



NANOAPP 2015
Nanomaterials & Application
23 - 26 June 2015, Maribor, Slovenia

BOOK OF ABSTRACTS

Maribor – Slovenija

23 – 26 June 2015

Book of Abstracts | Zbornik povzetkov

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NANOAPP Mednarodna znanstvena konferenca Nanomateriali & aplikacije**

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Aleksandra Lobnik
Andreja Gutmaher

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2. International Scientific Conference | 2. Mednarodna znanstvena konferenca

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

Venue | Prizorišče

Hotel Habakuk, Maribor, Slovenija

Dates | Datum

23 - 26 June 2015 | 23. – 26. junij 2015

Chair of the Conference | Predsedujoča

Prof. Dr. Aleksandra Lobnik, University of Maribor, Slovenia

Co-chairs of the Conference | So-predsedujoči

Prof. Dr. Michel Wong Chi Man, Institute Charles Gerhardt Montpellier, France

Prof. Dr. Stephane Parola, ENS Lyon, University of Lyon, CNRS, France

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IOS, Institute for Environmental Protection and Sensors, L.t.d, Slovenia

ENS Lyon, CNRS, Université de Lyon, France

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National Academy of Sciences of Ukraine, Ukraine

FOREWORD

Welcome to the NANOAPP 2015 Conference in Maribor, Slovenia

We are delighted to have you participate in the **NANOAPP 2015** (<http://nanoapp.ios.si/>) which the second NANOAPP conference in Hotel Habakuk in Maribor, Slovenia from 23. – 26. of June, 2015.

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 Tuesday, June 23rd and concluding on Friday, June, 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 Maribor, and that you experience a truly valuable and memorable meeting.

Chair of the NANOAPP 2015 Conference

Prof. Dr. Aleksandra Lobnik



NANOAPP 2015

Nanomaterials & Application
23 - 26 June 2015, Maribor, Slovenia

Day 1: Tuesday, 23 June 2015

15:00 - 19:00	Registration - Hotel Habakuk Congress Centre Foyer 1
Room	Turner
16:00 - 16:10	Welcome Remarks: Prof. Dr. A. Lobnik, Slovenia
Session Chair	Prof. Dr. Aleksandra Lobnik: NANOMATERIALS/HYBRID NANOMATERIALS
16:10 - 16:30	Invited Lecture I2: Prof. Dr. R. Zboril - Advanced nanoarchitecture of iron and carbon based materials for environmental, catalytic and biomedical applications
16:30 - 16:50	Invited Lecture I3: Prof. Dr. S. Bégin-Colin, Mathilde Menard - Core-shell nanoparticles designed for theranostics
Session Chair	Prof. Dr. Jean Olivier Durand: Young Scientists Session
16:50 - 17:10	Invited Lecture I4: Dr. P. Jenuš - Preparation of ferrite-based exchange-coupled hard/soft magnetic nanocomposites
17:10 - 17:25	Oral Presentation O1: A. Nouredine - Inkjet-printed mesoporous silica dots as biosensors for cancer diagnosis and therapy
17:25 - 17:40	Oral Presentation O2: M. Bračič - Patterned surface modification of ultra-thin PDMS films with polysaccharides for advanced biomedical sensoric devices
17:40 - 17:55	Oral Presentation O3: E. F. Grosu - Nanostructured mixtures of mixed oxides derived from layered double hydroxides reconstructed in $\text{Ga}_2(\text{SO}_4)_3$ and $\text{In}(\text{C}_2\text{H}_3\text{O}_2)_3$ aqueous solutions for efficient UV and solar-driven photocatalysis
17:55 - 18:10	Oral Presentation O4: M. Lakhane - Structural properties of novel zeolite-modified cellulose nanofibril composites, and their potential applications
18:10 - 18:25	Oral Presentation O5: C. Mansas - Synthesis of core-shell nanoparticles to capture radioactive cesium
18:25 - 18:40	Oral Presentation O6: U. Maver - Electrospun nanofibrous CMC/PEOX as a part of an effective pain relieving wound dressing
20:00 - 22:00	Welcome Reception - Hotel Habakuk Congress Centre Foyer 2
End of Day 1	

