the two components. So far we have developed methods for doping silver, copper, gold, magnetic cobalt, iron, platinum and palladium. Some of the useful applications which have been demonstrated, include alteration of classical metal properties (such as conductivity), induction of un-orthodox properties to metals (such as rendering a metal acidic or basic), formation of new metallic catalysts such as metals doped with organometallic complexes, creation of materials which are at the border between polymeric and metallic, formation of bioactive metals by enzymes entrapment, induction of chirality within metals, induction of corrosion resistance in iron, formation of efficient biocidal materials, new batteries and more. A variety of synthetic methods have been developed for creating the dopant@metals, including aqueous homogeneous and heterogeneous reductions of the metal cations, reductions in DMF, electrochemical entrapments, and thermal decompositions of metal carbonyls. The picture that has emerged is of entrapment within agglomerated nanocrystals. A useful property of the porosity is that the dopant is accessible for chemical reactions; this has been utilized for catalysis. Entrapment and adsorption are very different processes: Water-soluble entrapped molecules cannot be extracted by water, but the same molecules are easily washed away if only adsorbed. Likewise, most of the special properties that we have observed to date - such as major improvements or changes in catalytic activity, completely different TGA behavior, and more - are observed only in the entrapped cases.

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Catalytic Nanomachines: Design and Applications

Joseph Wang

Department of Nanoengineering, University California San Diego, La Jolla, CA 92093, USA

E-mail: josephwang@ucsd.edu

Abstract

The remarkable performance of biomotors is inspiring scientists to create synthetic nanomachines that mimic the function of these amazing natural systems. This presentation will discuss the challenges and opportunities facing the design and operation of artificial nanomotors and demonstrate their prospects for diverse biomedical applications. Particular attention will be given to catalytic nanowire and microtube motors propelled by the catalytic decomposition of a chemical fuel, as well as to fuel-free (magnetically or electrically-driven) nanomotors. While artificial nanomotors still pale compared to nature biomotors, recent advances indicate significant improvements in the velocity, power, motion control, cargo-towing force, scope and versatility of such catalytic nanomotors. The greatly improved capabilities of chemically-powered artificial nanomotors could pave the way to exciting and important applications ranging from drug delivery to nanosurgery, and to sophisticated nanoscale devices performing complex tasks.

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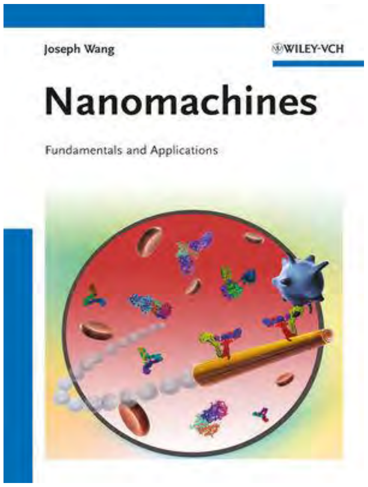


Figure 2. Capture of cancer cells (Ref. 1).

Joseph Wang is Professor in Department of Nanoengineering at University of California, San Diego (UCSD). He received Ph.D. from the Technion in 1978. He held Regents Professorship and a Manasse Chair positions at NMSU, and served as the director of Center for Bioelectronics and Biosensors of Arizona State University (ASU). Prof. Wang has published more than 900 papers, 10 books and he holds 12 patents (H Index=100). He received 2 ACS National Awards in 1999 and 2006 and 4 Honorary Professors from Spain, Argentina and Slovenia. He became the most cited electrochemist in the world and received the 4th place in the ISI's list of 'Most Cited Researchers in Chemistry' in 1996-2006. Prof. Wang is the Editor-in-Chief of *Electroanalysis (Wiley)*. His scientific interests are concentrated in the areas of nanomachines, bioelectronics, biosensors, bionanotechnology and electroanalytical chemistry.

Bistable control of electronic order on the femtosecond timescale in transition metal chalcogenide non-volatile memory devices.

D. Mihailovic[1,2], T. Mertelj[1], I.Vaskivskyi[1], L.Stojchevska[1] and S.Brazovskii[3]

1. Jozef Stefan Institute and Postgraduate School, Jamova 39, 1000 Ljubljana, Slovenia,
2. CENN Nanocenter, Jamova 39, 1000 Ljubljana, Slovenia,
3. LPTMS-CNRS, U. Paris-Sud, bat. 100, Cite Université, 91405 Orsay, France

dragan.mihailovic@ijs.si

Transition metal dichalcogenides (TMDs) have recently become a subject of both fundamental and technological interest as electronic materials exhibiting superior switching properties compared to other 2D materials, potentially challenging silicon in nano devices. Many TMD materials are well known for their spontaneous collective charge density wave ordering properties, but so far these effects have not been utilised in any kind of useful device. Here we report on a new potential application of TMD materials for non-volatile memory devices based on controllable switching of a CDW system between different collectively ordered states. Resistance switching is demonstrated in 1T-TaS_2 using single 35 fs laser pulses which sets a record in terms of switching speed for a non-volatile switching device. The device - a phasistor - switches between two different phases of the material allows unprecedented ultrahigh data writing rates, well beyond current nanosecond memory devices. The effect responsible for the swtiching is also of great fundamental interest as the first known example of bistable switching to and from a hidden metastable state under non equilibrium conditions, The hidden state is not reachable under thermodynamic conditions, and is shown to occur only with ultrashort laser pulses.

Inorganic Nanoparticles for medical applications

H. Hofmann

Powder Technology Laboratory, Ecole Polytechnique Fédéral de Lausanne, Station 12

CH-1015 Lausanne, Switzerland

heinrich.hofmann@epfl.ch

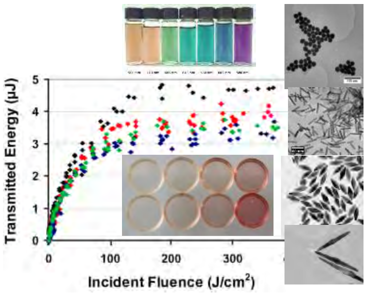
Nanoparticles with a superparamagnetic core are highly multifunctional instruments for biomedical applications, including contrast agent for MRI, vector for gene or drug delivery or as local heat sources, hyperthermia. For these mentioned applications, the particles have too fulfill several characteristics like high magnetization, high magnetic anisotropy, biocompatibility, specific targeting, high colloidal stability or simple and cost efficient production. It is impossible that a pure and simple nanoparticle can reach this goals, therefore complex coatings were necessary. In this talk the different method and processes to coat nanosized iron oxide particles (SPION) would be presented and discussed in spite of view of the target application. Additionally we have also to treat the key problems regarding clinical use of the particles which are missing understanding of the interaction between particle and the biological systems like cells or organelles. Also the comportment in blood is still not very well controlled. To investigate how functionalized SPIONs interact with cells and cell organelles, modified the surface with polyvinyl alcohol, silica, gold or even more complex with maleimide-PEG-NHS to the surface of the particle which allowed a further derivatisation by coumarin, c[RGDfK-(Ac-SH)] peptide and organelle targeting peptides. The proteins detected after re-separation of the particles from cell cultures and in vivo experiments give an important insight to the interaction of inorganic nanoparticles with biological systems and would allow the design of new biocompatible particles. These results show that we have developed a very useful tool for the investigation of the cell-particle interactions which will allow to conduct more detailed investigation regarding drug and gene delivery, toxicity of nanoparticles and the development of new diagnostic tools. The work presented is partially financed by ***the*** European Community's Seventh Framework Programme (FP7) under GRANT AGREEMENT No 228929, ACRONYM NanoDiaRA.

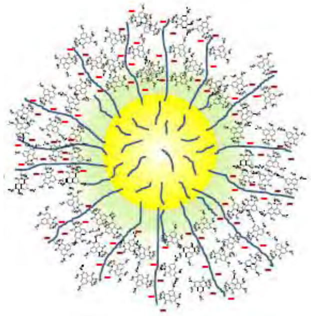
Metal nanoparticles as a tool for controlling the properties of dyes. Applications in bioimaging and optics.

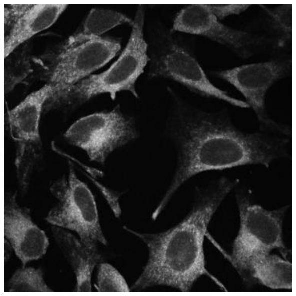
S. Parola

Laboratoire de Chimie, ENS Lyon, CNRS, Université Lyon 1, France,
stephane.parola@univ-lyon1.fr

The development of new hybrid nanoplatforms which can combine optical properties of chromophores with inorganic nanomaterials is of increasing interest for optical and biomedical purposes. In the last decade, noble metal nanoparticles have sparked wide interest for developing new optical applications in the context of bio-imaging, photo-thermal therapy, optical sensors and solar cells. This interest is essentially due to their unique optical properties related to their Localized Surface Plasmon Resonances (LSPR). This optical property at the nanoscale has been used to enhance the optical properties of molecular systems located close to noble metal nanostructures as, for instance, in SERS experiments. Numerous works are investigating the possibility of using the light interaction with metallic nanoparticles to improve the luminescence of chromophores. These nanoparticles can be used for bioimaging or phototherapy. Combination of metal nanoparticles and chromophores in composite materials (films, monoliths) is also a great challenge for optical applications but requires control of dispersion during the process in order to control molecule to particles interactions. This was successfully achieved and showed strong impact of the metal-molecule interactions on the overall optical properties. This will be illustrated by examples of applications in fluorescence imaging, dark field imaging, photodynamic therapy on cells and optical protection against lasers.







Biosensors Based on Surface Plasmons: Advances and Applications

J. Homola

Institute of Photonics and Electronics, Chaberská 57, 182 51 Prague 8, Czech Republic.

Surface plasmons are special modes of an electromagnetic field which may propagate along thin metal films (propagating surface plasmons) or exist on metal nanoparticles (localized surface plasmons). Surface plasmons are highly sensitive to changes in the local environment, which make them attractive for the development of (bio)sensors. In the last two decades, numerous sensors based on propagating surface plasmons (sometimes referred to as surface plasmon resonance (SPR) sensors) have been developed and SPR sensors have become a central tool for characterizing and quantifying biomolecular interactions. Moreover, SPR biosensors have been increasingly applied to detection of chemical and biological species [1]. In recent years, the sensing potential of localized surface plasmons has been extensively studied and various sensor platforms based on localized surface plasmons on metal nanoparticles or their arrays have been developed.

This paper reviews recent advances in the development of plasmonic biosensors, including advances in the method, optical instrumentation, microfluidics and functionalization methods. Special attention is given to evaluation and comparison of performance of plasmonic sensors based on spectroscopy of propagating surface plasmons and those based on spectroscopy of localized surface plasmons. Examples of bioanalytical applications illustrating performance and potential of plasmonic biosensors are presented. These include detection of analytes related to medical diagnostics (protein and nucleic acid markers), environmental monitoring (endocrine disrupting compounds), and food safety (drug residues, bacterial pathogens and toxins).

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Two-Dimensional Oxide Nanomaterials and Their Applications

M. Osada[1] and T. Sasaki[1]

[1]International Center of Materials Nanoarchitectonics (WPI-MANA),
National Institute for Materials Science, Tsukuba 305-0044, Japan

Two-dimensional (2D) nanosheets, which possess atomic or molecular thickness and infinite planar lengths, have been emerging as important new materials due to their unique properties. In particular, the recent development of methods for manipulating graphene has provided new possibilities and applications for 2D material systems; many amazing functionalities such as high electron mobility and quantum Hall effects have been discovered. This breakthrough has opened up the possibility of isolating and exploring the fascinating properties of 2D nanosheets of other layered materials, which upon reduction to single/few atomic layers, will offer functional flexibility, new properties and novel applications. We are working on the creation of new oxide nanosheets and the exploration of their novel functionalities in electronic applications [1,2]. Titania- or perovskite-based nanosheets exhibit superior high-□ performance (□$_r$ = 100–320) even at a few-nm thicknesses, which is an essential requirement for next-generation electronics. Additionally, nanosheet-based high-□ capacitors exceed textbook limits, opening a route to new capacitor devices. One more interesting concept using 2D oxide nanosheets is designing complex nanodevices and superstructured nanohybrids such as all nanosheet FETs, artificial ferroelectrics, spinelectronic devices, magneto-plasmonic metamaterials, Li-ion batteries, etc. With these unique aspects, 2D nanosheets will become an important research target in the form of “oxide graphene”.

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Porous Hybrid Networks Assembled from Cage-type Siloxanes and Organic Linkers

A. Shimojima

Waseda University, Ohkubo-3, Shinjuku-ku, Tokyo 169-8555, Japan.

Inorganic–organic hybrid porous materials have attracted great interest because of their wide range of potential applications. Covalent-linking of molecular building units is a promising route to produce porous materials with unique structures and properties. The double-four-ring (D4R) siloxane unit (Si_8O_{12}), known as a secondary building unit of zeolites, is useful as an inorganic building unit because of its rigidity, high symmetry, and hyperbranched architecture. Recently, significant progress has been made in the synthesis of hybrid porous materials from D4R siloxanes either by cross-coupling with organic linkers or by self-polymerization via C–C bonds [1]. The use of organic linker molecules allows facile variation of the pore characteristics depending on the length or the geometry of the linkers, although cleavage of the Si–O–Si bonds often occurs to give amorphous networks. To achieve well-defined hybrid porous networks, reactions that proceed under milder conditions have been examined. Synthesis of hybrid porous networks by imine (R^1–N=C–R^2, R = organic groups) formation between formyl-functionalized D4R units and phenylenediamine or by Si−O−R formation between hydrido-D4R units and various diols [2] have been achieved. Synthesis, characterizations and the properties of these new microporous materials will be presented

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Polymer-functionalized mesoporous silica: preparation using dynamic polymer micelles as structuring and functionalizing agents

C. Gérardin

Institut Charles Gerhardt Montpellier UMR 5253 CNRS-ENSCM-UM2-UM1
Montpellier, France.

A highly versatile and powerful preparation route of polymer-functionalized ordered mesoporous materials will be presented [1]: smart assemblies of hydrophilic diblock copolymers are used as innovative structuring and functionalizing agents for the direct synthesis, at room temperature and in water, of polymer-functionalized mesoporous silica. The concept consists in replacing the classical amphiphilic template by induced and reversible assemblies of water-soluble block copolymers. More precisely, the new functional assemblies are dynamic reversible PolyIon electrostatic Complex (PIC) micelles of double-hydrophilic block copolymers [2], whose micellization process can be easily controlled by pH or ionic strength variations. Such PIC micelles are used as porogens and as agents of homogeneous functionalization of mesopores with polyacid or polybasic chains. The new synthesis strategy allows the recovery and recycling of the porogen polymers in water [3]. It also permits the direct preparation of polymer-functionalized mesopores.

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Magnetic nanostructures towards elimination of heavy rare earth in Nd-Fe-B magnets.

Spomenka Kobe, Paul McGuiness
Jožef Stefan Institute

Permanent magnets based on rare earths (REs), in particular the neodymium-iron-boron (Nd-Fe-B) type, have revolutionized the worlds of computing, motors/actuators and electrical/electronic devices. Furthermore, they are increasingly important in environmentally critical technologies like hybrid and pure electric vehicles (HEVs and EVs) as well as for wind turbines.

Suggestions will be given on how to drastically reduce or totally eliminate the need to use scarce and most expensive heavy rare earths (HREs) like terbium (Tb) and dysprosium (Dy, which are indispensable in high coercivity, high temperature applications and represent by far the highest expense in production of Nd-Fe-B magnets:

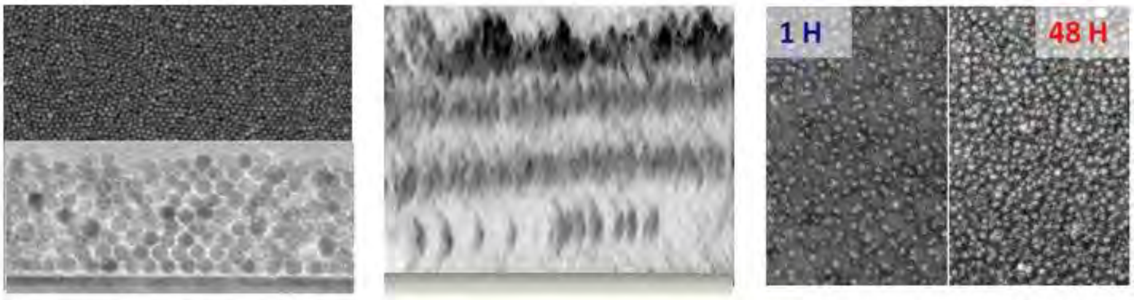
A typical magnet for automotive or moderately high-temperature use employs about 30-24 weight percent Nd and 4–10 weight percent Dy or Tb, i.e., Dy/Nd = 0.2. Therefore the real problem in terms of critical supply lies in the heavy rare earths, rather than REs in general. It will be presented how these heavy rare earths can be reduced or even totally eliminated by advanced synthesis, characterization and modeling focused on grain boundary engineering, introducing modified grain boundaries and sophisticate control of the microstructure towards the nanoscale, as one of the possible solutions.

Assemblies of Magnetic Iron Oxide Nanoparticles with tuneable Nanostructures and Magnetic properties

Benoît Pichon, [*,a] Xavier Cattoën [b,c] and Sylvie Begin-Colin,[a]
[a] Institut de Physique et Chimie des Matériaux de Strasbourg (UMR CNRS-UdS-ECPM 7504)
23 rue du loess - BP 43 67034, Strasbourg cedex 2
Benoit.Pichon@unistra.fr
[b] Institut Charles Gerhardt Montpellier, 8 Rue de l'Ecole Normale, 34296 Montpellier Cedex 5, France
[c] Institut Néel, UPR2940 CNRS/UJF, 25 rue des Martyrs, 38042 Grenoble, France.

The assembling of magnetic nanoparticles (NPs) into arrays represents a very exciting and important challenge with regards to their high potential in the development of new nanodevices for spintronic, magnetic and magneto-electronic applications. The physical properties of NPs assemblies being significantly dependent on their spatial arrangement, it is well argued that the key to successful applications of such nanoparticle-based devices is engineering well-defined nanostructures. Magnetic properties are strongly dependent on dipole-dipole interactions and can be finely tuned by controlling the interparticle distance. Therefore magnetic NPs may be considered as independent and non interacting elemental nano-magnets for high storage applications while tight packed NPs assemblies ruled by collective properties are suitable for sensors.

Here we report on the assembling of inorganic-organic hybrid NPs by using three different bottom-up techniques which are all based on specific interactions between functional organic groups at NP and substrate surfaces. Mono- and multilayer hybrid nanostructures with tuneable interparticle and interlayer distances have been prepared by the Langmuir-Blodgett [1] and the Layer by Layer techniques [2], respectively. In addition, sizeable domains of NPs and tuneable interparticle distance have been addressed by molecular patterning resulting from self-assembled monolayers (SAMs) of organic molecules. [3] More recently, we have developed e new approach based on click chemistry which enable the structuration of highly stable assemblies.[4] Finally, the nanostructure of these hybrid films has been correlated to their magnetic properties.