Day 2: Wednesday, 24 June 2015	
Room	Turner
Session Chair	Prof. Dr. Aleksandra Lobnik: Opening
9:00 - 9:30	Welcome Remarks: Prof. Dr. A. Lobnik, Slovenia Director-General of Science Directorate of the Ministry of Education, Science and Sport - Mag. U. Krajcar, Slovenia Vice Rector of the University of Maribor - Prof. Dr. N. Samec, Slovenia Dean of the Faculty of Mechanical Engineering, University of Maribor - Prof. Dr. B. Dolšak, Slovenia
Session Chair	Prof. Dr. Michel Wong Chi Man: NANOMATERIALS & APPLICATIONS
9:30 - 10:15	Plenary Lecture P1: Prof. Dr. Ha Chang-Sik, South Korea - Periodic Mesoporous Organosilicas for Drug Delivery and Metal Adsorption
Session Chair	Prof. Dr. Guillermo Orellana: NANOMATERIALS IN SENSORS
10:15 - 10:35	Invited Lecture I5: Prof. Dr. B. Mizaikoff, Germany - Molecularly Imprinted Nanoparticles for Advanced Biomimetic Assays
10:35 - 10:55	Invited Lecture I6: Prof. Dr. K. Katagiri, Japan - Nanoparticle-based nanohybrid materials for biomedical applications
10:55 - 11:40	Coffee Break and Posters
Room	Turner
Session Chair	Prof. Dr. Ulrich Schubert: NANOMATERIALS/HYBRID NANOMATERIALS
11:40 - 12:25	Plenary Lecture P2: Prof. Dr. J. Bartlett, Australia - Cooperative Physical and Chemical Interactions for the Sol-Gel Processing of Organised Films and Nanoparticles
12:25 - 12:45	Invited Lecture I7: Prof. Dr. H. Hofmann, Switzerland - New insight into the colloidal behavior of suspensions with nanoparticles
12:45 - 13:05	Invited Lecture I8: Prof. Dr. M. Osada, Japan - Hierarchically Structured Assembly of 2D Nanosheets for Tailored Artificial Materials
13:05 - 13:25	Invited Lecture I9: Prof. Dr. R. Šafarič - Using van der Waals force for gripping nano/micro sized objects
13:25-14:40	Lunch
Room	Turner
Session Chair	Prof Dr. Heinrich Hofmann: NANOMATERIALS IN BIO/MEDICAL APPLICATIONS
14:40 - 15:25	Plenary Lecture P3: Prof. Dr. K. Stana Kleinschek, Slovenia - Polysaccharide materials for biomedical applications
15:25 - 15:45	Invited Lecture I10: Prof. Dr. L. Vellutini, France - Functionalized core-shell γ -Fe ₂ O ₃ nanoparticles for bio-immobilization
15:45 - 16:05	Invited Lecture I11: Prof. Dr. C. Carcel - pH-operated hybrid silica nanoparticles for autonomous drug delivery
16:05 - 16:25	Invited Lecture I12: Prof. Dr. P. Nikitin - Biocomputing with nanoparticles for biomedical applications
16:25 - 16:45	Invited Lecture I13: Prof. Dr. J. O. Durand- Mesoporous Silica, Bridged Silsesquioxane, Periodic Mesoporous Organosilica Nanoparticles for drug delivery and two-photon Photodynamic Therapy
16:45 - 17:15	Coffee Break and Posters
Room	Turner
Session Chair	Prof. Dr. Masahide Takahashi: NANOMATERIALS IN BIO/MEDICAL APPLICATIONS
17:15 - 17:45	Keynote Lecture K1: Prof. Dr. A. Gedanken, Israel - Making the Hospital a safer place by the sonochemical coating of all the textiles with antibacterial NPs
17:45 - 18:05	Invited Lecture I14: Prof. Dr. S. Lambert - Efficient P- and Ag-doped titania for the photocatalytic degradation
18:25 - 19:00 Poster Session	Poster Session
	Free evening
End of Day 2	

Day 3: Thursday, 25 June 2015	
Room	Turner
Session Chair	Prof. Dr. Loïc Blum: NANOMATERIALS IN SENSORS
8:30 - 9:15	Plenary Lecture P4: Prof. Dr. L. Lechuga, Spain - Point-of-care photonic nanobiosensors for global health diagnostics: Challenges and opportunities
Session Chair	Prof. Dr. Laura Lechuga: NANOMATERIALS IN SENSORS
9:15 - 9:35	Invited Lecture I16: Prof. Dr. G. Orellana - Light, Molecularly Imprinted Polymers and Nanotechnology to Tackle Analytical Challenges
9:35 - 9:55	Invited Lecture I17: Prof. Dr. I. Klimant - High performance luminescence indicators and sensing materials
9:55 - 10:15	Invited Lecture I18: Prof. Dr. L. Blum - Nanostructuration of lipids for membrane biochip development
10:15 - 10:35	Invited Lecture I19: Prof. Dr. G. Mohr - Absorbance and fluorescence based indicator dyes for use in nanomaterials
10:35 - 10:55	Invited Lecture I20: Prof. Dr. D. Boyer - Up-Converting Nanoparticles for Smart Traceability
10:55 - 11:15	Invited Lecture I21: Prof. Dr. J. D. Brennan, Canada - A Biosensing Platform Based on Synergistic Release of DNA Probes from Reduced Graphene Oxide and Rolling Circle Amplification
11:15 - 11:35	Coffee Break and Posters
Room	Turner
Session Chair	Prof. Dr. Stephane Parola: NANOMATERIALS IN ENVIRONMENT
11:35 - 11:55	Invited Lecture I22: Prof. Dr. O. Solcova - Water Treatment by Various Methods – Advantages and Disadvantages
11:55 - 12:15	Invited Lecture I23: Prof. Dr. M. Franko - Coupling Photothermal Spectroscopy and Nanotechnology
12:15 - 12:35	Invited Lecture I24: Prof. Dr. R. Backov, France - Integrative Chemistry-based Rational Design of Advanced Porous Materials Dedicated to Energy Conversion and Storage
12:35 - 12:55	Invited Lecture I25: Prof. Dr. P. Trens - Combining experimental and theoretical approaches for studying the sorption of vapours by Metal Organic Frameworks
12:55 - 13:15	Invited Lecture I41: Dr. T. Feczko, Hungary - Latent heat storage by silica nanoparticles-coated polymer beads containing organic phase change materials
13:15 - 14:20	Lunch
Room	Turner
Session Chair	Prof. Dr. John Bartlett: NANOMATERIALS/HYBRID NANOMATERIALS
14:20 - 14:50	Keynote Lecture K2: Prof. Dr. L. Malfatti - Graphene nanostructures in self-assembled mesoporous films: towards the design of highly performing nanocomposites
14:50 - 15:10	Invited Lecture I26: Prof. Dr. K. Pirnat - Graphene nanoribbons in Li-ion batteries
15:10 - 15:30	Invited Lecture I27: Prof. Dr. A. Shimojima, Japan - Synthesis of Mesoporous Silica Nanoparticles with Controlled Architectures
15:30 - 15:50	Invited Lecture I28: Prof. Dr. D. Grosso - Nanostructured sol-gel coatings, preparation and application
15:50 - 16:10	Invited Lecture I29: Prof. Dr. M. Takahashi - Stimuli-responsive microarchitectures with peristaltic capabilities based on bilayered hybrid materials
16:10 - 16:30	Invited Lecture I30: Prof. Dr. X. Cattoën - Click chemistry: a powerful tool for the functionalization of nanoparticles
16:30 - 16:45	Oral Presentation O8: Prof. Dr. J. Causse - Facile one-pot synthesis of copper hexacyanoferrate functionalized silica monoliths for the selective uptake of ¹³⁷ Cs
18:30	Departure to the Cablecar - 5 minutes easy walk
19:00 - 22:00	Cablecar Dinner
End of Day 3	