Electronic micrographs of nanoparticle assemblies prepared by the Langmuir-Blogdett technique (left), the layer by Layer technique (center) and the SAM technique (right).

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Synthesis of Nanocomposite Particles by Coating Magnetic Spinel Ferrite onto Different Core Nanoparticles: Nanocomposite Particles Based on a Hexaferrite ($BaFe_{12}O_{19}$) Core and a Maghemite (γ-Fe_2O_3) Shell

D. Primc[1], M. Drofenik[1,2], D. Makovec[1]

[1]Department for Materials Synthesis, Jožef Stefan Institute, Ljubljana, SI-1000, Slovenia.
[2]Faculty for Chemistry and Chemical Technology, University of Maribor, Maribor, SI-2000, Slovenia.

With multifunctional nanocomposite particles, the useful properties of different materials are combined on a nanoscale. One way to synthesize such nanocomposite particles is by coating nanoparticles made of one material with a shell made of another material. A new synthesis route that yields a magnetic spinel ferrite shell on the surfaces of different core nanoparticles will be presented for the case of nanocomposite particles consisting of hard-magnetic, barium hexaferrite ($BaFe_{12}O_{19}$) core nanoparticles, and a soft-magnetic, spinel maghemite (γ-Fe_2O_3) shell. The formation of the shell is achieved by the heterogeneous nucleation of iron (oxide)hydroxide FeOOH on the surfaces of the core nanoparticles, with close control of the reaction kinetics during the precipitation of the Fe^{2+}/Fe^{3+} ions. Subsequently, the formed (oxide)hydroxide shell transforms into magnetic spinel ferrite. When ultrafine discoid hexaferrite nanoparticles are used as the cores, their reaction with the precipitating Fe species results in nanoparticles that differ in terms of the composition and structure, compared with any known compound. If the larger platelet core nanoparticles are coated, the spinel grows epitaxially on the structurally similar hexaferrite, forming sandwich-type nanocomposite particles. The magnetic exchange coupling between the two phases results in a large increase in the magnetic energy product $|BH|_{MAX}$.

Nanofabrication of composite materials for plasmonic sensing applications.

F. Romanato[1,2,3]

[1]University of Padova, Department of Physics and Astronomy, via Marzolo 8, 35131 Padova, Italy
[2]Laboratory for Nanofabrication of Nanodevices, LaNN – Venetonanotech, Corso StatiUniti 4,
35127 Padova, Italy
[3]CNR-IOM National Laboratory, Area Science Park, S.S. 14 km 163.5, 34012 Basovizza, Trieste,
Italy

In the last few years the interest in nanostructures for sensing application has grown increasingly leading to the development of new designs based on the surface plasmon resonance of metallic structures[1], [2],[3]. By carefully tuning the nanostructures taking into account the materials, their geometry, surface multilayer combination and electro-optical features it is possible to design highly specific and sensitive sensing platform suitable for many different analytes detection.

Several types of plasmonic nanostructures have been designed in order to adjust resonance frequencies, resulting in amplification and confinement of the electromagnetic field around specific areas of the structure. They have pyramidal, conical, wedge-like, undulated shapes fabricated controlling multilayer material and nanoscale each on them characterized by peculiar optical and bio functional properties. These complex array of nanostructures can be considered as metamaterials whose properties in term of analytes trapping, complex optical properties, nanofluidic properties that can be designed and carefully controlled. We will present the strategies of design, the physical models of plasmon resonance excitation, the nanomaterial synthesis, the nano fabrication processes as well as the bio-functionalization looking forward the detection optimization [4], [5], [6],[7].

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We will show specifically the realization of multiple large area arrays of nanostructures transparent substrate, in order to produce a substrate suitable for microfluidic experiments and transmission analysis. Multiple membrane mask has been produced and employed to fabricate large areas chips on a transparent substrate. One type of these nanostructred substrates was used for the development of innovative Grating-Coupled Surface Plasmon Resonance (GCSPR) sensor configuration based on polarization modulation. The grating surface was grafted with an antifouling layer of polyethylene oxide (PEO) in order to prevent non-specific interactions. The assembled nanostructured substrate becomes a model of bio-recognition assays based on biotin/avidin reaction and 22mer DNA/PNA binding were used as test validation. Output signal exhibits harmonic dependence on polarization and the phase term is exploited for sensing analysis achieving competitive performance in refractive index sensitivity with values down to 6 □ 10^{-7} RIU (Refractive Index Units).

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Luminescent thermometry at the nanoscale

Luís D. Carlos

Departamento de Física and CICECO, Universidade de Aveiro, 3810–193 Aveiro, Portugal

The assortment of luminescent and non–luminescent nanothermometers that have been proposed over the last five years clearly point out the emergent interest of nanothermometry in innumerable fields, such as electronics, photonics, micro and nanofluidics, and nanomedicine. Despite of the promising progress on micro/nanofluidics and intracellular thermometry, precision control of fluid temperature by accounting for local temperature gradients and accurate temperature distributions within living cells have not yet been satisfactorily addressed [1].

The talk presents distinct examples of lanthanide-based nanothermometers: i) a γ–Fe_2O_3 maghemite core coated with an organosilica shell co-doped with Eu^{3+} and Tb^{3+} β-diketonate chelates [2]; ii) a di-ureasil organic-inorganic film embedding Eu^{3+} and Tb^{3+} β-diketonate chelates [3] and iii) an all-in-one nanoplatform comprising $(Gd,Yb,Er)_2O_3$ nanorods (thermometers) that were surface-decorated with gold nanoparticles (heaters) [4]. Whereas for ii) the temperature profile of a microelectronic circuit recovered with the hybrid film is accessed with a high spatial resolution ($1\text{-}2\times10^{-6}$ m), in i) the design of the siloxane-based hybrid host and chelate ligands permits the working of the nanothermometers in nanofluids (water suspensions) at 293–320 K with an emission quantum yield up to 0.38±0.04, a relative sensitivity of ca. 1.5% K^{-1} and a spatio-temporal resolution of 64×10^{-6} m–150×10^{-3} s. Furthermore, the heat propagation velocity in the nanofluid was determined at 294 K using simply the nanothermometers Eu^{3+}/Tb^{3+} steady-state spectra. Moreover, we discuss that the all-in-one nanoplatform is a step forward towards assessing the local temperature of laser-excited gold nanostructures. The local temperature is calculated using either Boltzmann's distribution (300–1050 K) of the Er^{3+} up-conversion $^2H_{11/2}\rightarrow{}^4I_{15/2}/{}^4S_{3/2}\rightarrow{}^4I_{15/2}$ intensity ratio, or Planck's law (1200–2000 K) for a white-light emission ascribed to the blackbody radiation.

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Morphosynthese of nanoporous silicas from well defined particles to homogeneous coating

Makoto Ogawa
Department of Earth Sciences and Graduate School of Creative Science and Engineering,
Waseda University, 1-6-1 Nishiwaseda, Shinjuku-ku, Tokyo 169-8050, Japan
e-mail: makoto@waseda.jp

ABSTRACT

After the successful preparation of mesostructured and mesoporous silica films by the solvent evaporation method,[1,2] the preparation of mesoporous silica films have been extensively investigated partly due to the wide range of application of mesoporous silica films for low-*k* material for semiconductor electronics[3], nano-reactors for photochemical reaction[4], and membranes[5]. In addition to the solvent evaporation method, the deposition of mesoporous silica layer from acidic aqueous solution and vapor phase has been reported to prepare mesoporous silica layers on flat substrates toward with high structural regularity or controlled thickness.[6,7] Here, we report an alternative synthetic way to deposit homogeneous nanoporous silica thin layer on a variety of solids surfaces from flat substrate to micrometer size powders and, as to the materials, from oxide and hydroxides to carbon and organic polymers.[8-13] The present reaction is very simple, where substrates (both plate and powder) were put into a homogeneous solution containing tetraethoxysilane, hexadecyltrimethylammonium chloride, methanol, water and ammonia. The present synthesis is a new and versatile method to prepare nanoporous silica thin layers on solid substrate especially when the reported procedure is not applicable; substrate with complex morphology and/or unstable in acidic solutions such as hydrotalcite and ZnO. Mesoporous silica coating is regarded as a way to modify the surface properties of powders as well as to impart new functions such as molecular sieving one on catalysts and adsorbents.[14]

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Dendronized magnetic nano-objects for MRI and hyperthermia

Delphine Felder-Flesch,[a*] Claire Billotey,[b] Benoit Pichon,[a] Sylvie Begin-Colin,[a*]

[a] Institut de Physique et Chimie des Matériaux de Strasbourg IPCMS UMR CNRS-UdS-ECPM 7504 23 rue du loess BP 43 67034 Strasbourg cedex 2

Sylvie.Begin@ipcms.unistra.fr, Delphine.Felder@ipcms.unistra.fr
[b] Hospices Civils de Lyon - Service de Médecine Nucléaire Pavillon B, 5 place d'Arsonval, 69437 Lyon cedex 03, France.

Some of the significant and most promising applications for inorganic nanoparticles (NPs) lie in the fields of biology and biomedicine. Due to their magnetic properties tuned by their shape and/or composition, superparamagnetic iron oxide NPs (SPIO) with appropriate surface chemistry can be used in numerous in vivo applications such as MRI contrast enhancement, hyperthermia treatment, cell sorting, drug delivery...
In that context, we will present the main synthesis ways of iron oxide NPs and their functionalization and we will propose a concept combining a dendritic coating of magnetic oxide nanoparticles with phosphonate anchors. Indeed, phosphonates ensure a strong anchoring at the NPs surface while preserving their magnetic properties, and dendritic shells, in addition to their small and easily controllable size (as a function of their generation), are promising building blocks simultaneously solving the problems of biocompatibility, large in vivo stability and specificity. Dendronized iron oxide nanoparticles were demonstrated to induce any cytotoxicity. I*n vivo* and *in vitro* MRI measurements showed that the contrast enhancement properties of the dendronized NPs were higher than those obtained with commercial polymer-coated NPs. Moreover, both types of dendronized NPs were eliminated by urinary and hepatobiliary pathways without unspecific uptake especially in the RES organs and in the lungs. The design of dendronized NPs was further improved to obtain theranostic nano-objects (which can both identify disease states and simultaneously deliver therapy) by adjusting the morphology and the composition of the inorganic magnetic core and by designing multifonctionalized dendrons. These NPs were found suitable to combine imaging and therapy by hyperthermia.

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Iron-bearing materials in advanced environmental and biomedical nanotechnologies

Radek Zboril

Regional Centre of Advanced Technologies and Materials, Palacky University Olomouc,
17. listopadu 12, 771 46 Olomouc, Czech Republic
zboril@prfnw.upol.cz

Iron and its compounds show a huge potential in various nanotechnologies due to their low-cost, biocompatibility, non-toxicity, biodegradability, and environmentally friendly character. A broad spectrum of accessible valence states (0, II, III, IV, V, VI) and polymorphism of iron (III) oxides [1] contribute to the miscellaneous chemistry and variety of applications of Fe-bearing nanomaterials. Thus, nanoscale zero valent iron (nZVI) represents environmentally friendly tool for in-situ reductive treatment of ground water contaminated by, e.g., chlorinated hydrocarbons, uranium, and heavy metals. In the talk, selected results of large scale remediation with nZVI will be discussed together with some challenging applications including cyanobacteria removal [2]. Nanocrystalline iron (III) oxides in various structural forms are widely recognized as promising materials in biomedicine, biotechnologies or catalysis. The control of the structural, morphological, and surface properties of nanocrystalline iron oxides towards tailored applications in MRI contrast enhancement, targeted drug delivery, and direct solar splitting of water will be discussed [3,4]. Ferrates, iron oxides with high oxidation state of Fe (IV,V,VI) complete a broad portfolio of iron-bearing compounds having a significant potential in environmentally friendly technologies. Especially, ferrate(VI) is highly efficient oxidation/sorption material enabling to remove many organic compounds, cyanides, heavy metals or chemical warfare agents. In these applications, the formed nanocrystalline iron oxides play the crucial role. We will demonstrate and discuss the extraordinary efficiency of ferrate(VI)-induced removal of arsenic through its embedding in the structure of the in-situ formed iron(III) oxide [5]. In the last part, various multifunctional hybrids of iron oxides with carbon nanostructures and nanosilver will be introduced and their applications in advanced water treatment technologies and biomedicine will be analyzed [6].

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Next Generation of Magnetic Nanoparticles for Biomedical Applications

Nguyen TK
Thanh

UCL Healthcare Biomagnetic and Nanomaterials Laboratories, and Department of Physics & Astronomy, University College London, UK.

Email: ntk.thanh@ucl.ac.uk *http:www.ntk-thanh.co.uk*

Magnetic nanoparticles have many potential clinical applications, however, the currently available MNPs namely iron oxide are sub-optimal in terms of their physical and biochemical properties. They have lower saturation magnetisation and often are not well biofunctionalised for specific biological target. In this presentation, novel class of MNPs with different size, shape (cube, octopods, rods, multipods, star), chemical composition (e.g., metallic Co, alloy FePt, trimetallic FePtPd, etc..;), coating and surface chemistry have been fabricated using wet chemical methods.

Multifunctional/hybrid MNPs with noble metal Au and semiconductor quantum dots CdSe were also synthesised. Magnetic nanoparticles could be used to track neural stem cells after a transplant in order to monitor how the cells heal spinal injuries

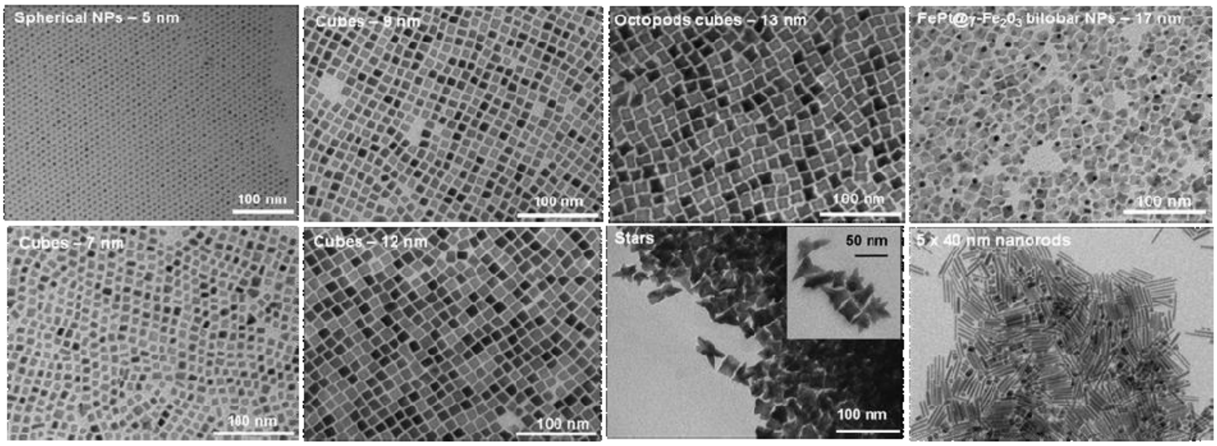

Fig 1: ***Tunable shapes of magnetic nanoparticles: Fe-Pt, Fe-Pd and Fe-Pt-Pd alloys***

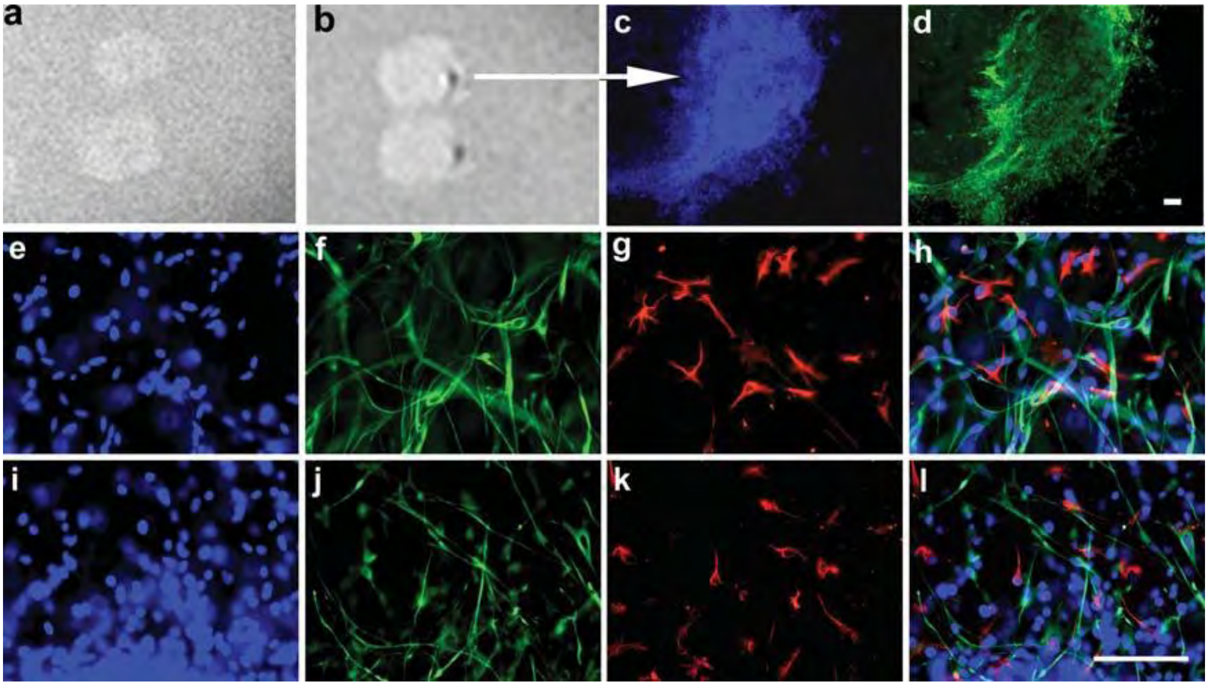

Fig 2. CoPt-labeled NSCs detected by MRI after transplantation into rat spinal cord slices