Day 4: Friday, 26 June 2015	
Room	Turner
Session Chair	Prof. Dr. Masahide Takahashi: NANOMATERIALS/HYBRID NANOMATERIALS
8:30 - 9:15	Plenary Lecture P5: Prof. Dr. U. Schubert, Austria - Metal oxide clusters as models for metal oxide nanoparticles
9:15 - 9:35	Invited Lecture I31: Prof. Dr. D. Portehault, France - Bridging the gap between solid state chemistry and nanoscale chemistry: from alloys to functional complex oxides
9:55 - 10:15	Invited Lecture I35: Prof. Dr. B. Pichon - Enhancement of magnetic properties in Fe ₃ O ₄ @CoO core-shell nanoparticles exhibiting exchange bias coupling
10:15 - 10:35	Invited Lecture I33: Prof. Dr. J.-L. Bantignies - 1D-confinement inside single-wall carbon nanotubes
10:35 - 10:55	Invited Lecture I34: Prof. Dr. D. Makovec - Synthesis of magnetic and multifunctional nanocomposites based on the colloidal processing of nanoparticles
10:55 - 11:25	Coffee Break and Posters
Room	Turner
Session Chair	Prof. Dr. John D. Brennan : NANOMATERIALS IN ENVIRONMENT
11:25 - 11:45	Invited Lecture I36: Prof. Dr. S. Parola - Hybrid sol-gel composite materials with microstructuration for photocatalytic applications
11:45 - 12:05	Invited Lecture I37: Prof. Dr. B. Heinrichs, Belgium - Doped oxide powders and films through low temperature syntheses for applications in water purification and anti-corrosion
12:05 - 12:25	Invited Lecture I38: Prof. Dr. N. Zabukovec Logar - Advanced heat storage materials for integrated storage solutions
12:25 - 12:45	Invited Lecture I39: Prof. Dr. U. Lavrečič Štangar - Towards efficient removal of contaminants from households grey waste water: Photocatalytic ozonation process
12:45 - 13:05	Invited Lecture I40: Prof. Dr. M. Lira Cantu, Spain - Solution processing Transition Metal Oxides and Graphene for Printed Organic Solar Cells
13:05 - 13:15	Conference Closing Remarks - Prof. Dr. A. Lobnik, Slovenia
13:15 - 15:00	Lunch
17:00 - 00:00	Timber rafting on river Drava , Wine tasting
End of the Conference	
End of Day 4	

Functionalized core-shell $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles for bio-immobilization

Liubov MITCOVA, Karine HEUZE, Thierry BUFFETEAU and Luc VELLUTINI

UNIVERSITE DE BORDEAUX, Institut des Sciences Moléculaires (UMR-5255) - C2M group, 351 cours de la libération, TALENCE, FRANCE

In the last two decades, substantial progress has been made in the development of technologies in the field of magnetic particles.^[1] Due to the simplicity in their use and the ease in their manipulation, magnetic particles are the most common solid phase for immobilization of biomolecules. They are widely used in applications such as high-throughput immunoassays, sample preparation, protein and nucleic acids purification and more generally life sciences research.