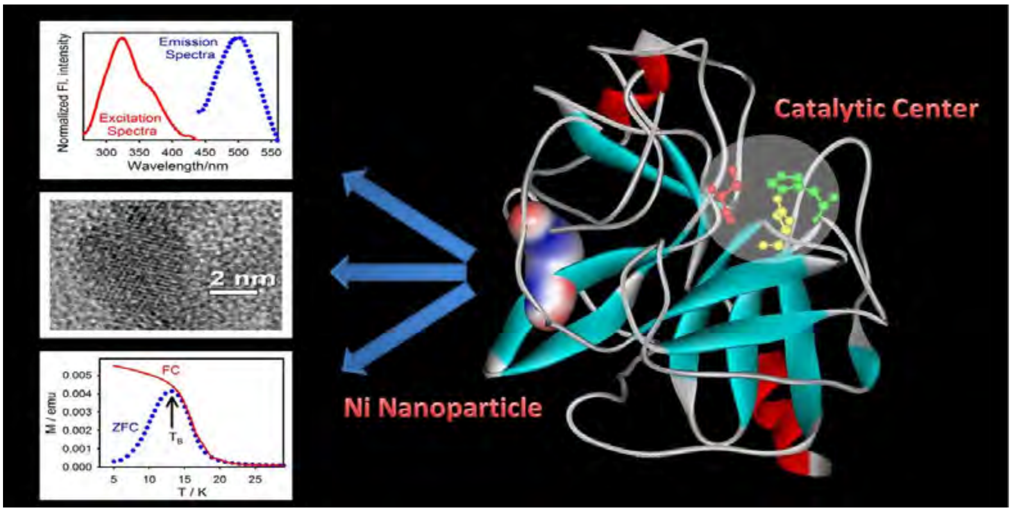

Fig 3. Superparamagnetic Fluorescent Nickel-Enzyme Nanobioconjugates

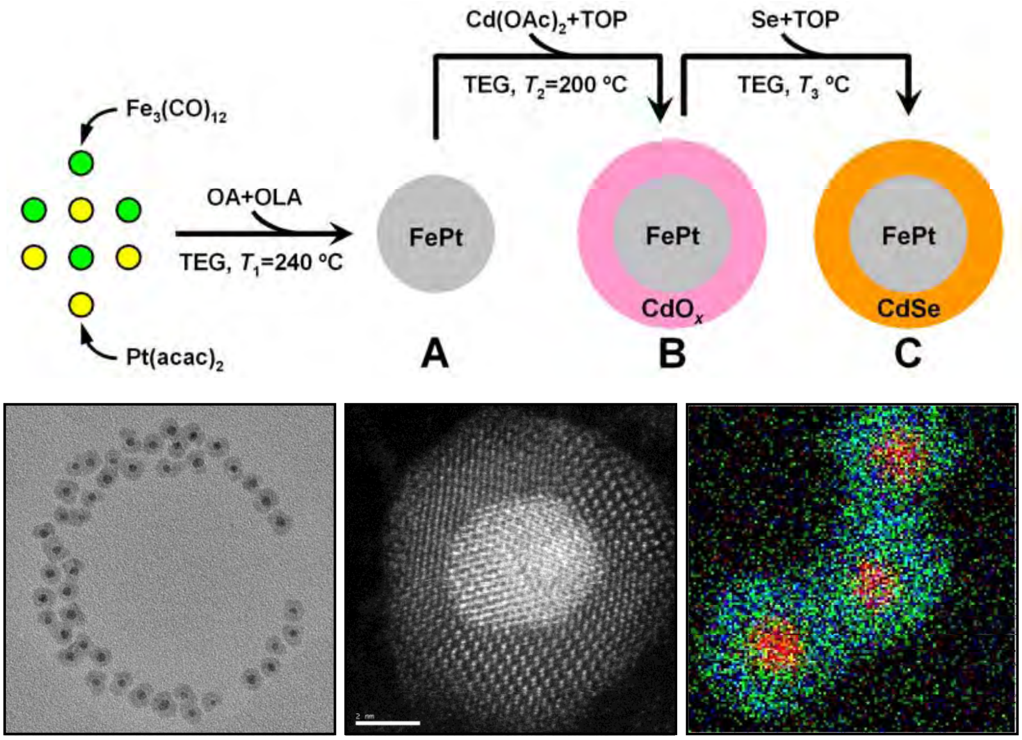

Fig 4. Core@Shell Structure of FePt@CdSe Nanoparticles

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Controlled caffeine transfer through light-responsive membrane

Lukas Baumann,[a,b] *Katrin Schöller,*[a] *Damien de Courten,*[c,d] *Martin Wolf,*[c] *René M. Rossi*[a] *and*
*Lukas J. Scherer**,[a]

[a]Empa, Swiss Federal Laboratories for Materials Science and Technology,
Lerchenfeldstrasse 5, St.Gallen, Switzerland. *lukas.scherer@empa.ch*
[b]University of Basel, Klingelbergstrasse 80, 4056 Basel, Switzerland.
[c]University Hospital Zurich, Frauenklinikstrasse 10, 8091 Zürich, Switzerland.
[d]ETH Zurich, Rämistrasse 101,8092 Zürich, Switzerland.
lukas.scherer@empa.ch

To avoid apnea, preterm neonates are treated nowadays with caffeine either orally or via infusion. This treatment leads to an over- dose shortly after application and an under-supply at a later stage. Since caffeine penetrates the skin of neonates, a controlled release and thus a constant up-take of caffeine by the neonates can be achieved by a transdermal drug-release system with a stimuli-responsive membrane as smart release unit.

Since light can be applied rapidly, locally, remotely and reversibly, it is the ideal trigger for such a system. In the presentation, the successful development of a highly flexible nanoporous light-responsive membrane will be discussed [1]. The membranes were based on copolymers made of different spirobenzopyran acrylates and 2-hydroxyethyl acrylate grafted from track-edged polycarbonate or polyester membranes. Different surface-induced polymerization techniques (plasma-induced random polymerization, different ATRP techniques) were compared and had a major influence not only on the switchability but also on the kinetics and the stability towards photobleaching of the membrane. Interestingly, the main reason for the change of the permeability resistance were electrostatic changes of the surfaces and not sterical changes of the membrane pores [2].

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Poplar seed fibers – Examples of the use of natural nano / micro materials in practice

I. Likon[1], A. Lobnik[2], M. Likon[3]

[1]Gimnazija Koper, Cankarjeva 12, Koper, Slovenia.
[2]IOS d.o.o., Beloruska ulica 7, Maribor, Slovenia.
[3]Insol d.o.o., Cankarjeva ulica 16a, Postojna, Slovenia.

In 2011 European Commission offered its definition of “nanomaterial”, it recommended to identify a nanomaterial only on the basis of its particle size [1] “The justification for this choice is that properties or risks posed by a nano-sized material are not determined by the intention of the manufacturer and do not differ depending on whether the nanomaterial is natural, produced incidentally, or the result of a manufacturing process with or without the explicit intention to produce a nanomaterial. There are many naturally occurring nanomaterials and they may exhibit similar properties to those that are manufactured. From a definition point of view it is therefore not logical to omit certain types of materials on the basis of their genesis.” [2]. A lot of efforts have been done during past years to extract and purified natural nanomaterials, especially natural nanofibers. Cellulosic nanofibers are of the special interests for the use in advanced nanomaterial applications. Especially for production of medical materials [2], biosensors [4], ultralight composite materials and hi-tech textile [5]. The Slovenian authors discovered special sorption and insulation characteristics of poplar seed fibers [6,7]. Additional researches showed that fibers have special morphological structure [8]. Actually, they take place in twilight zone between micro and nano world due to their length they are micro fibers but due of their wall thickness they are felt in nano world. Poplar seed hair fibers are hollow hydrophobic micro tubes with an external diameter between 3 and 12 μm, an average length of 4±1 mm and average tube wall thickness of 400±100 nm. 89 vol. % of those fibres represents empty void. The solid skeleton of the hollow fibers consists of lingo cellulosic material coated by a hydrophobic waxy coating. The exceptional chemical, physical and microstructural properties of poplar seed hair fibers enable super-absorbent behavior with high absorption capacity for heavy motor oil and diesel fuel. The absorption values of 182-211 g heavy oil/g fiber and 55-60 g heavy oil/g fiber for packing densities of 0.005 g/cm^3 and 0.02 g/cm^3, respectively, surpass all known natural absorbents. Their thermodynamic conductivity depends from package density but in general is lower than 0,03 W/m^{2}K what is comparable with advanced insulation materials.

Up to now the Poplar seed fibers obtained from the trees of Populus nigra italica are generally treated as waste material or, at best, as low-quality fertilizer. The fibers are extremely light, hydrophobic, possess large active specific surface area and float on water surfaces without long-term degradation, even when soaked with hydrophobic liquids. The micro tubular morphology and the resistant and resilient chemical structure of the tube walls make poplar seed fibers an extremely promising natural source for the production of an oil super sorbent and insulation. The use of poplar seed fibers for the production of oil absorbents and insulation materials is sustainable, has a low (even negative) carbon footprint, has a low energy demand and is very clean. At the end of its life cycle, when an oil absorbent based on poplar seed fibers becomes a waste product, it can be used as a high-energy fuel, burning without the emission of noxious fumes.

Due to their exception characteristics those fibers are promising materials to be used as bracket for actives substances used in medical applications.

The Poplar trees, which includes poplars, cottonwoods and aspen trees, represents a huge natural source of fibers with exceptional physical properties which are an extremely promising natural source for the production of advanced materials with high added value.

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Preparation, characterization and application of photochromic nanocapsules

B. Voncina[1], B. Neral[1] , T. Feczko[2,3]

[1]University of Maribor, Faculty of Mechanical Engineering, Institute for Engineering Materials and Design, Maribor, Slovenia

[2]Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, Pusztaszeri u. 59-67., Budapest, 1025, Hungary

[3]Research Institute of Chemical and Process Engineering, University of Pannonia, Egyetem u. 10.,Veszprém, 8200, Hungary

Photochromic compounds change colour on exposure to light, while the reversion may be attributable either to radiation or may be thermal. The use of photochromism on fabrics can provide new opportunities to develop smart textiles; for example, sensors and active protective clothes.

Ethyl cellulose-1,3-dihydro-1,3,3,4,5 (and 1,3,3,5,6) -pentamethyl-spiro-[2H-indole-2,3'-(3H)naphtha(2,1-b)(1,4) oxazine] composites were prepared by an oil-in-water emulsion, solvent evaporation method in order to form easily suspendable and fatigue-resistant photochromic nanoparticles/nanocapsules in screen-printing paste. Their size was well below 1 μm and did not change substantially over a wide range of dye concentrations.

After screen-printing, a homogenous photochromic layer was built on a cotton substrate surface, which represented substantial blue colour development in CIELab colour space measurements because of ultraviolet light, even at a dye concentration of 0.045% w ⁄ w. The addition of a photodegradation inhibitor, Tinuvin 144, further increased the coloration of the printed fabric.

Nanomaterials for batteries and fuel cells

Miran Gaberscek[1,2,3]

[1]National Institute of Chemistry, Hajdrihova 19, SI-1000 Ljubljana, Slovenia

[2]Centre of Excellence Low Carbon Technologies, Hajdrihova 19, SI-1000 Ljubljana, Slovenia

[3]Faculty of Chemistry and Chem. Tech., University of Ljubljana, Slovenia

The functioning of modern batteries and fuel cells relies almost exclusively on the use of appropriate electrochemically-active nanomaterials. Even more, the typical electrode in these devices consists of up to 5 different phases, each usually appearing in a nanoform. These phases are not arbitrarily intermixed but need to be structurised in a carefully prescribed way to provide optimised transport pathways for electrons and ions – the essential energy carriers. Thus, it is quite appropriate to use the term nanoarchitectures when speaking about the smallest units of such electrodes.

We will first present the synthesis and preparation approaches that can lead to well defined battery and fuel cell electrode nanoarchitectures. After that we will explain on practical examples the role of each of the phases in functioning of battery or fuel cell. The importance of size (micro vs. nano) will be demonstrated experimentally and theoretically. Special nanoeffects will be presented and commented in some detail. Finally, the first model taking into account the collective effects of nanoparticles will be presented and illustrated on a practical example of ordinary rubber balloons mounted on a common pressure vessel (a couple of movies will serve as a basis for theoretical and practical explanation).

The Potential of Nanoporous Materials in Heat Storage Applications

N. Zabukovec Logar

National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia

Thermochemical heat storage (TCS) utilises the reversible chemical and physical sorption of gases, mostly water vapour, in solids. It is considered the only storage concept with a potential for long-term, also seasonal, low-temperature (up to 150 ^{o}C) thermal energy storage. Under the influence of a heat supply, water is removed from the material that is then stored separately (activation of material). When water vapour and sorbent are put into contact, there is a heat release (material's discharge or deactivation). The essential breakthrough that is still needed to commercialise the storage concept is precise design and engineering of new storage materials, as well as energy and resource efficient and environmentally benign synthesis routes.

The current S&T activities are targeted at the development of porous adsorbents with optimized physical-chemical properties for maximum heat storage capacity and suitable interactions with vapours**.** The quick and fully reversible hydration processes in micro- and meso-porous materials is considered superior to those in crystallohydrates, which are also attractive TCS materials at a relatively low cost, but suffer from very slow sorption kinetics and severe materials degradation. In the lecture, some recent studies of the structure/sorption-behavior relationship in microporous solids with the aim of improving the design of storage materials, will be presented [1]. The highlights will be on the role of chemical composition, pore size, hydrothermal stability and thermal conductivity of selected microporous aluminophosphates and metal-organic framework materials.

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Smart lighting devices based on the combination of luminescent nanocomposites with UV or blue emitting LEDs

D. Boyer, G. Chadeyron, N. Pradal, A. Garrido, S. Thérias, R. Mahiou

Clermont Université, Institut de Chimie de Clermont-Ferrand, UMR 6296 CNRS / UBP / ENSCCF, 24 avenue des Landais, BP 80026, 63171 Aubière, France.

Nanophosphors with different compositions and shapes were prepared by soft chemistry routes. They were dispersed in polymer matrices in order to achieve luminescent nanocomposite films. These films were combined with blue or UV excitation to produced white light with suitable chromaticity coordinates.

Nowadays, the white light emitting diodes (WLEDs) are considered as one of the most promising eco-friendly light sources, not containing mercury and more energy efficient than conventional lighting devices (incandescent and compact fluorescent light bulbs). Current commercial WLEDs use a 460 nm blue GaN LED chip covered by a $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce) yellowish phosphor coating. However, this association suffers from some weaknesses such as a low stability of color temperature and a poor color rendering index (CRI) due to a weak contribution in the red wavelength range. Combining deep-ultraviolet (DUV – 200 nm $\leq \lambda_{em} \leq$ 300 nm) or ultraviolet (UV – 300 nm $\leq \lambda_{em} \leq$ 400 nm) diode chips with a mixture of red, green and blue phosphors to produce white light would be a relevant alternative but presently these types of LEDs still exhibit inadequate performances. In this work, lanthanides based nanophosphors with different shapes were synthetized by soft chemistry routes i.e. sol-gel process and hydrothermal method. Depending on the synthesis procedures, TEM analyses have revealed the achievements of nanoparticles, nanorods or nanowires with narrow size distributions. Their structural, morphological and optical properties were investigated and compared. Luminescent nanocomposite films were prepared by dispersing these nanomaterials in polymer matrices like silicon. Their mechanical properties as well as their optical properties upon blue or UV excitation were investigated.

Nanomaterials for Photocatalytic Reactions

O. Solcova, L. Spacilova, Y. Maleterova, M. Matejkova, M. Morozova

Institute of Chemical Process Fundamentals of the ASCR, v. v. i., Prague, Rozvojova 135,
16500, Czech Republic

Nowadays, photocatalysis has been applied as a promising technique for the wastewater decontamination and/or purification. It is well established that titanium oxide and related nanostructure materials in the presence of UV light (in dependence of condition also in the presence of visible-light) can create very active species that are able to restore and preserve a clean environment by decomposition of the harmful organics.

Endocrine disruptors represent the group of chemical substances disrupting the hormonal indication of vertebrates and thereby they could encroach on the organism function. To the group of endocrine disruptors belong surfactants, softeners, fungicides, insecticides and some kinds of medications and hormonal contraception. They are commonly presented not only in the waste water but also in the natural water. Endocrine disruptors are persistent to degradation by common chemicals as well as biological and photolytic processes. The necessity of finding the alternative solutions leads to development and use of the new technologies. Photo-catalysis using semiconductor particles have found increasing interest to solve the endocrine disruptors remove problems.

This study is focused on verification of the specially designed photoactive materials and their modified versions suitable for photo-processes carried out upon illumination in the UV-light. Ethynylestradiol, Nonylphenol and Bisphenol A were chosen as typical compounds belong to the endocrine disruptor group. In this work the water decontamination with various concentrations of endocrine disruptors in the two types of reactors; batch and plug flow arrangement on the titania thin layers were studied.

The financial support of the Technology Agency of the Czech Republic No. TA01020804 and Competence Centre BIORAF, Grant No.TE01020080 is gratefully acknowledged.

Bifunctional silica nanoparticles as new nanoprobes for biofilms exploration

Léïla MAULINE[a], Marie GRESSIER[a], Christine ROQUES[b] and Marie-Joëlle MENU[a]

[a] Centre Interuniversitaire de Recherche et d'Ingénierie des Matériaux, UMR-CNRS 5085,
Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex 9, France

[b]Laboratoire de Microbiologie Industrielle- Faculté de Pharmacie, LGC, UMR 5503
Université Paul Sabatier, 35 chemin des Maraîchers, 31062 TOULOUSE cedex 7, France

menu@chimie.ups-tlse.fr

The development of imaging techniques, in particular fluorescence microscopy coupled with functionalized nanoprobes, allows in situ investigations of the 3D structure of biofilms with submicron resolution. For nearly two decades, luminescent latex nanoparticles combined with confocal laser scanning microscopy (CLSM) have been intensively employed for the investigation of mass transport, particle spatial distribution, and diffusion inside biofilms. Studies revealed the heterogeneous diffusion of particles inside biofilms (Guiot et al. 2002; Morrow et al. 2010; Habimana et al. 2011; Forier et al. 2012). Among the variety of available probes such as organic molecules, transition metal complexes or quantum dots (QD), luminescent silica nanoparticles (LSNPs) have been of scientific interest due to their applications in biological and medical fields; such as the rapid and hypersensitive detection of pathogenic bacteria (Zhao et al. 2004; Wang et al. 2010, 2011), cancer cell detection (Santra et al. 2001; Herr et al. 2006), and cell imaging (Voisin et al. 2007; Yang et al. 2008). However, silica nanoparticles are still not widely used in the exploration of biofilms. Compared to latex nanoparticles, they are amenable to chemical modification because of the presence of silanol groups at the silica surface which allow covalent grafting of different functional groups. Furthermore, appropriate dye can be covalently bound in the core of the silica matrix. For biological applications, covalent anchoring is favored as it prevents dye release, non-specific labeling, and loss of fluorescence signal intensity. Several compounds are described as displaying luminescent properties when covalently incorporated into silica nanoparticles, such as modified QDs (Qian et al. 2010), organic dyes (Yang et al. 2003; Kumar et al. 2008), or transition metal complexes (d or f) (Jiang et al. 2010). Similar to tris(2,2′-dipyridyl)ruthenium(II) chloride, which is one of the most popular dyes, the synthesis of several silylated ruthenium(II) complexes incorporated into the core or grafted onto the surface of silica nanoparticles has been recently described. These ruthenium(II)–silica nanohybrids display advantages, in particular by exhibiting very interesting photoluminescence properties (Cousinie et al. 2012).

We have evaluated the effect of the surface functionalization of nanoparticles on their spatial distribution in bacterial biofilms. In this work, bifunctional silica nanoparticles (BSNPs) are designed by incorporating a silylated ruthenium(II) complex [Ru(bpy)2(bpy-Si)]Cl2 in silica nanoparticles with two different particle sizes, and by modifying the surface of LSNPs with various organosilanes. After checking that LSNPs were non-toxic to P. aeruginosa, the effects of surface modification on the penetration and the distribution of BSNPs in biofilms of that species were investigated.

Nanostructured catalysts with enhanced properties for pollutant and waste treatment

B. Heinrichs, S. Lambert

Laboratoire de Génie Chimique, B6a, Université de Liège, B-4000 Liège, Belgium

The conversion of pollutants and wastes into harmless or even useful products is one of the main outlet of catalysts manufacturing. To be efficient for a specific application, a catalyst must combine adequate structure and porous texture especially at the nanoscale. The aim of this talk is to show, through two processes of environmental interest (hydrodechlorination of chlorinated wastes and photooxidation of pollutants), that sol-gel process is a very powerful tool to design nanostructured catalysts with desired properties.

On the one hand, active and selective hydrodechlorination catalysts have been produced through a cogelation method. The xerogels obtained are constituted of Pd-Ag, Pd-Cu or Ni-Cu alloy nanocrystallites (3 nm) located inside microporous silica particles (10-50 nm) arranged in larger aggregates, themselves constituting the macroscopic pellet. Such a structure allows converting selectively chlorinated alkanes into reusable alkenes while avoiding diffusional limitations. Moreover, while being accessible through micropores, alloy crystallites are trapped in silica particles which makes them sinter-proof at high temperatures.

On the other hand, the cogelation method has been used to produce P-doped TiO_2-anatase photocatalysts for the oxidation of organic pollutants. The presence of P in the anatase structure favours the activity through additional activation with the visible range of the light source. Interestingly, that presence allows to keep small anatase nanocrystallites despite the high temperature thermal treatment, which favours again a high activity.

Finally, an aqueous sol-gel method has allowed to produce nanocrystalline photocatalysts exhibiting a remarkably high photocatalytic activity without requiring any calcination step. It has been found that, while produced at ambient temperature, the catalysts are exclusively composed of doped nanocrystallites of anatase.

Porous silicon nanoparticles functionalized for 2-photon photodynamic therapy of cancer cells.

Emilie Secret,Marie Maynadier, Audrey Gallud, Magali Gary-Bobo, Arnaud Chaix, Philippe Maillard, Michael J. Sailor, Marcel Garcia, Jean-Olivier Durand and Frédérique Cunin.

Photodynamic therapy (PDT) has arisen as an alternative to chemo and radio therapy for non-invasive selective destruction of tumours. PDT involves the use of a photosensitizer which, in the presence of oxygen, upon irradiation at specific wavelengths, leads to the generation of cytotoxic species and consequently to irreversible cell damaging. PDT has been in clinical use for over a decade but, despite the advantages of the therapy itself, photosensitizers in use today induce a long photosensitivity of the patient that limits their use. To overcome this issue, encapsulation of the photosensitizers into nanoparticles is a promising new approach[1]. In addition, replacing classical one-photon excitation in the visible region by two-photon excitation in the NIR range (700-1200 nm spectral range) is also currently of high interest and offers new perspectives for the treatment of tumours due to the increased penetration depth, less scattering losses and 3D spatial resolution. In this work, we studied the use of porous silicon nanoparticles (pSiNP) functionalized with both a photosensitizer and a targeting agent. Porous silicon is a biocompatible and biodegradable[2-4] material which can generate $^1O_2$ when excited by visible light due to quantum-confinement effect[5, 6]. pSiNP had been shown to be degraded into non-toxic silicic acid byproducts *in vivo*[4]. The multi-functionalized pSiNP studied here were able to target, image and kill cancer cells *in vitro* by photodynamic therapy mechanisms both with 1-photon and 2-photon excitation.

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Glycine Nitrate Process: a suitable route to elaborate complex oxide nanoparticles for biomedical applications

G. Goglio, R. Epherre, C. Pepin, N. Penin, G. Kaur, M.H. Delville, E. Duguet

CNRS, University of Bordeaux, ICMCB, Pessac, France.

Complex oxide nanoparticles are thrust to the forefront due their potentialities for biomedical applications [1]. For example, manganite perovskites could be used as thermal mediators for magnetic hyperthermia either to destroy directly tumour cells by necrosis or to improve drug or radiation efficiency without overheating of safe tissue. Besides the size and absence of aggregation, Curie temperature (related to manganese valency) is a crucial to be controlled. As another example, (complex) gadolinium oxides may be used as contrast agents for Magnetic Resonance Imaging. Here the challenge will consist in finding more efficient agents for the detection and diagnosis of tumours tuning composition, size and structure.

For the elaboration of such oxides, Glycine Nitrate Process (GNP) was selected [2]. This aqueous solution combustion process is particularly suitable for the preparation of multicomponent oxide materials as it ensures the cationic homogeneity in the combustion residue. Moreover it takes advantage of exothermic, fast and self-sustaining oxido-reduction reactions which makes it particularly interesting to elaborate highly divided materials. So our main goal is to optimize and validate the suitability of the GNP to easily prepare complex oxides as nanoparticles, with a perfect control of the cationic composition of the material, of the flame temperature (related to cristallinity and particles size) and of the transition metal valency when any [3]. In the case of manganites, the influence of conditions synthesis will be discussed considering their influence on non-stochiometry effects and consequently on magnetic properties.

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A nanodesigned silica surface for biotechnology applications

H. Rahma, T. Buffeteau, G. Le Bourdon, M. Degueil, B. Bennetau, K. Heuzé, L. Vellutini

University of Bordeaux, ISM UMR 5255 CNRS, F-33400 Talence, France

Controlling surface properties and biological interfaces at the nanometer scale have become essential challenges in biotechnology for biosensing applications and biological studies (culture or interactions). The key element for molecular recognition and specific interactions studies is to control biomolecules distribution onto the surfaces. A number of techniques currently exist, generally lithographies techniques, to generate nanopatterned surfaces. These methods require highly specialized devices such as lasers for ablation, scanning probe or e-beam which are often expensive and used for a limited number of biological studies. So, investigations in new strategies of surface modifications are critical for the development of controlled, easily scaled-up and repeatable modified nanopatterned surfaces.[1] Self-Assembled Monolayers (SAMs) on silicon based surfaces provide molecularly defined platforms for chemical derivatization. We reported recently the preparation of a dense and well-packed grafting of a functional dendritic silylated coupling agent, inserted in a decylorganosilane monolayer.[2] Thus, we show that, depending on experimental parameters, particularly the solvent, it is possible to obtain a nanodesigned surface *via* a bottom-up approach.[3] Moreover, we succeed in the formation of both homogeneous dense monolayer and a heterogeneous dense monolayer, the latter being characterized by a nanosized volcano-type pattern (4-6 nm of height, 100 nm of width and around 3 volcanos/μm^2) randomly distributed over the surface.

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Correlative qualitative and quantitative aspects of titanium oxide nanoparticles fate and toxicity in skin cells and multicellular living specimens

M.H. Delville,*[1] Q. Le Tréquesser,[1,2] M. Simon,[2] G. Devès[2], G. Saez[2] P. Barberet,[2] H. Seznec,[2]
1CNRS/ICMCB, Université de Bordeaux, France; 2CNRS/IN2P3, CENBG, France;3IECB, Université de Bordeaux France

Corresponding author: delville@icmcb-bordeaux.cnrs.fr

[1] *CNRS, Université de Bordeaux, ICMCB, 87 Av. du Dr. Schweitzer, 33608Pessac, France*
[2] *Université de Bordeaux, CNRS/IN2P3, CENBG Ch. du Solarium, BP120, 33175 Gradignan, France*

Nanomaterials are of great interest from both academic and industrial points of view, with numerous applications in domains such as medicine, catalysis and material sciences.[1] Their issues in nanotoxicology have also attracted attention worldwide and established methods of chemical safety assessments must be modified to address their characteristics and more especially to assess the biological effects of these highly reactive materials.

These nanoparticles being produced for several decades on industrial scale, there is an urgent need to evaluate their risks and to ensure their safe production, handling, use, and disposal. Moreover, a comprehensive study is clearly needed to fully explore the toxicity of nanoparticles, which may help to better understand their deleterious health effects and create environmentally friendly and biologically relevant nanoparticles. In particular, the behavior of nanoparticles inside living cells is still an enigma, and no metabolic responses induced by these particles are understood so far.

This presentation concerns the potential toxicity due to exposure of chemically modified hybrid TiO_2 NPs used in sunscreens and cosmetics. We propose to apply an original imaging

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[1] Quentin Le Trequesser, Hervé Seznec and Marie-Hélène Delville *Nanotechnol Rev 2013; 2, (2), 125–169.

methodology (Ion Beam Analysis, TEM, and Confocal Microscopy) to in vitro studies, combining technologies for not only detection, tracking, and quantification of TiO_2 nanoparticles but also for use of indicators for ion homeostasis, cell metabolism, or fate.[2]

The main goal is to precisely identify the molecular and cellular mechanisms involved in the nanotoxicity of TiO_2 nanoparticles in eukaryotic cells and multi-cellular organisms such as C. elegans, focusing on parameters such as size, morphology and surface modification of the TiO_2 nanoparticles.

We address the current knowledge gap of human cells and C. elegans responses to TiO_2 nanoparticles exposure. Since nematodes feed on bacteria and are considered as particle-ingesting organisms, this study will offer new perspectives in nanoparticles-related risk assessment and food web accumulation modeling.

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Nano- and micro-structuration of the sensing layers for chemiluminescence-based biosensors and electrochemical sensors.

Loïc J. BLUM,[a] Cloé DESMET,[a] and Christophe A. MARQUETTE,[a, b]
[a]Institut de Chimie et Biochimie Moléculaires et Supramoléculaires
ICBMS UMR 5246 – Université Lyon 1/CNRS- 69622 Villeurbanne - FRANCE
[b]AXO Science SAS - 66 Bd Niels Bohr - 69100 Villeurbanne – FRANCE

When developing sensors and biosensors much attention must be paid to the sensing layer since in most cases, it is the key element of the sensor giving the specificity/selectivity and the sensitivity. Nano- and micro-structuration can have ground-breaking effect through the amplification of the detected signal and two examples are presented below.

1- Because of its great sensitivity, the luminol chemiluminescence (CL) reaction catalyzed by peroxidase is often used as the detection system for biosensors and biochips. Although the light emission can be enhanced by chemical compounds such as 4-iodophenol, a physical approach has been also developed to enhance the light emission of the peroxidase-catalyzed luminol CL. Peroxidase was immobilized on biochips at the surface of flat "bulk-like" and rough "cluster-like" metal films at a distance controlled by a peptide chain with a length between 1.3 and 7.8 nm. When the CL of the luminol/H_2O_2 system is catalyzed by peroxidase in the presence of a metal-corrugated film (Fig. 1), a strong CL enhancement is observed. The magnitude of enhancement depends on different factors such as the morphology of the thin metal film, the nature of the metal, the pH value of the reaction medium as well as the distance between peroxidase and the surface. Exploiting this enhancement phenomenon, DNA chips and immunochips have been designed using nano-structured gold-modified carbon microarrays.

2- A multiplex electrochemical sensor for on-site simultaneous detection of four explosive precursors (hexamine, hydrogen peroxide, sodium hypochlorite, ammonium nitrate) have been also designed. The disposable electrochemical chips combine ease of use and portability thanks to a simple and inexpensive carbon paste screen-printing fabrication technique. The chips were composed of one counter electrode, one pseudo-reference electrode and eight working electrodes (Fig. 2) which were modified with different electrodeposited metals: gold, palladium and platinum. These different micro-structured coatings give its selectivity to the multi-sensor through a "fingerprint"-like signal of the multiplex detection.

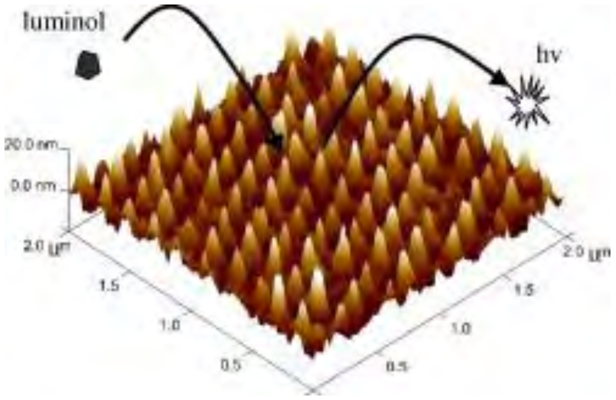


Figure 1. Gold nano-structured surface.

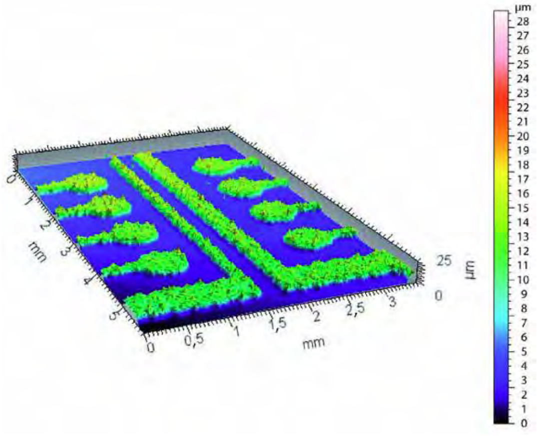
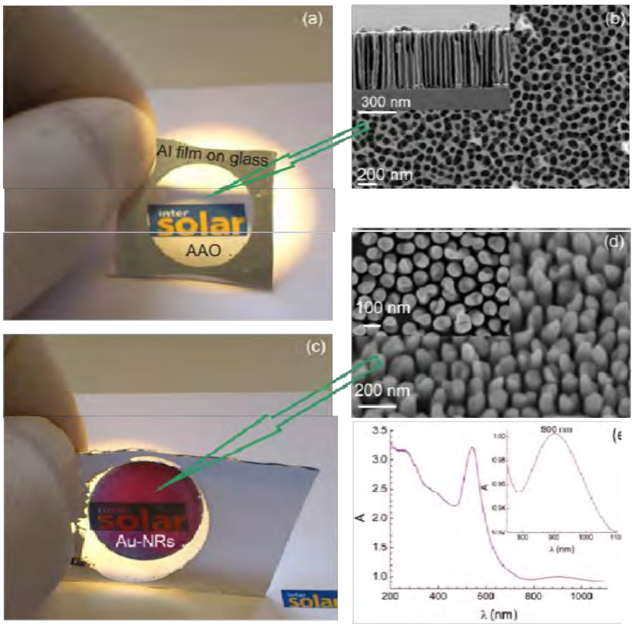


Figure 2. Screen-printed electrodes of the multiplex electrochemical sensor.

Template synthesis of Nanomaterials for energy and sensing applications

Mohammed Es-Souni Institute for Materials & Surface Technology, University of Applied Sciences Kiel, Germany

Template synthesis of nanomaterials using supported anodized alumina (AAO) template films offers a versatile and cost-effective way of producing ordered structures of tunable aspect ratio. These structures can be processed on large area substrates including ITO-glass, silicon wafers and polymeric supports making this method of high practical interest. In the present talk I first briefly introduce template synthesis of nanomaterials using anodized alumina (AAO) templates and show exemplarily on noble metal nanostructures how morphology and properties can be tuned. In the second part advanced AAO-template films supported on different substrates, e.g. silicon and glass, are presented as robust and easy-to-handle alternatives to free standing AAO-templates. First results using these templates for the processing of Ag and Au-Nanorods and the tunimg of their optical properties via varying their aspect ratio, as well as their SERS applications are discussed. Finally, nanocomposites of VO_2 and TiO_2@Au-nanorods are discussed with emphasis on optical properties and energy applications.



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Hybrid organic-inorganic nanocomposites and their applications in optical sensing

M. Čajlaković
JOANNEUM RESEARCH, Forschungsgesellschaft mbH – Materials
MATERIALS, Sensorsystems,
Franz-Pichler-Straße 30,
Weiz, Austria

Abstract

Sol-gel chemistry is based on the polymerization of molecular precursors such as metal alkoxides $M(OR)_n$ [1]. With the development of sol-gel science and technology, one of the attractive features of the sol-gel process is that it allows the preparation of numerous types of new organic-inorganic hybrid materials possible under the mild conditions [2]. Organically modified silicates (ORMOSILs) are kinds of such materials in which organic fragments are built into silicon-oxide networks. A typical process of preparing such ORMOSILs is by co-hydrolyzing from a mixture of a Tetraethoxysilane and alkyl-substituted silicon alkoxides. Inorganic and organic components can then be mixed at the nanomeric scale, in virtually any ratio leading to so-called hybrid organic-inorganic nanocomposites. The nature of the interface has been used to grossly divide these materials into two distinct classes. Class I corresponds to all the systems where there are no covalent or iono-covalent bonds between the organic and inorganic components. In such materials, only weak bonds (hydrogen, van der Waals or ionic bonds) between the various components give the cohesion to the whole structure. In contrast, in class II materials, the two phases are linked together through strong chemical bonds (covalent or iono-covalent bonds).

In order to obtain sensing devices, the chemical or biological recognizing elements can be added to the sol during different steps of the process, remaining firmly retained in the matrix, yet sterically accessible to small molecules and ions that may diffuse into the porous structure. The mild conditions of the process, together with the chemical inertia of sol-gel glass, make these materials ideal for the immobilization of numerous organic, organometallic and biological molecules. Characteristics such as polarity, porosity and ion exchange capacity can be easily tailored by simple modification of the polymerization protocol. The apparent decrease of brittleness may be one of the most important advantages of ORMOSILs, which makes them suitable as matrices for chemical sensing. Sol-gel thin films-based optical sensors for determination of pH, gases, ionic species as well as biosensors have been experiencing a rapid growth, as a reflex of the increasing demand for stable, robust and specific devices for

applications in areas such as a food industry, diagnostics, in vivo monitoring, environmental control and biotechnology.

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Tailoring the size and morphology of nanoparticles by chemical substitution for specific applications

D. Lisjak[1]

[1]Jožef Stefan Institute, Department for Materials Synthesis, Ljubljana,
Slovenia.

The size, size-distribution and morphology of nanoparticles, together with their crystal structure, determine their physical properties and, consequently, their application. Apart from the synthesis parameters, the above-mentioned properties are usually tailored by surfactants. As an alternative, a chemical substitution during the hydrothermal synthesis of different oxide nanoparticles was considered in this contribution.

First, the possibility to narrow the particle-size distribution of barium ferrite nanoplates by the substitution of Fe^{3+} in $BaFe_{12}O_{19}$ (Fig. 1a) will be presented. As suggested by kinetic studies, this was possible by the suppression of the secondary crystal growth due to the partial substitution of Fe^{3+} with larger In^{3+} or Sc^{3+}. The resulting nanoparticles showed applicable magnetic properties and colloidal stability in polar solvents. Consequently, they were assembled into anisotropic magnetic films for self-biased applications and incorporated into polymers for magneto-optic applications.

Second, the substitution of Er^{3+} in Er_2O_3 with other lanthanide ions was studied. In this case, not only the size but also the morphology of the nanoparticles changed with the substitution (Fig. 1b, c). The effect of the morphology on the assembly of nanoparticles in thin films will be presented. The latter are suitable for optical communication technologies, while the nanoparticles can be used as new, fluorescent bio-labels.