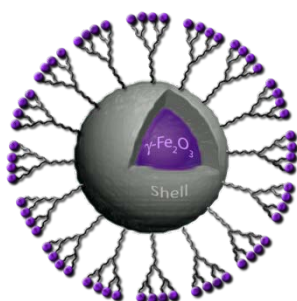


Figure 1. $\gamma\text{-Fe}_2\text{O}_3$ NPs by functional dendritic coupling agents

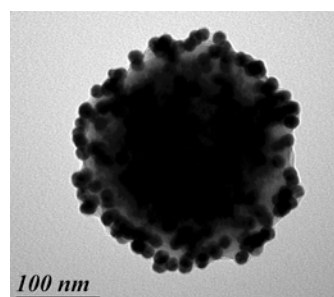


Figure 2. TEM image of biotin functionalized core-shell $\gamma\text{-Fe}_2\text{O}_3$ nanoparticle with gold-SA NPs immobilized on its surface.

We are developing innovative customized surfaces with dendritic functional structures to open new biofunctionalization perspectives.^[2] The grafting of functional dendritic coupling agents is proposed to multiply the number of functional groups and their flexibility at the magnetic particles surface (Figure 1). Indeed, the improvements of surface coverage of magnetic particles will influence accessibility to biological targets and will strongly increase recognition kinetics while reducing non-specific binding. In that context, highly functionalized biotin core-shell $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles (300 nm) have been synthesized. Then, the immobilization of 15 nm streptavidin coated gold nanoparticles (gold-SA NPs) has been performed *via* affinity recognition and used as nanoscale marker on the core-shell $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles surface (Figure 2). We demonstrated a positive dendritic effect on the surface functionalization.

References

1. (a) R. J. Koopmans et al. *Current Opinion in Microbiology* (2010) 12, 327. (b) J. Kim et al. *Cell Trends in Biotechnology* (2008) 26, 639. (c) J. Kim et al. *Biotech. Adv.* (2006) 24, 296.
2. H. Rahma et al. *ACS Appl. Mater. Interfaces* (2013) 5, 6843.

pH-operated hybrid silica nanoparticles for autonomous drug delivery

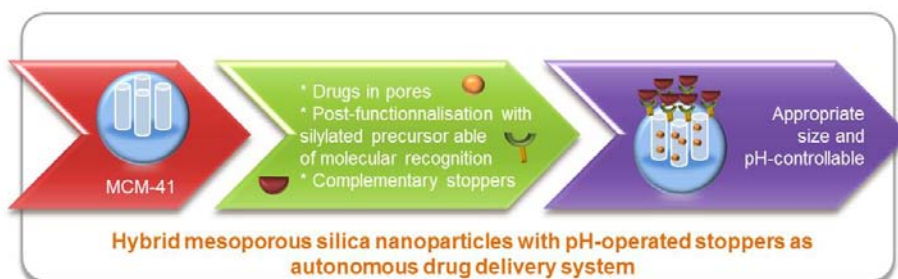
C. Carcel¹

¹Institut Charles Gerhardt Montpellier UMR-5253 CNRS-UM2-ENSCM-UM1, Ecole Nationale Supérieure de Chimie de Montpellier, 8 rue de l'école normale, 34296 Montpellier Cedex 05, France, carole.carcel@enscm.fr

In the past decades, several smart nanomaterials have been developed particularly as drug delivery systems for application in medical fields. Appropriately designed drug carriers with controlled delivery triggered by stimuli, without premature release, to the targeted cells can overcome some issues of conventional therapy (limited side-effects) and enhance the therapeutic performance of a given drug. Among several strategies, silica nanoparticles (SNP) appear as one of the most promising drug carrier.

Following our work on the development of pH-responsive hybrid silicas^[1] we have considered the possibility to prepare new hybrid silica nanoparticles as pH-operating nanomachines for drug release. The key challenge is to develop an autonomous system with a self-triggered release liable to occur inside the infected cells without external control. Since SNP can enter in infected cells due to EPR effect and via endocytosis route to the acidic lysosome compartment, a mild pH operating strategy may afford such autonomy to prevent leakage and avoiding premature release of the drug before reaching the target cells.

The strategy presented here will describe the preparation of hybrid mesoporous silica nanoparticles with pH-operated stoppers. Selected stoppers will be a commercially non-toxic available compound^[2] and a cytotoxic compound derived from an anticancer drug^[3].



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Biocomputing with nanoparticles for biomedical applications

P. I. Nikitin

General Physics Institute, Russian Academy of Sciences, 38 Vavilov St, 119991 Moscow, Russia

e-mail: nikitin@kapella.gpi.ru

Nanoparticles have a variety of useful intrinsic properties and significant potential for biomedical applications both in vitro and in vivo. However, the biocomputing capacity of particle-based systems is relatively unexplored. We have shown that almost any type of nanoparticle or microparticle can be transformed into biocomputing structures that can implement a functionally complete set of Boolean logic gates (YES, NOT, AND and OR), and can be made to bind to a target as a result of a computation¹. The logic gating functionality is incorporated into self-assembled particle/biomolecule interfaces, and the logic gating is achieved through input-induced disassembly of the structures (Fig. 1).