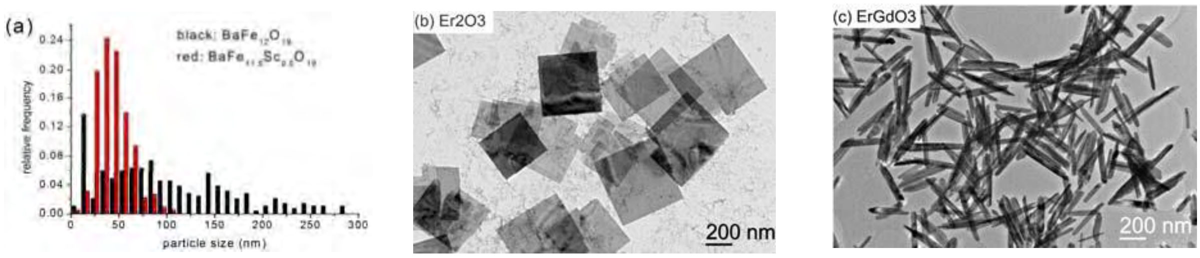

Figure 1: The effect of chemical substitution on the particle-size distribution of

$BaFe_{12}O_{19}$ (a) and on the morphology of $Er_{1-x}Gd_xO_3$ (b, c).

Features of the Formation of Functional Polysiloxane Nanolayer on the Surface of Ceramic Membranes

V.V. Tomina[1], I.V. Melnyk[1], Yu.L. Zub[1], A. Kosak[2,3], A. Lobnik[2,3]
[1]Chuiko Institute of Surface Chemistry, NAS of Ukraine, 17, General Naumov Str., Kyiv 03164 Ukraine
[2]University of Maribor, Faculty of Mechanical Engineering, Centre of Sensor Technology, Smetanova 17, 2000 Maribor, Slovenia
[3]Institute for Environmental Protection and Sensors, Beloruska 7, 2000 Maribor, Slovenia

This report examined the use of hydrolytic polycondensation reaction of tetra- and trifunctional silanes to create polysiloxane layer with complexing groups on the surface of ceramic membranes. This approach allows one to obtain new functionalized ceramic membranes that can be used to remove heavy metals in the filtration process. However, the first results [1,2] showed that the formation of functionalized polysiloxane layer has its features.

Indeed, there was observed the formation of comlexing layer with $\equiv Si(CH_2)_3SH$ groups on the surface during the functionalization of planar ceramic (Al_2O_3) membranes. When using an equimolar ratio of $Si(OEt)_4$ and $(MeO)_3Si(CH_2)_3SH$ in the initial sol, the surface layer formed with nanoparticles of 55-70 nm (Fig. 1a). The decrease in two times of trifunctional silane in the initial sol resulted in the formation of vitreous coating on the membrane surface (Fig. 1b,c). Dilution of the initial sol with alcohol promotes the formation of more uniform polysiloxane layer with adsoption sites (Fig. 1d). The highest sorption capacity with respect to ions of silver(I) was observed for such layer.

Hence, factors that influence the surface structure of the polysiloxane layer and the size of nanoparticles in this layer are: a) the ratio of reacting tetra- and trifunctional silanes; b) the concentration of alkoxysilanes in the initial sol.

Using these factors, one can be directed to form a functional layer on the surface of the filtration membranes. Apparently, this approach can be used for the functionalization of polymer membranes.

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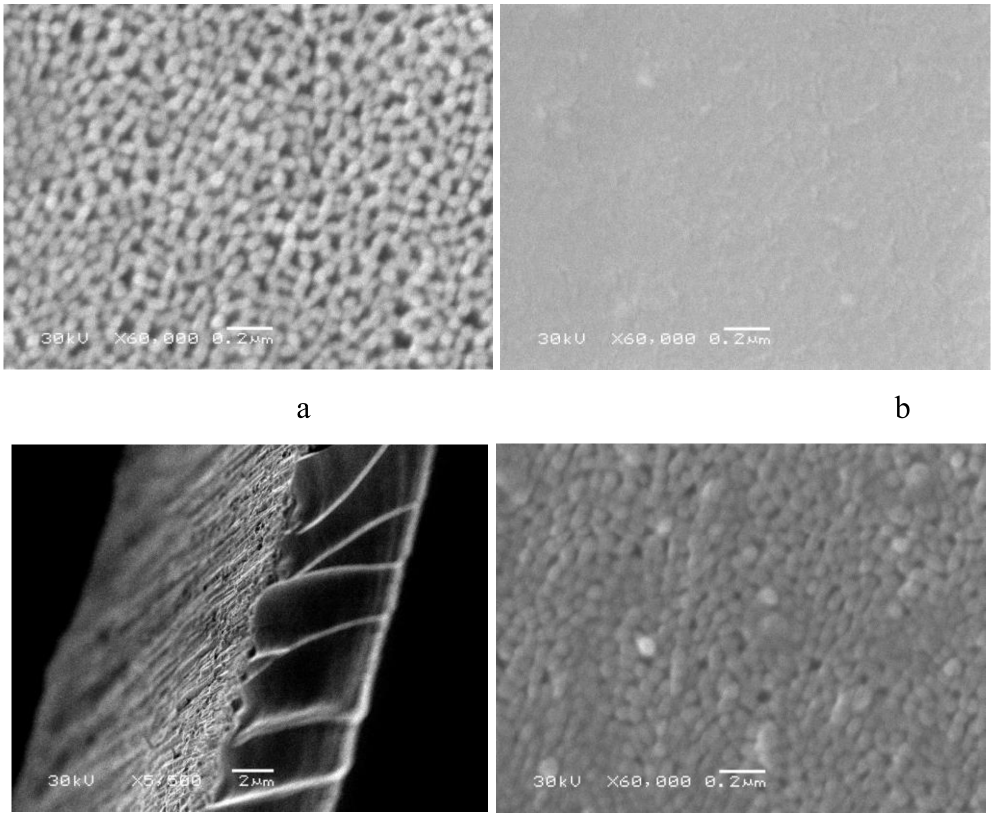

a b

c d

Fig. 1. SEM images of ceramic membranes containing $SiO_2/O_{3/2}Si(CH_2)_3SH$ layer.

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Synthesis of iron oxide magnetic nanoparticles and their heating properties

S.Gyergyek[1,2], D. Makovec[1], M. Drofenik[1,3], O. Jordan[4], H. Hofmann[2]

[1]Department for Materials Synthesis, "Jožef Stefan" Institute, Ljubljana, Slovenia.
[2]Powder Technology Laboratory, Ecole Polytechnique Fédéral Lausanne, Switzerland.

[3]Faculty of Chemistry and Chemical Engineering University of Maribor, Slovenia.

[4]School of Pharmaceutical Sciences, University of Geneva-University of Lausanne, Genève.

Magnetically induced hyperthermia is a promising and minimally invasive procedure for treatment of tumours. Despite the fact that it is a relatively old concept and is in clinical trial it is still far from being optimized and fully employed. One of the most important reasons for that is the lack of the synthesis methods that would enable precise control over the nanoparticles' size, size distribution and surface properties. Magnetic iron oxide nanoparticles with narrow size distribution were synthesized by hydrothermal treatment of suspensions of iron oxide nanoparticles. Ricinoleic-acid-coated magnetic nanoparticles were co-precipitated at room temperature from aqueous solution of Fe^{2+}/Fe^{3+} cations. Presence of the ricinoleic acid on the nanoparticles' surface strongly suppress their growth under hydrothermal conditions. Because of strong dependency of the particles growth on their size the size distribution significantly narrowed during hydrothermal treatment. By varying experimental conditions, nanoparticles of average size between 10 and 18 nm with narrow size distribution were synthesized. Ricinoleic-acid-coated nanoparticles were homogeneously dispersed in PMMA matrix. Influence of the nanoparticles size and magnetic properties nanocomposite on heating in alternating magnetic field was examined.

Influence of an applied magnetic field on the magnetic nanoparticles assembly

P. Jenuš[1,2], D. Lisjak[1], A. Mertelj[3], D. Križaj[4], D. Kovačič[5], D. Makovec[1]

[1]Jožef Stefan Institute, Department for Materials Synthesis, Ljubljana, Slovenia.

[2]Jožef Stefan International Postgraduated School, Ljubljana, Slovenia.

[3]Jožef Stefan Institute, Complex Matter Department, Ljubljana, Slovenia.

[4]University of Ljubljana, Faculty of Electrical Engineering, Ljubljana, Slovenija.

[5] LPKF Laser & Elektronika d.o.o, Naklo, Slovenija.

The focus of nanoscience and nanotechnology is increasingly shifting from the synthesis of individual components to their assembly into larger systems. Hereby, the use of external fields (electric, magnetic) has an enormous potential in the preparation of nanoparticles assemblies. We report a study on magnetically directed assembly of cobalt ferrite and maghemite nanoparticles. As-synthesized nanoparticles of both compositions were dispersed in water with citric acid as a surfactant. 3-dimensional assemblies of ferrite nanoparticles were prepared by drying their dispersions under an applied magnetic field with different strengths using two different set-ups: with and without soft-magnetic template. The assemblies were examined with the scanning electron microscope (SEM), which revealed differences in their morphologies (Fig. 1), depending on the set-up and magnetic properties of materials used. The mechanism of the nanoparticles assembly was studied in-situ with optical microscopy.

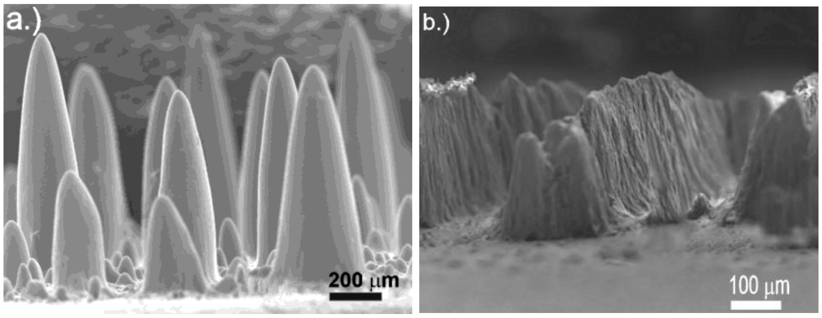

Fig. 1: 3-dimensional structures of cobalt ferrite nanoparticles assembled under an applied magnetic field: a.) without and b.) with soft-magnetic template.

Textiles meet Light

Marek Krehel,[a,b] *René M. Rossi*[a] *and Lukas J. Scherer**,[a]

[a]Empa, Swiss Federal Laboratories for Materials Science and Technology,
[b]ETH Zurich, Rämistrasse 101,8092 Zürich, Switzerland.
lukas.scherer@empa.ch

Body-monitoring through an iHealth system would decrease the medical costs enormously. By implementing the body-sensors in a wearable textile, important body parameters as e.g. the electrical activity of the heart, the SpO2 or the blood perfusion can be monitored.

The integration of sensors in textiles can be done either by miniaturizing electrical components or by producing “smart” fibers. Our research activities are based in the second approach using polymeric optical fibers. Polymeric optical fibers fabrics have been produced for a wide range of medical implementations in illumination for photodynamic therapy and sensing. Articles of polymeric optical fibers (POFs) for a wide range of applications, especially for networks in buildings, automobiles, railways, aviation or in industrial plants are numerous, while publications where POFs are used for medical purposes are rather rare [1]. Herein, the focus will be on textiles with integrated POFs and their medical applications. Our activities in the field of medical sensing using POFs are wound-monitoring, pulse-oximetry and photopletismography as well as gas sensing. Special attention will be given to the features of differences in textile structures resulting in flexible and lightweight structures. Recent applications in the field of optical textiles given in this report demonstrate practicability and usefulness for flexible two-dimensional illumination and sensing areas. The presentation also discusses a novel approach to produce POFs which are ideally suited to integrate them in textiles.

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Application of V_2O_5 Xerogel as Hole-Transport Layer in Organic Solar Cells: Towards Low Cost Printed Optoelectronic Devices

G. Terán-Escobar, J. Pampel, J. M. Caicedo, M. Lira-Cantú

Centre d'Investigaciò en Nanociéncia i Nanotecnologia (CIN2, CSIC-ICN). Campus
UAB, Edifici ICN2, Bellaterra, Barcelona, Spain E-08193

The predicted maximum power conversion efficiency (PCE) of Organic solar cells (OSCs) has been empirically estimated at around 10-12%, and theoretical at around 20-24%, comparable with that of crystalline Si solar cells.[1] Yet, OSCs must also be cost-competitive and show long lifetimes. To achieve the low cost estimates, OSCs must be fabricated by inexpensive and large-scale technologies, and an attractive option is the application of solution-processing printing techniques, like roll-to-roll.[2-8] Additionally, the envisaged mass-production of OSCs indicates that toxic organic solvents will have to be circumvented and substituted for non-toxic, alcohol or water-based, solutions and inks. In this work, water-based V_2O_5 xerogel has been applied as hole transport layer, HTL, in stable organic solar cells (OSCs). The V_2O_5 is processed from sodium metavanadate solution in water followed by an ion exchange process. A thin film was fabricated from the sol gel solution by spin coating, resulting in a final $V_2O_5 \cdot 0.5H_2O$ formula. XPS, UPS and optical characterization were used to further characterize the work function (WF) and band gap energy (BG) of the V_2O_5 thin films. Results revealed different WF for the V_2O_5 thin films prepared from a fresh and an 24h-aged V_2O_5/isopropanol (IPA) solution with WF values of 5.15 eV and 5.5 eV respectively. This difference is due to the reaction between the IPA with the V_2O_5 in solution with time, which reduces the V^{+5} to V^{+4}. Thus the photoactivation of the solar cells was required. Outdoor stability analyses of sealed inverted and normal configuration OSC applying the V_2O_5 as the HTL, revealed high stability for both devices, with the retention of the 80% of its initial photovoltaic response for more than 1000h [1].

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Surface modification of core-shell $NaYF_4$:Yb,Tm@SiO_2 nanoparticles for the early prostate cancer diagnosis in the NIR range

N. Francolon[1], D. Boyer[1], P. Adumeau[1], J.-L. Canet[1], C. Hesling[2], L. Morel[2], R. Mahiou[1]

[1] Clermont Université, Institut de Chimie de Clermont-Ferrand, UMR 6296 CNRS / UBP
/ ENSCCF, 24 avenue des Landais, BP 80026, 63171 Aubière, France.

[2] Clermont Université, Génétique Reproduction et Développement, CNRS, UMR 6247, INSERM, U931, BP 10448, F-63000 Clermont-Ferrand, France.

Targeted fluorescent nanoparticles (NPs) are currently attracting a strong interest since they can decrease the time needed to diagnose a cancer allowing an earlier medical care of patients. In this work, we developed new multifunctional NPs based on core-shell $NaYF_4$:Yb,Tm@SiO_2 to target the prostate specific membrane antigen (PSMA), a protein which is overexpressed on prostate cancer [1]. The fluoride NPs were prepared by the thermolysis process in acid oleic [2]. The combination of Yb^{3+} ions with Tm^{3+} ions is responsible of a near infrared emission (800 nm) upon infrared excitation at 980 nm. Unlike UV photons, excitation with infrared photons within the weak absorption range of tissues (0.9–1.2 μm) leads to a diagnosis in depth without damaging the living cells. In order to modify easily their surface, these fluoride NPs were coated with a silica shell by a reverse sol-gel emulsion method. The effect of this embedding on the photoluminescence properties was studied upon infrared excitation. The NPs surface was further functionalized using various alkoxysilanes in order to graft polyethylene glycol (PEG) molecules to increase the biocompatibility as well as targeting molecules. Their cytotoxicity was assessed by determining the viability of Hela cells as a function of NPs concentration. Eventually, several promising targeting molecules have been synthesized based on the glutamyl-urea which is a ligand of the PSMA.

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Adsorption of heavy metal ions by highly functionalized SiO_2 particles

M. Bauman[1], A. Košak[2], M. Kolar[3], M. Poberžnik[1], A. Lobnik[1,2]

[1]IOS, Ltd., Institute of Environmental Protection and Sensors,
Beloruska 7, SI-2000 Maribor, Slovenia
[2]University of Maribor, Faculty of Mechanical Engineering, Centre of Sensor
Technology, Smetanova 17, SI-2000 Maribor, Slovenia
[3]University of Maribor, Faculty of Chemistry and Chemical Engineering,
Smetanova 17, SI-2000 Maribor, Slovenia

Art of manipulating matter at the nanoscale (1-100 nm), offers the potential of novel nanomaterials. Recently, nanomaterials with a high surface-to-volume ratio proved to be very promising material for environmental applications, because of their nontoxic nature, high specific surface area regular pore structure and the possibility to modify their surface [1, 2, 3]. Highly functionalized silica particles have also the potential to contribute novel solutions to an enormous range of problems currently facing water contaminated with toxic heavy metals [4]. In this work a novel systematic approach towards the synthesis of mercaptopropyl coated silica (SiO_2) nanoparticles used for selective adsorption of heavy metal ions (Hg^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+}) from aqueous solutions is presented. According to the Stöber's process almost monodisperse silica (SiO_2) nanoparticles with a narrow particle size distribution of around (85±5) nm were formed. Functionalization of the prepared SiO_2 nanoparticles was successfully performed in a one-step procedure by the covalent bonding of mercaptopropyl groups ($-(CH_2)_3-SH$) onto the surface of nanoscale SiO_2 particles. FTIR spectra analysis confirmed the bonding of mercapto-silane molecules onto the surface of the silica nanoparticles mediated Si–O–Si and -SH vibrations. TEM/EDXS micrographs indicated nearly monodispersed and spherical morphology of the prepared particles with a strong signal of Si and S, confirming a successful functionalization procedure of mercapto groups onto the silica surface. Adsorption rate of heavy metal ions after 1h was as follows: Hg^{2+} (99.9%) > Pb^{2+} (55.9%) > Cd^{2+} (50.2%) > Zn^{2+} (4%). An influence of the contact time and pH value of the medium for the adsorption of heavy metals from wastewater, were investigated. Optimal conditions for adsorption were determined and results were fitted with Langmuir isotherm model [5].

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Sub 25nm mesoporous silica nanoparticles for retinoblastoma cells labeling and two-photon photodynamic therapy.

D. Warther,[1] D. Brevet,[1] M. Gary-Bobo,[2] M. Maynadier,[2] A. Gallud,[2] A. Morère, M. Blanchard-Desce,[3] O. Mongin,[3] M. Garcia,[2] L. Raehm,[1] J.O. Durand.[1]

[1] ICGM, UMR 5253 CNRS, place Eugène Bataillon, cc1701, 34095 Montpellier, France.
[2] IBMM, UMR 5247 CNRS, 15 av. Charles Flahault, 34093 Montpellier, France.
[3] ISM, UMR 5255 CNRS, 351 cours de la libération, 33405 Talence, France

Retinoblastoma is the most common intraocular malignancy in childhood. It occurs during fetus development and induces high morbidity rate. Although early diagnosis is well established, the very low drug-permeable blood-retinal barrier limits its treatment by systemic medication, requiring very invasive treatments leading to vision impairment or blindness [1].

One promising strategy to overcome this limitation is the use of nanoparticles. Indeed, it appears that small nanoparticles could pass through the blood-retinal barrier. 20nm gold nanoparticles have been described to be distributed in all retinal layers after systemic injection in mice while 100nm nanoparticles were not [2].

100nm silica nanoparticles with very efficient two-photon photodynamic properties on retinoblastoma Y-79 cell cultures were previously described in our laboratory [3]. These nanoparticles also showed an interesting enhanced effect in inducing cellular death while combining photodynamic therapy and camptothecin delivrery. For the use of these nanoparticles through a systemic pathway, their size should be reduced so they could pass the blood-retinal barrier.

Here we describe the synthesis and the development of sub 25nm mesoporous nanoparticles carrying both our two-photon photosensitizer and a recognition pattern (mannose or antibody) to target retinoblastoma cells. Their small size was obtained through sol-gel synthesis by adjusting several parameters such as base or temperature. They were then functionalized by organic surface grafting. The photodynamic activity of these nanoparticles was assessed through live cell experimentations. After incubation, Y-79 cells were irradiated with two-photon laser and cell death was established. Further experiments on animal model will be needed to insure the relevancy of our small sized nanoparticles for systemic treatment of retinoblastoma.

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Benefits of Using Mesoporous Materials for Heavy Metal Optical Detection

Š. Korent Urek[1], M. Turel[1], N. Frančič[2], A. Lobnik[2]

[1]IOS, Institute for environmental protection and sensors, Beloruska 7, Maribor, SI.
[2]University of Maribor, Faculty of Mechanical Engineering, Maribor, SI.

The monitoring of heavy metals within the environment, drinking water, food, and biological fluids has become essential due to the raising of environmental awareness and increasingly stringent regulations for pollution control. Heavy metals, by definition, are metals with densities of > 5 g cm^{-3}. They are released into the environment mainly by industrial activities. In small quantities, certain heavy metals such as iron, copper, manganese, and zinc are nutritionally essential for a healthier life. However, heavy metals such as Hg, As, Pb, and Cd, are highly toxic and carcinogenic, even at the trace level. Therefore, there is a constant demand for the development of new optical chemical sensors with improved sensor performance.

Mesoporous materials are a class of nanostructures with well-defined mesoscale (2–50 nm diametres) pores, surface areas up to 1000 m^2/g and large pore volumes (~1.0 mL/g). The use of mesoporous materials as a solid support for the fabrications of optical chemical sensors has many advantages: they allow high indicator concentration loading without self-interactions, size exclusive selectivity, improve analyte diffusion and may serve as in-situ preconcentrator for analyte.

Over the years different optical chemical sensors have been introduced based on silica mesoporous materials for the determination of mercury, copper, zinc, and other heavy metal ions [1], which will be presented.

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Thin Sol-gel TiO_2 Layers as the Simple Chemical Sensor

M. Morozova[1], P. Kluson[1], P. Dzik[2], J. Krysa[3], O. Solcova[1]

[1]Institute of Chemical Process Fundamentals of the ASCR, v. v. i., Rozvojova 2/135, 16502
Prague 6, Czech Republic
[2]Brno University of Technology, Purkynova 464/118, 61200 Brno, Czech Republic
[3]ICT Prague, Technicka 5, 16628 Prague 6, Czech Republic

Titanium dioxide (TiO_2) is a semiconductor oxide with a wide range of applications due to its non-toxicity, photochemical stability, photocatalytic activity and low cost. Especially, thin films as the nanostructured electrode materials have evoked a great interest in fields of photovoltaic, energy storage, sensing, photo-electrocatalysis etc. These applications require excellent charge separation and electron transport. Efficiency of the charge separation as well as the successful electron migration through the layer are strongly dependent on the layer morphology, crystallinity, particle size, crystallographic form and on the type of used dopant. The conductive properties of TiO_2 arise from the ability of the light quantum absorption which causes the charge carriers (electron-hole pairs) generation.

This study is focused on the thin sol-gel TiO_2/ITO electrode preparation and on the characterisation of their structural and photo-electrochemical properties by series of physical and electrochemical methods.

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Recent progress on fabrication of nanomaterials for the optical detection of explosives and chemical threat agents

M. Turel[1], B. Viltužnik[1], Š. Korent Urek[1], A. Lobnik[1,2]

[1]Institute for Environmental Protection and Sensors, Beloruska 7, 2000 Maribor, Slovenia
[2]University of Maribor, Centre of Sensor Technology, Smetanova 17, 2000 Maribor, Slovenia

The sensitive and selective detection of warfare threats is very important for military as well as for homeland security. All of the current commercially available detectors for explosives (EXPs) and chemical warfare agents (CWAs) have their advantages and disadvantages and many of them utilize technologies that are adapted from classic analytical chemistry techniques. However, there is still much room for improvement. Nanotechnology and nanomaterials play an important role, since they make it possible to provide sensor devices with rapid, sensitive, simple and low-cost on-field detection. Moreover, nanoparticle-based sensors are suitable for the mass fabrication of miniaturized devices, and they could be integrated into existing multiplex detection systems, such as sensor arrays, including electronic noses. Therefore, intense research efforts have been directed over the years to develop sensitive and selective schemes. Optical chemical nano-based sensors offer the potential for orders-of-magnitude improvements in sensitivity, selectivity, response time and affordability. Several different approaches have been investigated, including, but not limited to, fluorescence methods, surface plasmon resonance (SPR), surface enhanced Raman scattering (SERS) and colorimetric detection (UV/Vis). It is primarily gold nanoparticles (AuNPs) and quantum dots (QDs) that have been explored for this purpose [1].

The presentation will focus on the nanomaterials that have recently been fabricated and used in probes and sensors for the optical and spectroscopic detection of EXPs and CWAs.

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Nanoporous carbon and silica materials as sorbents of heavy metal ions and biomolecules

M. Barczak, P. Borowski, K. Michalak, K. Gdula, M. Oszust, D. Pietras-Ożga

Faculty of Chemistry, Maria Curie-Sklodowska University
Maria Curie-Sklodowska Sq. 3, 20-031 Lublin, POLAND
e-mail: mbarczak@umcs.pl

Ordered mesoporous carbons (OMC) and silicas (OMS) are particularly important nanomaterials in many areas of modern science and technology, such as water and air purification, gas separation, catalysis, chromatography, energy storage, etc. These groups of nanomaterials exhibit many advantages over traditional activated carbons and silicas mainly due to their ordered structure and uniform pore size distributions. In addition, it also possible to create desired surface chemistry, what is extremely useful in designing new adsorbents for selective removal of many contaminants including heavy metals ions, phenols or pharmaceuticals. Thus, there is currently an appreciable interest in the synthesis, and characterization of OMC and OMS, as well as in their assessment for applications ranging from electronic devices to adsorbents and catalyst supports.

In this work CMK-3 and SBA-15 porous materials were synthesized and characterized by broad range of instrumental techniques including infrared spectroscopy, powder X-ray diffraction, thermogravimetry, nitrogen sorption measurements, electron microscopy and elemental analysis. Selected materials were tested as sorbents of heavy metal ions and biomolecules to investigate their potential applications for removal of these substances from waters and wastewaters.

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Nanomaterials as Sorbents for Water Treatment

M. Matejkova[1], K. Soukup[1], J. Grabowski[2], O. Solcova[1]

[1]Institute of Chemical Process Fundamentals of the ASCR, v. v. i., Prague, Rozvojova 135,
16500, Czech Republic
[2]Central Mining Institute, Katowice, Plac Gwarkow 1, 40166, Poland

Phenols belong to the most common water pollutants in the industrial effluents thus contamination of ground waters is not so sporadic. The other source of phenols as contaminants used to be the application of the underground coal gasification technology (UCG). Moreover, phenols as a class of organics are similar in structure to the more common herbicides and insecticides which reveal the high resistance to biodegradation. [1]

Nanomaterials as zeolites (Bentonite, Montmorillonite) titania and another mixed metal oxides, nanoiron (Nanofer) and active carbon (Supersorbon, Norit) have been employed as packing into the reactive barrier for the ground water contaminant removal. The efficiency of the individual sorbents was also tested on the model contaminated waters with the different concentration of phenol. Applied sorbents have been thoroughly characterized by various methods as Nitrogen physical adsorption, Mercury porosimetry, Helium pycnometry, Scanning electron microscopy, XRD, Raman spectroscopy. Experiments were carried out under varying experimental condition of particle size, pH, temperature, etc. To obtain the sorption capacities of individual sorbents relevant to the real conditions after UCG process the laboratory reactor designed for formation and release of the UCG contaminants was applied.

This study is focused on evaluation of the individual sorbent efficiency and capacity for phenol removal from UCG post-processing water.

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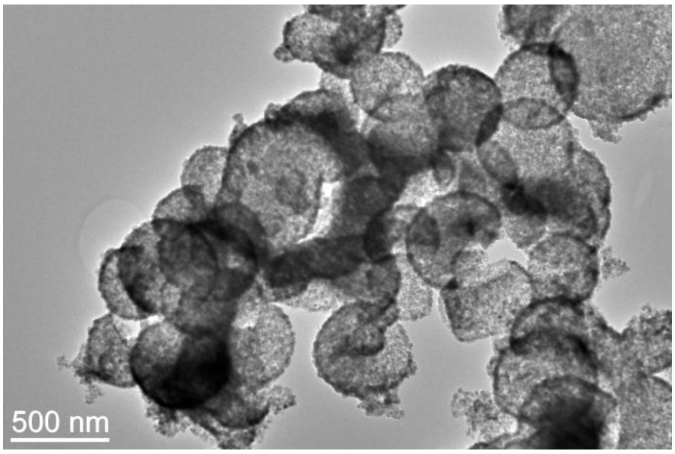
Synthesis and characterization of superparamagnetic iron-oxide hollow spherical structures

M. Lakić[1], A. Košak[1,2*], A. Lobnik[1,2]
[1]University of Maribor, Faculty of mechanical engineering, Smetanova 17, Maribor, Slovenia
[2]Institute for Environmental Protection and Sensors, Beloruska 7, Maribor, Slovenia
lakic.marijana@gmail.com; aljosa.kosak@siol.net*

Superparamagnetic iron-oxide hollow spherical structures, with dimensions ranging from the nanometer to micrometer scale, have recently attracted attention over a wide range of modern medicine, pharmacology, catalysis, optoelectronics, information storage, and environmental protection. Their internal hollow space may be used as hosts for the encapsulation of guest molecules such as specific drugs or dyes, while their large specific surface areas, very low densities, and also strong magnetic responses, make them interesting candidates for use in targeted drug or gene delivery [1].

Among the many available preparation methods such as the conventional hard-templating method, sacrificial-templating method, soft-templating method, and template-free method, the hard-template method has been shown to have a very effective approach for achieving hollow spherical structures. In general, this method involves four steps; the preparation of hard templates, functionalization of template surface for achieving favorable surface properties, coating the templates with designed materials to form compact shells, and selective removal of the templates to obtain hollow structures [2].

This study presents a novel systematic approach for the fabrication of superparamagnetic hollow spherical structures based on the hard-template method. In the first step of this method, mono-dispersed silica (SiO_2) particles as hard templates were prepared using the method of Stöber, which was based on the hydrolysis and condensation of a tetraethoxysilane (TEOS) precursor in the presence of ammonia within an alcoholic solution. After the Stöber synthesis, the primary surface engineering of the prepared SiO_2 particles was performed in the next step by the precipitation and subsequent oxidation of Fe(II)/Fe(III) hydroxides in order to ensure an homogenous superparamagnetic maghemite (γ-Fe_2O_3) coating, and a simultaneous dissolution of the hard SiO_2 templates was achieved using an acidic aqueous solution of a pH value 3 (Fig.1). The obtained samples were characterized using the X-ray diffractometry (XRD), electron microscopy (TEM/SEM), Fourier transform infrared



spectroscopy (FTIR), and specific surface area measurements (BET). A specific magnetization (VSM) of the prepared samples was measured at a room temperature.

Figure 1 Superparamagnetic γ-Fe_2O_3 hollow spherical structures.

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Influence of sol-gel process parameters and alkoxide precursors on the formation and morphological properties of hybrid SiO_2 nanoparticles

P. Nedeljko[1], A. Košak[1,2], M. Turel[1], A. Lobnik[1,2]

[1]Institute for Environmental Protection and Sensors, Beloruska 7, Maribor, SLO.
[2]University of Maribor, Faculty of Mechanical Engineering, Centre for Sensor Technology, Smetanova 17, Maribor, SLO.

Monodispersed, nanostructured hybrid materials based on silica (SiO_2) particles are attracting growing fundamental and technological interest in different fields of applications. These materials have high specific surface area, they are inert and optically transparent, and have tunable and controllable porosity. The chemistry of silica provides the opportunity for a variety of surface functionalities (with hydroxyl, amino, thiol, carboxyl groups, etc.), which can be used to attach targeting molecules. In addition, SiO_2 nanoparticles can be conjugated to any desired organic dye as well as they can incorporate various bioactive molecules. In recent years various organic-inorganic schemes that make use of either a) tetraalkoxysilanes in a combination with organo-alkoxysilane precursors or b) only organosilane precursors were presented for the fabrication of SiO_2 nanostructured composites. Since the organofunctional precursors contain a non-hydrolizable organic component, nanostructures including these materials can exhibit a variety of important properties that find numerous applications in coatings, separation and environmental protection, catalysis, sensor design, etc. In particular, the use of hybrid organosilica for the fabrication of hollow nanostructures recently attracted considerable interest, because of the simple controlling of size/morphology and surface functionalizations of these structures. Here, the ratio between the tetraalkoxysilane and the organoalkoxyisilane component and the synthesis order showed to be critical parameters for final morphology and size distribution of the nanospheres.

However, in this study, several silica based hybrid nanomaterials were prepared via Stöber’s process, which is based on the hydrolysis and co-condensation of alkoxysilane precursors in the presence of ammonia in alcoholic solution. Influence of sol-gel process parameters and various molar ratios of alkoxysilane precursors, such as tetraethoxysilane (TEOS), 1,2-bis(triethoxysilyl)-ethane (BETA), aminopropyltremethoxysilane (APTriMOS), 3-glycidoxypropyltrimethoxy-silane (GPTriMOS) and 3,3,3-trifluoropropyltrimethoxysilane (F-TriMOS), on the size and morphology of the prepared product were investigated. Obtained nanoparticles were characterized using infrared spectroscopy (FTIR), transmission and scanning electron microscopy (TEM/SEM/EDXS) and thermogravimetric methods (TGA/DTA/DSC). The specific surface area and porosity (BET) were measured for all the prepared samples.

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Adsorption of Pb^{2+} and Hg^{2+} ions from aqueous solutions by mercaptosilane coated Co-ferrite nanoparticles

B. Viltužnik[1], A. Lobnik[2], A. Košak[1,2]

[1]Institute for Environmental Protection and Sensors, Beloruska 7, 2000 Maribor, Slovenia.

[2]University of Maribor, Faculty of Mechanical Engineering, Centre for Sensor Technology, Smetanova 17, 2000 Maribor, Slovenia.

In this work, nanocrystalline $CoFe_2O_4$ nanoparticles with a narrow particle size distribution (10±2) nm and specific magnetization (55±2) emu/g were prepared using classical co-precipitation method. Prepared magnetic nanoparticles were stabilized using citric acid to avoid agglomeration. Obtained nanoparticles were surface modified using 3-(trimethoxysilyl)-1-propanthiol (MPTMS) alkoxysilane molecules to obtain functional surface layer with a high affinity to Pb^{2+} and Hg^{2+} ions.

Surface functionalized $CoFe_2O_4$ nanoparticles were suspended in aqueous solution containing Pb^{2+} and Hg^{2+} ions. The influence of various experimental parameters (concentration of reactants, temperature and time of reaction, molar ratios between water and alkoxide precursors, the adsorption time, etc.) on the morphology and adsorption characteristics of mercaptopropyl coated $CoFe_2O_4$ nanoparticles was investigated. An optimal conditions for adsorption of Pb^{2+} and Hg^{2+} ions from aqueous solutions were determined. Equilibrium data were fitted using two-parameter isotherm models and kinetic models were used to analyze the kinetic data for Pb^{2+} and Hg^{2+} removal from aqueous solutions.

Application of SiO_2 based spherical nanostructures on NF/UF membrane surface – opportunity to enhance heavy metal retention

M. Bauman[1], V.V. Tomina[2], A. Košak[3], M. Kolar[4], M. Poberžnik[1], Y.L. Zub[2], A. Lobnik[1,3]

[1]IOS, Ltd., Institute of Environmental Protection and Sensors,
Beloruska 7, SI-2000 Maribor, Slovenia
[2]Chuiko Institute of Surface Chemistry, NAS of Ukraine, 03164 Kyiv, Ukraine
[3]University of Maribor, Faculty of Mechanical Engineering, Centre of Sensor Technology
[4]University of Maribor, Faculty of Chemistry and Chemical Engineering,
Smetanova 17, SI-2000 Maribor, Slovenia

Recently membrane filtrations become considered suitable and feasible method for recovering valuable heavy metal ions, especially from various waste streams. [1], [2] It is also known that the surface chemistry of SiO_2 structures enables the membrane surface modification of (UF/NF membranes) with a thin polymeric layer of functional silanes, e.g. tetraethoxy-silane (TEOS) and 3-mercapto-propyl-trimethoxy-silane (MPTMS) via sol-gel direct, one-pot synthesis. [3]
Applying convenient deposition methods and well-defined synthesis parameters, it is possible to prepare the desired microporous silica layers in the nano range with the porous structure, controlled particle size distribution [4],[5],[6] which affects the sorption affinity towards heavy metal species and enables their selective removal during filtration process. [7]
The commercially available NF/UF membrane was surface functionalized by sol-gel deposition method. [3] Various synthesis parameters (TEOS:MPTMS ratio at ~25/50°C in alkaline pH~10, 3hrs/7hrs/24hrs/5days) were applied to achieve the desired 3D microporous silica surface coating with the controlled particle distribution and particle size in the nano range (~80 to 100 nm for NF and ~300 to 500 nm for UF membrane). Spherical nanoparticles were tested for sorption of lead ions in three stages: as particles, loose membranes, and membrane coupons in filtration module. AAS analytics was applied to determine Pb^{2+} concentration in supernatant to calculate the adsorption rate on modified nanoparticles and loose membranes and to determine the UF/NF membranes Pb^{2+} retention rate after filtration.

Model solution ($PbNO_3$; c=100 mg/L) filtrations with non-modified and modified membrane coupons in flat sheet module were performed at various pressures: 5; 20; 44 bar (NF) and 5; 8 and 10 bar (UF), at constant cross-flow velocity in acidic pH ~4 in order to avoid the formation of insoluble metal hydroxides. During the extensive research the relevant materials (sol-gel particles, loose membranes) were subjected to complex analytical methods, such as SEM/TEM/EDXS microscopy, ATR-FTIR spectroscopy, zeta potential of colloids and membranes, specific surface area and porosimetry (BET) in order to get the most comprehensive insight into the innovative approach for NF/UF functionalization.