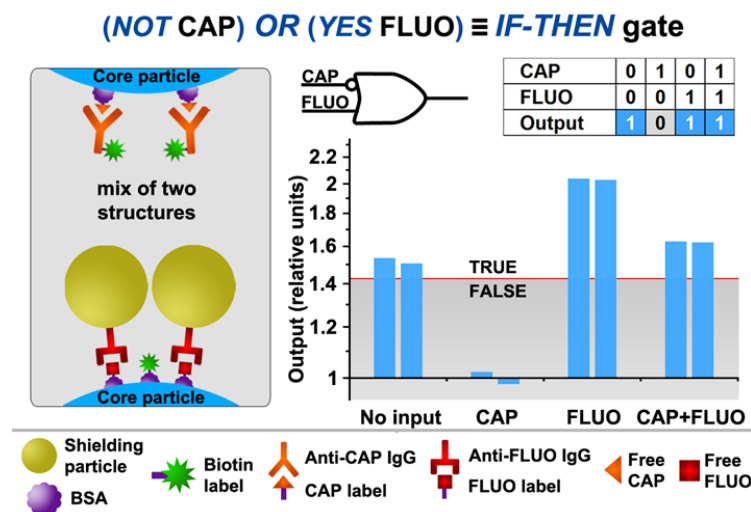


Fig. 1. Example of the self-assembled structure for complex logic gate of two inputs (left) and its results in log scale (right). The inputs are presence of chloramphenicol (CAP) and/or fluorescein (FLUO) molecules

We have demonstrated that nanoparticles with biocomputing capabilities are prospective for creation of sophisticated nanorobotic devices ranging from intelligent sensors to smart programmable theranostic agents. The approach was experimentally illustrated for advanced immunoassays and logic-gated cell targeting.

For developments of biocomputing schemes based on various nanoparticles, the following original research methods have been optimized and effectively used such as:

- magnetic immunoassays that employ magnetic nanoparticles (MNP) as the labels detected by the

magnetic particle quantification (MPQ) method^{2,3};

- spectral correlation interferometric (SCI) method for investigation of affinity constants of receptors deposited on nanoparticles to the ligands immobilized on glass cover slips⁴;
- optical methods for development of nanoagents with Boolean logic gating capabilities based on gold nanoparticles (GNP).

In particular, the reversible processes of self-assembly and disintegration of the multifunctional structures based on GNP were investigated. To this end, a real-time technique for monitoring the status of GNP association with or dissociation from various colloidal objects of non-metallic nature, e.g., with MNP based on iron oxides, was developed. For verification of the results on interaction of various functionalized nanoparticles and for quantitative monitoring of their binding to biomolecules on a sensor surface, the SCI method⁴ was used, which is insensitive to the bulk refractive index of solutions, provides information on the average thickness of surface layer expressed in metrology units (pm or nm) and uses low cost cover slips as the sensor chips⁴.

In the experiments, the preference to MNP was given because of their prospects for real medical applications as many types of MNP were already approved for injection to humans for various procedures such as contrast enhancement of MRI, etc. Besides, the MNP behavior in vivo could be effectively studied by the MPQ method, e.g. for non-invasive magnetic particle mapping in organs of experimental animals for long-term investigation of biotransformation, clearance and redistribution of MNP in animal's body, for quantification of aerosol delivery of nanodrugs to animal lungs⁵.

Our biocomputing structures based on stimuli responsive composite nanoparticle/biomolecule interfaces allow remarkably complex information processing. The signal transduction between several orthogonal receptors that do not share any specific biochemistry was achieved, among other means, by spatial entanglement of the receptors. The proposed platform can be applied to the development of autonomous nanodevices as intelligent biosensors with built-in biochemical data analysis for multiplex point-of-care diagnostics, field testing, etc. Furthermore, with the progress in metabolomics for the identification of new small molecule biomarkers, the platform could be used to construct bionanorobotic agents for complex stimuli-controlled targeted drug delivery, early diagnostics and health monitoring as a part of preventive medicine solutions.

Different aspects of the work were supported by RFBR grants No. 14-29-07271, 13-03-12468, 14-02-00840 and 15-02-07791.

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2. P.I. Nikitin, P.M. Vetoshko. *Russian patents* RU2177611 & RU2166751 (2000), *European patents* EP1262766 & EP2120041 (2001).
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Mesoporous Silica, Bridged Silsesquioxane, Periodic Mesoporous Organosilica Nanoparticles for drug delivery and two-photon Photodynamic Therapy.

Jean-Olivier Durand

Mesoporous silica nanoparticles (MSN) have attracted much attention the last decade for nanomedicine applications due to their biocompatibility, flexible functionalisation, tunable pore size and diameter. We describe here MSN engineered for two-photon triggered drug delivery in MCF-7 breast cancer cells. The two-photon triggered drug delivery system was based on a FRET mechanism from a two-photon dye in the walls of the MSN to an azobenzene moiety in the pores of the MSN (nanoimpellers). Concerning photodynamic therapy, a two-photon photosensitizer possessing four triethoxysilyl groups was used to perform the synthesis of Bridged Silsesquioxane Nanoparticles and core-shell systems with a gold core. Two-photon photodynamic therapy was performed in vitro on MCF-7 cancer cells. Alternatively, the synthesis of biodegradable Periodic Mesoporous Organosilica Nanoparticles (nanoPMOs) was realized and the nanoparticles were efficient in delivering doxorubicin in cancer cells. Multipod-based nanoPMOs were also synthesized from bis-triethoxysilylbenzene and bis-triethoxysilyl ethylene.