The preliminary research results show that the retention rate of Pb^{2+} increased the most using modified NF membrane, namely by Pb^{2+} 143% at 44 bar in comparison to non-modified membrane. So far UF modified membranes showed only minor improvement of Pb^{2+} ions retention. One-pot sol-gel synthesized silica systems could improve filtration membranes' rejection of specific heavy metal ion e.g. retention of Pb^{2+} by NF membrane with TEOS:MPTMS 1:1 (r525/24h/25°C) coating, while for UF membrane 1:2 (r525/24h/25°C) the optimization of modification is still the challenge.

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Ormosil-derived thin-film membranes for the colorimetric detection of dissolved ammonia

M. Turel[1], T. Mastnak[2], Š. Korent-Urek[1], A. Lobnik[1,2]

[1]Institute for Environmental Protection and Sensors, Beloruska 7, 2000 Maribor, Slovenia.
[2]University of Maribor, Faculty of Mechanical Engineering, Centre of Sensor Technology, Smetanova 17, 2000 Maribor, Slovenia.

Due to the deleterious effects of ammonia to environment and humanity, there is a growing demand to diligently monitor the NH_3 level in drinking water, environmental samples and for industrial surveillance. In order to meet the increasing demand for methods suitable for monitoring ammonia in various applications, a variety of sensors has already been described [1].

Organically modified silicates (ORMOSILs) have been attracting great interest in the area of optical chemical sensors. The conventional sol-gel is usually rather hydrophilic and suitable for sensing polar ions. Alternatively, several types of organosilicon precursors can be hydrolyzed and co-condensed with tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS) to form an organic-inorganic hybrid. When using organomodified sol-gel glasses, the enhanced lipophilicity of the sol-gel affects the response of the sensor layers in that ions are restricted in their diffusion, whereas gases are not. In this study, several indicator dyes (Bromocresol Purple (BCP), Bromothymol Blue (BTB), Bromocresol Green (BCG) and Bromophenol Blue (BPB)) were incorporated into various sol-gel hybrid matrices and subsequently tested to their response on dissolved ammonia. In this respect, the BPB-based membranes showed the best sensitivity and limit of detection, while the BCG-based membranes showed the best reversibility.

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Novel-dye functionalized dendrimer

E. Soršak[1], J. V. Volmajer[1], M. Kočevar[2], A. Lobnik[1,3]

[1]University of Maribor, Faculty of Mechanical Engineering, Maribor, Slovenia.
[1]University of Ljubljana, Faculty of Chemistry and Chemical Technology, Ljubljana, Slovenia
[2]Institute for Environmental Protection and Sensors, Maribor, Slovenia.

Dendrimers are highly branched, nanosized macromolecules of defined three-dimensional size, shape and topology, which can be prepared with very narrow distribution. In recent years, they have been receiving increased attention mainly because of their symmetry, high degree of branching and high density of the termal functional groups, which can participate in different reaction. They find application in different fields such as chemistry, physics, biology and medicine. Bonding a dye to the dendrimer structure gives the compounds new properties and new areas of applications.[1]

The present study describes newly synthesized first generation dendrimers, whose peripheries have been modified with low molecular weight dye. The photophysical characteristics of dye-functionalized dendrimer have been investigated.

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Sol-gel Synthesis of Neodymium, Terbium, Praseodymium and Cerium Iron Garnets and Orthoferrites

O. Opuchovic, A. Beganskiene, A. Kareiva

Department of Inorganic Chemistry, Vilnius University, Naugarduko 24, LT-03225 Vilnius, Lithuania

Synthetic and inorganic pigments are widely used in ceramics industry as colour agents for glazes and pottery [1]. Despite the fact that there is a huge variety of colorific inorganic materials, the producers are still interested in creation of pigments with new properties [2]. Natural and synthetic ceramic pigments are colour giving materials for glazes, enamels and unglazed products [3].

Synthesis of neodymium, terbium, praseodymium and cerium iron garnets and orthoferrites was performed by sol-gel method. X-ray diffraction (XRD) analysis showed that formation neodymium orthoferrite and iron (III) oxide instead of desirable neodymium iron garnet took place. The sol-gel derived neodymium orthoferrite contained some impurities of iron (III) oxide. The single phase terbium iron garnet was successfully obtained using the same synthetic technique. However, during the synthesis of terbium orthoferrite the terbium iron garnet has formed as side phase. It was demonstrated that formation of praseodymium iron garnet was problematic. On the other hand, almost monophasic praseodymium orthoferrite was synthesized. In case of cerium, neither cerium iron garnet nor cerium orthoferrite were obtained using sol-gel processing route. The surface morphological features of synthesized materials were estimated using scanning electron microscopy (SEM).

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CuNi nanoparticles prepared by sol-gel method for Curie temperature-limited hyperthermia therapy

J. Stergar[1], I. Ban[1,2], G. Ferk[1], M. Drofenik[1,3], D. Makovec[3]

[1]Faculty of Chemistry and Chemical Engineering, University of Maribor, 2000 Maribor, Slovenia.
[2]Center of Excellence NAMASTE, 1000 Ljubljana, Slovenia.
[3]Jožef Stefan Institute, 1000 Ljubljana, Slovenia.

In the last years, magnetic nanoparticles have become very important in biomedical applications because of their unique multifunctional properties. Magnetic hyperthermia is a therapeutic method that uses magnetic nanoparticles as mediators for cancer tissue heating using an alternating magnetic field [1]. In this paper we present the synthesis of magnetic Cu_xNi_{1-x} (x= 32,5; 35; 37,5; 40) nanoparticles, which were carried out by sol-gel method, a process which involves four steps: preparation of starting precursor in SiO_2 matrix and subsequent decomposition, annealing and reduction. The reduction include two purposes: first is reduction of the Cu and Ni oxides to a Cu_xNi_{1-x} alloy and second is the homogenization of a CuNi alloy nanoparticles under Ar/H_2 atmosphere. The Cu_xNi_{1-x} alloy nanoparticles size and morphology were determined with X-ray diffraction (XRD) and TEM analyses. Thermal demagnetization in the vicinity of the Curie temperature of the nanoparticles was studied using a modified TGA-SDTA.

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Tailoring of Multifunctional Cellulose Fibres with Antibacterial Activity, Superhydrophobicity and Increased Thermo-Oxidative Stability by Application of Two-Component Inorganic-Organic Hybrid Coating

J. Vasiljević[1], I. Jerman[2], L. Černe[1], B. Tomšič[1], J. Medved[3], B. Orel[2], B. Simončič[1]

[1]University of Ljubljana, Faculty of Natural Sciences and Engineering, Department of Textiles, Aškerčeva 12, 1000 Ljubljana, Slovenia
[2]National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia
[3]University of Ljubljana, Faculty of Natural Sciences and Engineering, Department of Materials and Metallurgy, Aškerčeva 12, 1000 Ljubljana, Slovenia

In this research, the two-component sol-gel inorganic-organic hybrid coating was created on the cotton fibre surface. To this aim, an equimolar sol mixture of the hydrolysed precursors 1H,1H,2H,2H-perfluorooctylethoxysilane (SiF) and P,P-diphenyl-N-(3-(trimethoxysilyl)propyl) phosphinic amide (SiP) was applied to fabric samples at two different concentrations by the pad-dry-cure method. Energy dispersive X-ray spectroscopy and scanning electron microscopy revealed the formation of the uniform nanocomposite coating which did not influence the surface morphology of fibres. The functional properties of the finished cotton fabric were investigated using the static contact angles of water and n-hexadecane, the antibacterial test against gram-positive Staphylococcus aureus and gram-negative Escherichia coli and the thermogravimetric analysis in air atmosphere. The obtained results indicated that the presence of the SiP component in the two-component inorganic-organic hybrid coating did not hinder the functional properties imparted by the presence of the SiF component and vice versa which proved their compatibility in the two-component coating. The presence of the coating on the fibres surface induced the following properties of cotton fabric: superhydrophobicity and high oleophobicity which resulted in the passive antibacterial activity, and improved thermo-oxidative stability.

Bio-hybrid sol–gel thin films for organophosphate determination

N. Frančič[1], I.V. Lyagin[2], E.N. Efremenko[2], A. Lobnik[2]

[1]University of Maribor, Faculty of Mechanical Engineering, Centre of Sensor
Technology, Smetanova 17, 2000 Maribor, Slovenia.
[2]The M.V. Lomonosov Moscow State University, Chemical Faculty, Chemical
Enzymology Department, Lenin's Hills, 1/11 Moscow 119992, Russia.

The present work describes the development of bio-sensing films for the detection of organophosphorous compounds using sol–gel technology. A novel sol–gel immobilization method employing hybrid material was developed to immobilize the hexahistidine-modified OPH (His_6-OPH) enzyme in a porous membrane by retaining its catalytic activity. The sol–gel process is performed under mild conditions and the properties of the final framework (diffusion within the matrix, porous structure, thickness, etc.) may be modulated by the chemical nature of the precursors, the water-to-silane molar ratio, the reaction medium and the enzyme concentration [1-3]. The properties of silica gels can also be modified by the hydrolysis and condensation of organosilicon derivatives (ORMOSILs), such as glycidoxypropyltrimethoxysilane (GPTMS) or methyltrimethoxysilane (MTMOS). The resulting gel has a better structure, porosity and regular distribution of immobilised biomaterial than the conventional one [3]. All these parameters were optimized in this investigation. Bio-sensing layers with encapsulated His_6-OPH of various structures, where we have varied water/silane and precursor ratios (TEOS/GPTMS [4] or TMOS/MTMOS) have been prepared.

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Hierarchical mesoporous titania thin films as enzyme carriers for paraoxon detection and/or detoxification

Nina Frančič[1], Martín G. Bellino[2], Galo J. A. A. Soler-Illia[2], Aleksandra Lobnik[1]

[1]University of Maribor, Faculty of Mechanical Engineering, Centre of Sensor Technology, Smetanova 17, 2000 Maribor, Slovenia.

[2]Gerencia Química, Comisión Nacional de Energía Atómica, Av. Gral. Paz 1499, San Martín, B1650KNA, Argentina

Organophosphorous (OP) derivates are a massive and highly diverse family of organic chemicals, with many uses. These include pesticides (e.g. paraoxon, parathion) widely used in agriculture that accumulate in the ground and in water sources, as well as neurotoxic chemical warfare agents, (e.g. sarin, soman, and VX) [1].

OPH (EC 3.1.8.1) is one of the most studied enzymes related to its activity towards pesticides and nerve agents. OPH catalyzes hydrolysis reactions of various organophosphoric compounds containing P–O, P–F, and P–S bonds [2]. Fusing a hexahistidine (His_6) tag to OPH changed enzyme's catalytic and physical chemical properties [3], improving the catalytic efficiency, especially towards P–S containing substrates, and the stability under alkaline hydrolysis conditions compared to native OPH.

Enzyme immobilization on inorganic mesoporous materials is an interesting method to improve enzyme functionality [4-6]. The main advantages of these materials are their pore diameters (2–40 nm) and high pore volume (approximately 1 cm^3g^{-1}). Additionally, these materials are inert and stable at elevated temperatures giving the prepared biocatalysts the possibility of easy separation from products, its reuse, and less sensibility to pH changes as well as minimized denaturation. It is conceivable that large-pore mesoporous films with wide interpore necks could provide an appropriate environment to grant biological activity [7]. Recently, it has been shown that titania thin films with tuned hierarchical pore-size distribution and pores rainging between 10 and 100 nm can indeed be manufactured [8]. Moreover, titania films are biocompatible and stable under most physiological conditions [9].

In present work, His_6-OPH was immobilized onto mesoporous titania films in a phosphate buffer medium. Mesoporous thin films used as enzyme support were produced following the procedure reported by Malfattti et al. [8] by adjusting carefully the relative proportions of the precursor ($TiCl_4$), water, template (Pluronic F127), co-template (PPG), solvent (butanol), and co-solvents (THF) in the sols. Characterization of the thin films as well as immobilized biocatalyst (His_6-OPH/TiO_2) included FE-SEM, elipsometry and FTIR techniques. The enzymatic activity (performance of K_M and V_{max} measurements, pH profile, etc.) was determined spectrophotometrically, where the accumulation of the p-nitrophenolate anion as a hydrolysis product of paraoxon was monitored.

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Synthesis of mesoporous silica particles suitable for enzyme immobilization applicable in bio-sensing or detoxification processes of organophosphates

Nina Frančič, Aleksandra Lobnik

[1]University of Maribor, Faculty of Mechanical Engineering, Centre of Sensor Technology, Smetanova 17, 2000 Maribor, Slovenia.

In the past decade, interest in mesoporous materials has developed dramatically since they can be useful in a number of applications, including adsorption and sensor technology. Mesoporous materials are a class of nanostrustures with well-defined mesoscale (2–50 nm) pores, surface areas up to 1000 m^2/g and large pore volumes (~1.0 mL/g) [1]. Owing to their structural properties and regular morphology, mesoporous silicas (MPS) are promising materials for applications in the immobilization processes or as supports for bulky bio-molecules, such as enzymes.

We report on the synthesis of mesoporous silica (MPS) particles and their potential use for immobilization of the enzyme hexahistidine tagged OPH (His_6-OPH) [2]. Particle characterization points out a strong influence of the synthesis parameters (e.g. structure of precursors, water/silane ratio, precursors ratio, addition of surfactants, etc.). Preliminary results indicate significant potential in use of immobilized enzyme His_6-OPH for the purpose of bio-sensing or in the detoxification processes of organophosphates.

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The Adsorption of Ag-NP onto Cellulose Influenced by Plasma and Different Gas Used for Dyeing and Ag-NP Synthesis

M. Gorjanc[1], M. Mozetič[2], F. Kovač[3], M. Gorenšek[1]

[1]University of Ljubljana, Faculty of Natural Sciences and Engineering, Aškerčeva 12,
1000 Ljubljana, Slovenia.
[2]Jozef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia.
[3]University of Ljubljana, Faculty of Chemistry and Chemical Technology, Aškerčeva 5,
1000 Ljubljana, Slovenia.

For research low-pressure plasma was used for a treatment of cellulose to increase the adhesion of silver nanoparticles (Ag-NP) synthesised under different gaseous conditions. Bleached and mercerized cotton fabric was used as the representative cellulose material. Cotton fabrics were treated with a low-pressure water vapour plasma system for 10 seconds. The synthesis of Ag-NP was performed by reducing $AgNO_3$ with $NaBH_4$ in bi-distilled water at 20°C under argon or nitrogen gaseous conditions. After Ag-NP synthesis the untreated and plasma treated cotton fabric were immersed into the colloidal solution and treated for 5 min. The reduced form of vat dye was added into the same solution and dying of cotton took under air, argon or nitrogen gas at 60°C for 60 min. The functionalized and dyed samples were then rinsed twice in deionised water, post-treated in HCOOH 85% and rinsed in deionised water. The amount of adsorbed Ag-NP was determined using inductively coupled plasma mass spectroscopy (ICP-MS). The results show which of the conditions is the most appropriate for a higher Ag-NP adhesion onto cellulose and the importance of plasma treatment and used gas for Ag-NP synthesis and dyeing. The ICP-MS results show that the highest amount of Ag on cotton was achieved on plasma treated cotton and when argon gas was used for a synthesis of Ag-NP and dyeing.

Application of novel two-step nanosilver-silica coating to different textile fibres

D. Klemenčič[1], B. Tomšič[1], B. Simončič[1], F. Kovač[2]

[1] University of Ljubljana, Faculty of Natural Sciences and Engineering, Department of Textiles, Askerceva 12, Ljubljana, SI.

[2]University of Ljubljana, Faculty of Chemistry and Chemical Technology, Askerceva 5, Ljubljana, SI.

The aim of this research was to study the possibility of the application of a novel antimicrobial finishing procedure, developed in our previous study [1], to different textile fibres as well as to investigate its antimicrobial efficiency. The chemical modification of cotton (CO), silk (SE), wool (WO), viscose (CV), polyester (PES) and polyamide (PA) fibres was performed in two steps, where the pad-dry-cure method was used to create a functional silica matrix through the application of an inorganic–organic hybrid sol–gel precursor (RB) followed by the *in situ* synthesis of AgCl particles on the RB-modified fibres. The bulk concentration of Ag on the modified fibres was determined by inductively coupled plasma mass spectroscopy. The antimicrobial activity was determined for the bacteria *E. coli* and *S. aureus*, and the fungus *A. niger*. The results showed that the new procedure was suitable for the chemical modification of different textile fibres, in which the application of nanosilver-silica coating to the fibres provided excellent antimicrobial properties. It was also found that the Ag sorption capacity of the fibres was directly influenced by their chemical and morphological properties. The concentration of adsorbed Ag on the fibres increased in the order PES < PA < CO < SE < CV < WO. The lowest Ag sorption capactity on the PA and PES fibres was due to their high hydrophobicity and crystallinity.

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Ceramic Membranes with a Surface Nanolayer Containing 3-Aminopropyl and 3-Aminopropyl/Methyl Functional Groups

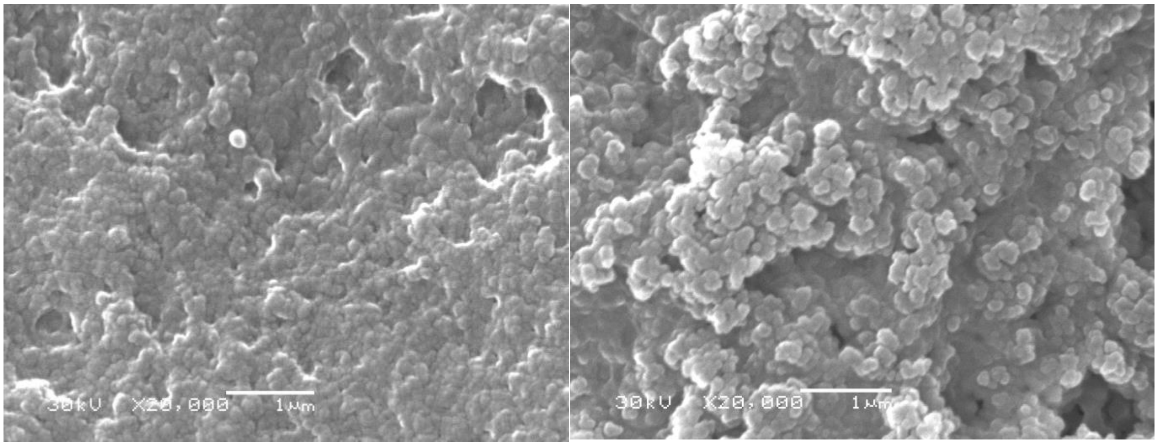
I.V. Melnyk[1], I.S. Stemkivska[2], L.M. Solodka[2], V.V.Tomina[1], Yu.L. Zub[1],
A. Kosak[3], A. Lobnik[3]

[1]Chuiko Institute of Surface Chemistry, NAS of Ukraine, 17, General Naumov Str.,
Kyiv 03164 Ukraine
[2]National University of “Kyiv-Mogyla Academy”, 2, Grygorii Skovoroda Str.,
Kyiv 04070 Ukraine
[2]University of Maribor, Faculty of Mechanical Engineering, Centre of Sensor
Technology, Smetanova 17, 2000 Maribor, Slovenia

The main objective of membrane technology is the separation of the components with minimal energy cost. Modern membranes typically consist of several layers of different materials, each with its own structural organization at the micro- and nanoscale. It provides a range of technological characteristics of the membrane as the high and selective transport properties, the ability to regenerate and so on. Sol-gel method is one of the most promising methods for inorganic and hybrid organic-inorganic membranes for process gas separation, dehydration of organic liquids by pervaporation, proton-conducting membranes for fuel cells and membranes with the "memory effect" [1]. This method also allows one to get the membranes with thin upper active layer, which determines their selectivity and transport properties.

This report examined functionalization of ceramic ultrafiltration membranes (〈-Al_2O_3, “Anodisc”) by sols obtained during hydrolytic polycondensation of tetraethoxysilane and 3-aminopropyltriethoxysilane (and metyltriethoxysilane). It was found the influence of the ratio of the reacting components, their concentration and drying regime on the structure of functional surface layer. Thus, the active layer of the membrane is formed by spherical particles of 50 nm (Fig. 1a) when two-component systems were used under optimal conditions, and in the case of ternary systems it is formed by spherical particles of 60 nm (Fig. 1b).

Depending on the ratio of the reacting components content of 3-aminopropyl groups was 0.55-2.1 mmol/g. DRIFT spectra confirm the presence of functional groups and polysiloxane skeleton in the active surface layer of membranes. The resulting membrane (its surface nanolayer) can sorb copper(II) ions from their aqueous solution. The composition of the coordination sphere of Cu^{2+} ions was studied using ERS and EPR spectroscopy. On the basis of these results the conclusions about the structure of the functional layer of membranes were done at the molecular level.



a b

Fig 1. The morphology of the surface layer of ceramic membranes functionalized by amino- (a) and amino/methyl (b) groups (according to SEM).

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Creation of superhydrophobic properties on cotton fabric by forming double-layered surface roughness

B. Tomšič[1], A. Maloprav[1], I. Jerman[2], Kristina Žagar[3], B. Orel[2] in B. Simončič[1]
[1]University of Ljubljana, Faculty of Natural Sciences and Engineering, Department of Textiles, Ljubljana, Aškerčeva 12, Slovenia.
[2]National Institute of Chemistry, Laboratory for Materials Chemistry, Ljubljana, Hajdrihova 19, Slovenia.
[3]Jozef Stefan Institute, Nanostructured Materials, Ljubljana, Jamova 39, Slovenia.

The aim of the study was to create a double-layered roughness on cotton fibres in order to mimic topography of lotus leaf for achieving superhydrophobic self-cleaning properties. A double layered roughness on cotton fibres was tailored by a combination of silica (SiO_2) nanoparticles, synthesised by Stöber's method, and aminopropyl isooctyl polyhedral oligomeric silsesquioxane (POSS), distinguished by its cubic like silicon-oxygen nanostructured skeleton, having one corner attached to a functional organic group. Functionalization of cotton fabric was obtained by a two-step process. In the first step, silica nanoparticles were applied to cotton fabric using pad-dry cure method, followed by a deposition of 4% POSS in the second step. For comparison only 4% POSS was also applied to cotton fabric. TEM, SEM and AFM techniques were exploit for studying morphological properties of the samples, while measurements of static contact angel of water and sliding angel were obtained for determination of functional properties before and after five consecutive washings of the samples. Rubbing fastness of the coatings as well as influence of the coatings on the air permeability and rigidity were also studied. By combining the unique structure of POSS molecules with SiO_2 nanoparticles supehydrophobicity of cotton fabric was achieved. Formation of double-layered roughness on the surface of the fibres resulted in an increase of static contact angel from 144.5°, determined for POSS finished sample, to 153.2° on SiO_2+POSS finished sample. Despite this, the adhesion between water droplet and the surface of the fabric was too high to obtain self-cleaning ″lotus effect″, resulting in a sliding angle of 16° on SiO_2+POSS cotton sample. Both studied coatings showed satisfactory washing and rubbing fastness. In comparison to the unfinished cotton sample, application of POSS and SiO_2+POSS slightly impaired air permeability as well as rigidity of the finished samples.

Photocatalytic porous coating obtained by sol-gel process on flexible substrates

D. Gregori[*,1,2], I. Benchenaa[2,3] , D. Léonard[3], C. Guillard[2], S. Parola[1]

[1] *Laboratoire de Chimie (LC), UMR 5182 ENSLyon, CNRS, Université Claude Bernard-Lyon 1, 46 allée d'Italie 69364 Lyon cedex 07, France*

[2] *Institut de recherche sur la catalyse et l'environnement (IRCELYON), 2 avenue Albert Einstein 69626 Villeurbanne cedex, France*

[3] *Institut des Sciences Analytiques (ISA), UMR 5280, 5 rue de la Doua 69100 Villeurbanne, France*

In recent years, the important development of the heterogeneous photocatalysis as depolluting technique induced new challenges especially for the applications with organic substrates. Coatings have to protect the organic substrates from the photocatalytic reactions and preserve their flexibility for the industrial uses. New materials must be stable in time and not release pollutants or photocatalysts. In this context, we have developped a composite hybrid film with homogeneous dispersion of TiO_2 nanoparticles into a silica based matrix. The matrix is prepared using the sol-gel process, at low temperature, which allows introducing organic groups in the inorganic network. Such modification of the structure induces increase of flexibility of the final material.

A hybrid silica sol is prepared by acidic catalysis of alkoxysilanes. A TiO_2 nanoparticles dispersion is introduced into the silica sol and the final solution is sonicated. Then, the film is deposited by various methods: dip-coating, spraying or padding, and dryed at 120°C. A final step of UV pre-treatment is applied on the material. The sample, immersed on an aqueous solution, is irradiated during 24 hours on a UV exposure chamber.

Modifications of the layer are controlled by contact angle, solid Si NMR, XPS and ToF-SIMS analysis. Concentrations for the pollutant released and the depolluting properties using formic acid as model are followed by HPLC as a function of the UV irradiation time.

To have an efficient material, many parameters are important to study and control: the choice of the photocatalyst, understand the photoctalyst/pollutants interactions, verify the stability of the coating and the substrate protection with time. With our synthesis we obtain a porous material spontaneously generated with the self organization of the TiO_2 nanoparticules and the growth of the silica network around them. The layer shows a macroporosity with a pore size between 50 and 300 nm. The last step, the UV pre-treatment, is used to create microporosity by degrading the organic groups present near the photocatalyst. These spaces allow increasing the accessibility of the pollutants to the photocatalyst and thus improving the film photoactivity. We compare the photoactivity of our coating with a commercial reference, a photocatalytic paper. Similar degradation rate is observed for both, but the quantity of TiO_2 presents on the commercial reference is twenty times superior.

A hierarchically porous material was obtained at low temperature, without templating agent using the sol-gel process followed by a properly adapted UV treatment. This composite has shown extremely promising properties in terms of protection of the organic substrates, flexibility, stability and photocatalytic behavior. This work led to a patent [1] and industrial development of these materials is running for various indoor and outdoor applications.

[1] Damia Gregori, Chantal Guillard, Frederic Chaput, Stephane Parola, Patent FR 13 53122, 2013

Effect of charge and coating on superparamagnetic iron oxide nanoparticles (SPION) proteins interactions: in vitro and biodistribution studies

Lionel Maurizi[1], Usawadee Sakulkhu[1], Lindsey Crowe[2], Azza Gramoun[2], Jean-Paul Vallee[2], Heinrich Hofmann[1]

[1]Powder Technology Laboratory, École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland
[2]Department of Radiology, University of Geneva and Geneva University Hospital, 1211 Geneva 14, Switzerland

Superparamagnetic iron oxide nanoparticles (SPION) have become important for various *in vivo* and *in vitro* biomedical applications such as imaging, magnetic separation, biosensor devices and therapy. To be used in biomedical applications, SPION are usually stabilized in physiological media with biocompatible surface coating[1] which could be used for specific targeting or detection[2]. It is commonly observed, *in vivo*, that the SPION are taken up by liver, spleen and the reticulo-endothelial system (RES) a few minutes after injection. Many studies have revealed that the chemical composition of the SPION surface, its charge or size influence biodistribution. However, studying SPION biological interactions, especially with body fluids proteins, is more important and a main challenge to understand their *in vivo* behavior.

In this study, maghemite SPION (□-Fe_2O_3) were surface modified with differently charged (positive, neutral and negative) polyvinyl alcohol (PVA) polymers. PVA was used to prevent agglomeration and improve biocompatibility of the magnetic nanoparticles[2]. Surface modified SPION were then characterized with classical methods (crystallite's and hydrodynamic mean diameters and Zeta potential) before incubation with biological media. *In vivo* studies were performed in the rat. The SPION were then injected, in the same conditions, for 15 minutes before sacrificing the animals. The SPION were removed from the rat's blood and the protein distribution was determined in 10 different organs and in the blood.

The *in vivo* protein interactions for different particles were compared revealing the influence of charge and coating on SPION uptake.

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Biochemical modification and functionaliaztion of nanocellulose surface

M. Božič, D. Jaušovec, V. Vivod, V. Kokol

University of Maribor, Institute for Engineering Materials and Design, Maribor, Slovenia

Cellulose nanofibers (CNFs) and nanowhiskers (CNWs) have been receiving a great importance in the last decade due to their specific aspect ratio and huge surface area as well as being renewable, nontoxic, sustainable and biodegradable nanomaterials. Moreover, the chemical character of the cellulose molecule enables the creation of new functional groups or even introduction of new molecules, giving them higher added-value and thus may additionally govern the final material properties made of them, as well as broadens their applications.

By this contribution, some advanced bio-catalytically induced strategies for surface modification and functionalization of nanocellulose will be presented as ecologically-friendly and substrate-specific alternative to aggressive chemical approaches: i) specific glucosidal-bond hydrolysis of nanocellulose by endo-cellulase to increase or modify their surface area (size, shape) *vs.* reactivity (hydroxyl groups) through evaluation of glucose release, particles zeta-size analysis and TEM; ii) the introduction of aldehyde *vs.* carboxyl functional groups on nanocellulose surface using laccase/TEMPO systems in combination with additional oxidation procedure-s being confirmed by spectrsoscopies and potentiometri titration; iii) the phosphorylation of nanocelluloze using hexokinase-mediated modification being confirmed by spectroscopies, potentiometric titration and DCS/Tg analysis, showing also metal-ions adsorption, flame-resistance and hydroxyapatite-growth properties; iv) finally, hydrophobical functionalization of nanocellulse using acetic anhydride and lipase in organic solvent being proved.

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Targeting of antimicrobial activity via micro/nano-structured surfaces using bio- and nano-technology

M. Božič[1], D. Jaušovec[1], R. Vogrinčič[1], J. Štrancar[2], V. Kokol[1]

[1]University of Maribor, Institute for Engineering Materials and Design, Maribor, SI
[2]Jožef Štefan Institute, Department of Solid State Physics, Ljubljana, SI

Clean surface maintenance still requires a continuous use of large quantities of detergents, disinfectants and antibiotics, but promising alternatives involve novel micron and nano-sized materials with more general mechanisms of action, which interfere with the basic cell supramolecular organization and processes.

By this contribution, a strategy for creating an antimicrobially-protected material surface using bio- and nano-technology will be presented. In that respect, titanate nanotubes (TiNTs) generating short-lived radicals in the process of photocatalisys that affect the bacterial membrane or act directly on the bacterial respiratory chain, and thus prevent bacterial growth, was used. The long-term and stable antimicrobial activity of polymeric-material (PES) chemically-inert surfaces was solved by the development of innovative and environmentally friendly techniques as enzyme-based and/or plasma-based pre-treatment methods, following by specific TiNTs deposition. On the other hand, TiNTs were surface pre-modified using pre-defined phenolic acids, denoting new reactive groups, being used for reaction with pre-modified PES surface in the second step; highly resolution capillary electrophoresis (CE) was introduced as innovative technique for characterization of surface chemistry and its stability, as well as aggregation of TiNTs in that respect. The photocatalytic behavior and stability of functionalized TiNTs as well as TiNT-nanostructured PES surfaces, before and after being excited with irradiation of UV light in aqueous environment, were also defined through radicals detected using spin-trapping EPR.

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Optical, electrical and structural properties of aluminium doped zinc oxide thin films by sol–gel method

P.Obreja, D.Cristea, M.Danila, A.Dinescu

National Research and Development Institute for Microtechnologies, Bucharest, RO

Zinc oxide is an inexpensive n-type semiconductor with many applications in solar energy conversion, light emitting diodes, nanolasers, varistors, photocatalysis and thin film chemical sensors. ZnO films can be fabricated by various methods [1-3]. The paper presents an experimental study on the preparation and physical properties of the aluminum doped zinc oxide (AZO) thin films on glass and silicon substrate by a multi-step sol-gel technique using spin coating process.

AZO thin films were prepared by sol–gel spin-coating method, starting from zinc acetate solutions (0.1M and 0.5 M) in ethanol stabilized by ethanolamine and doped with aluminum nitrate (1-3 at.%). AZO films were spin coated at a speed of 2000 rpm for 60 s and dried 10 min at 200°C to evaporate the solvent and to remove the organic compounds. The process was repeated 3-8 times to obtain the desired thickness. Finally, AZO multilayer samples were post-heated at 350°C for 30 min and their optical, electrical and structural properties were investigated by X-ray diffraction, UV–visible spectrophotometry, scanning electron microscopy and electrical resistance measurement. The as prepared AZO thin films are polycrystalline, preferentially oriented along the <002> direction, transparent in near ultraviolet and visible and have a grain size between 4-9 nm and a thickness between 200-620 nm. The resistivity values of AZO films were 1-20 ohm.cm.

The measurements on n-AZO/p-Si heterojunctions, obtained by AZO films deposited onto p-silicon show that this material can be used for fabrication of photodetectors with improved responsivity in UV.

Key Words: Aluminum-doped zinc oxide, Sol-Gel, Optical properties, Electrical properties;

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Preparation of hybrid silica nanoparticles

P. Nedeljko[1], A. Košak[1,2], M. Turel[1], A. Lobnik[1,2]

[1]Institute for Environmental Protection and Sensors, Beloruska 7, Maribor, SLO.
[2]University of Maribor, Faculty of Mechanical Engineering, Centre for Sensor Technology, Smetanova 17, Maribor, SLO.

Hybrid nanomaterials based on silica (SiO_2) particles are attracting growing fundamental and technological interest in different fields of sensor applications, particularly because of their unique properties which are dominated by tunable and controllable porosity, high specific surface area, transparency, nontoxic and inert nature and the possibility to treat their surface with various organic materials. The chemistry of silica provides the opportunity for a variety of surface functionalities with hydroxyl, amino, thiol, carboxyl groups, etc., which can be used to attach targeting biological molecules.

In this study, several silica based hybrid nanomaterials were prepared via Stöber's process, which is based on the hydrolysis and co-condensation of alkoxysilane precursors, such as tetraethoxysilane (TEOS) and 3-(Trimethoxysilyl)-1-propanethiol (MPTMS) in the presence of ammonia in alcoholic solution. We used alkoxide precursors at different molar ratios (P), while the molar ratios between water and tetraalkoxide (TEOS) precursor (R) was kept constant. An influence of the molar ratio (R), the molar ratio (P), the reaction temperature and the time of reaction on the particle size and morphology of the prepared product was investigated. The tendency of the surface -SH groups to bind the organic dye molecules, used for sensing biologically active compounds, was finally evaluated. Obtained nanoparticles were characterized using infrared spectroscopy (FTIR), transmission and scanning electron microscopy (TEM/SEM/EDXS) and thermogravimetric methods (TGA/DTA/DSC). The specific surface area and porosity (BET) were measured for the prepared samples.

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Development of experimental methods for determining magnetic fluid heating power

M. Beković, M. Trlep, M. Jesenik, A. Hamler

University of Maribor, Faculty of Electrical Engineering and Computer Science,
Smetanova ul. 17, Maribor, Slovenia

The objective of the work is to present the development of the experimental systems for determining magnetic fluid heating power when exposed to magnetic field. Systems are capable of generating homogeneous magnetic field of amplitudes up to 25 kA/m and frequencies from 10 kHz to 1 MHz. The application of the heated magnetic fluids is for medical purposes for the treatment of cancerous tissues and for that it is necessary to determine the heating power precisely. It can be determine by three methods which details are explained in the paper. The first one is called the calorimetric method where key parameter is temperature rise of the fluid. Second approach is using the magnetic measurement, where the key parameters are time dependent magnetic field strength H and appurtenant magnetic flux density B and determination of hysteresis loop area whilst the third method basis on determining the complex susceptibility between the measured magnetic field strength and magnetic polarization J. We will present two measurement systems as well as their strengths and weaknesses and how they affect the individual mentioned measuring method as reported in [1] and [2].

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Nanosized biocatalysts hydrolyzing organophosphorus toxins *in vivo*

E. Efremenko, I. Lyagin, A. Kabanov

The M.V. Lomonosov Moscow State University, Moscow, 119991 Russia

E-mail: elena_efremenko@list.ru

Organophosphate hydrolase with genetically introduced hexahistidine tag (His_6-OPH) was used to elaborate nanosized biocatalysts to hydrolyze organophosphorus toxins *in vivo*. Applying molecular modeling of surface charge of dimer molecule of OPH it was reveled that most density of positive charge was localized on the opposite side to the active center of the enzyme. Therefore, the polyanions were used to stabilize His_6-OPH and to develop its polyelectrolyte complexes [1]. The samples of stabilized His_6-OPH, prepared using various ratios between charges localized at the surface of enzyme and chosen anionic polymer were characterized by 30%-increased residual activity of the enzyme in interval of pH from 7.5 to 9.5 as compared to native enzyme. Comparison of catalytic properties of prepared samples with literature data known for OPH treated by polyethylene glycol testified to as minimum twice-time higher efficiency of catalytic action of obtained His_6-OPH-samples.

Analysis of AFM-images of obtained His_6-OPH-samples revealed the presence of nanoparticles with size close to 30-40 nm in all tried samples. The pharmacokinetics of developed samples in the blood of rats was researched *in vivo* after intravenous injection of the nanoparticles. Administrated His_6-OPH-biocatalysts circulated in blood for longer time than native enzyme.

The elaborated His_6-OPH-biocatalysts were tried *in vivo* as protective agents against the neurotoxic action of Vx and Paraoxon taken at LD_{50} and LD_{100}. The developed His_6-OPH-samples guaranteed the increase in amount of survived animals and provide the significant delay in appearance of convulsions in contaminated animals. The very effective use of the His_6-OPH-biocatalysts as antidotes also was demonstrated with animals contaminated by $1.2\times LD_{100}$-dose of Paraoxon. All animals survived with catalytic treatment by His_6-OPH-biocatalysts.

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