Efficient P- and Ag-doped titania for the photocatalytic degradation of waste water organic pollutants

C. J. Bodson¹, B. Heinrichs¹, L. Tasseroul¹, C. Bied², M. Wong Chi Man², S. D. Lambert¹

¹Department of Chemical Engineering – Nanomaterials, Catalysis, Electrochemistry, B6a, University of Liege, B-4000 Liege, Belgium. E-mail address : Stephanie.lambert@ulg.ac.be

²Charles Gerhardt Montpellier Institute, F-34296 Montpellier Cedex 5, France

TiO₂-based materials present a wide bandgap (3.20 eV) which corresponds to a wavelength $\lambda = 387$ nm for the anatase form. Consequently, only a small fraction of the solar spectrum in the near-UV region is absorbed and useful for photocatalysis. In view to improve the photocatalytic efficiency, various studies have been conducted on the doping of TiO₂ with non-metallic elements, particularly with phosphorus. The introduction of P in the TiO₂ indeed allows the formation of porous xerogels and stabilizes the TiO₂-anatase at higher temperatures up to 650 °C ; Moreover it was shown that the presence of P increases the photocatalytic activity of TiO₂-anatase under visible light through the introduction of an energy band just below the conduction band of TiO₂. However, the recombination degree of electrons (e⁻) and photogenerated holes (h⁺) remains high. This significant recombination limits the redox capacity of the surface of the material and is thus detrimental for its photocatalytic activity. In order to slow down the recombination rate of e⁻-h⁺ pairs, and thus to increase the photocatalytic activity of TiO₂, the incorporation of transition metallic nanoparticles such as Ag, Pd or Pt have been performed.

A simple method to tightly introduce Ag in TiO₂, is to co-condense titanium tetraisopropoxide (TTIP) with 3-(2-aminoethylamino) propyltrimethoxysilane (EDAS) in the presence of Ag salts. Indeed the formation of covalent Ti-O-Si ensures the anchorage of the amino group which easily form complexes with Ag cations. Nevertheless, in this case the doping of TiO₂ materials *via* a silylated linker does not favor the absorption of visible wavelengths, unlike doping with phosphorus. More recently, we synthesized, P-doped TiO₂ materials by the co-condensation of TTIP with EDAP. EDAP differs from EDAS bearing a phosphonate group, P(O)(OEt)₂, instead of a triethoxysilyl group which forms covalent bonds with TiO₂ matrix during the co-condensation step *via* P(O) group. Additionally, complexation of Ag⁺ ions *via* its ethylenediamine group is expected as in the case of EDAS. The cogelification of TTIP and EDAP in presence of a silver salt is therefore adequate to synthesize P and Ag co-doped TiO₂ xerogel photocatalysts. The influences of silver doping on physico-chemical properties of TiO₂ xerogels and the evaluation of the combined effect of P and Ag on the photocatalytic activity under visible light for *p*-nitrophenol degradation will be presented.

Curcubituril-Modified Iron-Oxide Nanoparticles for Combined Cancer Therapies

A. Trabolsi

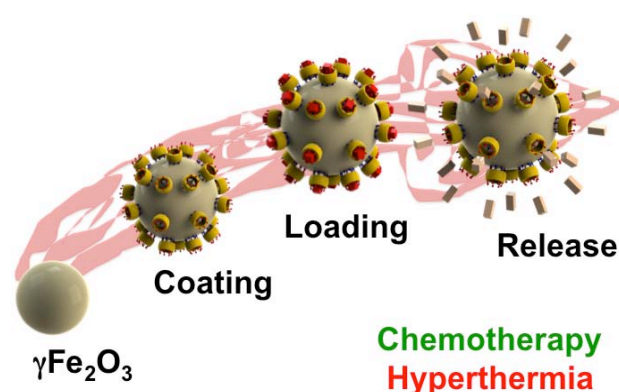
New York University Abu Dhabi, Abu Dhabi, United Arab Emirates

Chemotherapy seeks to minimize tumor progression and increase patient survival. However, the main problem is to find a balance between the drugs therapeutic effect on cancer cells and their deleterious effect on healthy cells. Due to their high hydrophobicity or rather their high hydrophilicity, these molecules must be injected in high and frequent doses, to avoid a rapid elimination and overcome their lack of specificity. Unfortunately, the high chemotherapeutic doses have side effects that patients find difficult to tolerate. Additionally, the diagnosis and imaging of tumor evolution remain a challenge.

In this aim, we developed¹ a theranostic platform consisting of iron oxide ($\gamma\text{-Fe}_2\text{O}_3$) nanoparticles (NPs) coated with water soluble and biocompatible cucurbit[7]uril (CB[7]) macrocycle (Figure 1). The inner cavity of CB[7] is hydrophobic, and allows the encapsulation and the transportation of hydrophobic drugs. Nile Red (NR), a hydrophobic dye, was first loaded into the cavities of the surface-adsorbed CB[7]s, and intracellular delivery of the dye to colon cancer cells was observed by confocal laser scanning microscopy. Powerful anticancer drugs (Paclitaxel, Doxorubicine and Cis-Platine) had been successfully encapsulated improving drastically their solubility. In solution, the release of Doxorubicin (Dox) can be triggered by (i) decreasing the pH, (ii) addition of a competitive guest (glutathione), and increasing the temperature. *In vitro* results demonstrate that encapsulation of drugs in the CB[7] cavities on the NP surfaces facilitates the cellular internalization of the drug, thereby enhancing its anti-cancer properties.

Finally, subjecting these nanoparticles to an alternating magnetic field increases the temperature of the cells, and make them more responsive to anticancer drugs.

Keywords: drug delivery, iron-oxide nanoparticles, cucurbituril, cancer therapy, biomedical applications.



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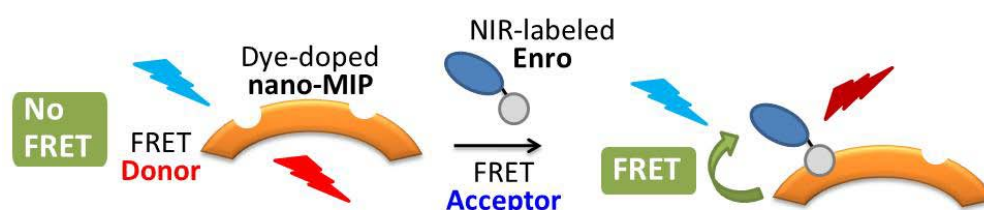
Light, Molecularly Imprinted Polymers and Nanotechnology to Tackle Analytical Challenges

G. Orellana,*¹ A.B. Descalzo,¹ J.L. Urraca,¹ V. Canalejas,² C.A. Barrios,² M.C. Moreno-Bondi¹

¹ Chemical Optosensors & Applied Photochemistry Group (GSOLFA), Faculty of Chemistry, Complutense University of Madrid, CEI Moncloa, 28040 Madrid, Spain; orellana@quim.ucm.es

² Institute of Optoelectronic Systems and Microtechnology (ISOM), ETSI Telecomunicación, Universidad Politécnica de Madrid, CEI Moncloa, 28040 Madrid, Spain

Nanotechnology has provided relevant benefits to *optical sensing* such as (metal) plasmon absorption, quantum confinement emission, accelerated response, high surface-area-to-volume ratio and savings of precious reagents, among others. *Molecular imprinting* is able to bring about the key analyte recognition with tailored polymer materials lacking the limitations of biomolecules used in biosensor development^[1]. Therefore, the combination of both areas seems a logical step for advanced chemical optosensors development. This lecture will introduce some recent examples from our Group demonstrating the analytical challenges that may be tackled by molecularly imprinted nanostructures: (i) luminescent core-shell imprinted *nanoparticles* engineered for analyte-targeted Förster resonance energy transfer (FRET)-based sensing (competitive MIP assay, see Figure below)^[2]; (ii) nano-MIP *arrays* fabricated by photoinduced local polymerization within metal subwavelength apertures, the size of which is finely tuned by the dose of 532 nm laser light^[3]. The enrofloxacin antibiotic and Rhodamine 123 dye have been selected as *templates*, respectively, to demonstrate the recognition capability of the nano-MIP structures, which has been evaluated by steady-state emission or fluorescence lifetime imaging microscopy (FLIM).



Acknowledgements

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High performance luminescence indicators and sensing materials

Ingo Klimant

Institute of Analytical Chemistry and Food Chemistry, Graz University of Technology, Stremayrgasse
9, 8010, Graz, Austria.
E-mail: klimant@tugraz.at

Optical chemosensors became very widespread in the last decades and are nowadays routinely used in numerous fields of science and technology. Optical sensors rely on the use of smart materials, which include e.g. indicators, polymers and other additives. State-of-the-art sensing materials do not always fulfill the requirements of sensitivity, selectivity, stability etc. Therefore, development of novel high performance materials still remains very important.

Our group recently developed a variety of novel materials which enable more reliable sensing of important parameters such as oxygen, temperature, pH etc. Particularly, we developed a series of novel red light-excitable oxygen indicators and sensors based on Pt(II) and Pd(II) benzoporphyrins. They enable virtually interference free measurements in the NIR window and benefit from excellent luminescence brightness. Also, different classes of porphyrin related compounds are introduced to enable more specific applications. For example, the complexes of azatetrabenzoporphyrins are fully compatible with red laser diodes and possess unmatched photostability. The photophysical properties (absorption and emission spectra, luminescence decay times) of the hybrids of tetrabenzo- and tetranaphthoporphyrins can be tuned over a wide range. We also reported a new NIR emitting temperature phosphor (Cr(III)-doped yttrium aluminum borate) which possesses good luminescence brightness (also at high temperature) and high temperature coefficients of the decay time at ambient temperatures. New pH indicators rely on perylene, diketopyrrolo-pyrrol, and azabodipys which are made pH sensitive by introducing functional groups responsible for Photoinduced Electron Transfer (PET). New smart materials developed in our group also comprise nanoparticles for various applications e.g. for extra- and intracellular monitoring of oxygen. Novel water-dispersible pressure sensitive paint is presented. A variety of magnetic nano- and microparticles as well as magnetic macrospheres are reported.

Nanostructuration of lipids for membrane biochip development

L. J. Blum, S. Rebaud, C. A. Marquette, A. Girard-Egrot

Institut de Chimie et Biochimie Moléculaires et Supramoléculaires (ICBMS), UMR CNRS 5246,

Université Lyon1, France.

Loic.Blum@univ-lyon1.fr

Biomimetic membranes are ideally suited to investigate many issues in membrane biology like membrane/protein interactions. Several systems such as Langmuir monolayers or supported lipid bilayers (SLB) are now widely accepted as reference methods for such investigations.

Beside these studies, biomimetic membranes are appropriate supports for protein interaction screening biochips. To that end, we develop a new simple and versatile technique for creating tethered Bilayer Lipid Membranes (tBLM), an attractive platform thanks to its quasi-natural assembly. In this approach, the lipid bilayers are achieved by small unilamellar vesicles fusion triggered by a synthetic fusogenic peptide to obtain tBLM on peptide spacers grafted on gold surfaces. Surface Plasmon Resonance (SPR), Atomic Force Microscopy (AFM) and Fluorescence Microscopy (Fluorescence Recovery After Photobleaching (FRAP)) have been used to characterize and to visualize the membrane formation process, as well as the interaction between proteins and these membrane models.

The main original feature of this simple methodology for forming tBLM on gold is that the lipid composition of the bilayer can be easily tuned. Several compositions have been tested which can mimic biological membranes as desired. Considering that this new approach is a versatile tool for investigating membrane/protein interactions, we first used Nucleoside-DiPhosphate Kinase B (NDPK-B), a monotopic enzyme interacting with the negatively charged lipids of the cell membrane, to evaluate the potentiality of this system.

Absorbance and fluorescence based indicator dyes for use in nanomaterials

G. J. Mohr

JOANNEUM RESEARCH Forschungsgesellschaft mbH – Materials, Franz-Pichler-Straße 30
A-8160 Weiz, Austria, e-mail: gerhard.mohr@joanneum.at

Indicator dyes are widely used for the development of optical chemical sensors. Typically, these dyes are immobilized into polymer materials, similar to well-known pH indicator test strips, and exposed to analyte solutions. Furthermore, sensor devices are built where a polymeric sensor layer is immobilized on top of an optical fibre. Fluorescent nanosensors have recently found increasing interest in medical and biological research because they enable continuous monitoring of analytes in living cells, tissues and microorganisms. The sensor materials and optical sensor devices find application in medical research, process control, biotechnology, environmental monitoring and food quality control.

In this presentation, examples for the use of indicator dyes in combination with nanoparticles, nanofibres and textiles are given and performance parameters, especially with respect to the different behaviour in nanomaterials are discussed. For example, sensor nanoparticles for pH or ATP can be used for continuous measurements in living cells,^[1] while nanofibre based sensors for oxygen exhibit a dramatically improved response time.^[2] Sensor textiles enable analyte monitoring on the skin and in wounds.^[3] For a stable and reversible response, indicator dyes should be covalently immobilized and accordingly, possible approaches for the design of new dyes will be discussed.



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Advanced nanoarchitecture of iron and carbon based materials for environmental, catalytic and biomedical applications

Radek Zbořil

Regional Centre of Advanced Technologies and Materials, Palacký University in Olomouc,
17. listopadu 1192/12, 771 46 Olomouc, Czech Republic, e-mail address: radek.zboril@upol.cz

Iron and carbon represent the key elements of current nanotechnologies with a huge application potential in biomedicine, environmental technologies, chemical industry, catalysis, energy storage technologies, food industry and biotechnologies. This broad portfolio of applications is related not only to biocompatibility, non-toxicity, and environmentally friendly character of iron- and carbon-based nanomaterials but also to a unique scale of valence states offered through iron chemistry, polymorphism of iron(III) oxide and amazing structural diversity of carbon and its nano-allotropes involving fullerenes, nanotubes, graphene and its derivatives, nanodiamonds or carbon dots. Moreover, the advanced nanoarchitecture based on sophisticated combination and functionalization of iron and carbon nanostructures allows to develop quite new technologies and/or to improve dramatically the performance of existing applications.^[1-5]

The superior performance of nano-Fe@C and Fe@Fe-O hybrids in environmental technologies will be demonstrated with treatment of groundwaters polluted with arsenic, chlorinated ethenes or chromium, including the results of full-scale remediation. The applicability of carbon dot-based fluorescent hybrids with graphene oxide and magnetic iron oxide for selective and multimodal cell labeling will be also presented.^[6] Among other biomedical applications, the use of magnetic iron oxide hybrids with silver nanoparticles for highly selective and sensitive SERS diagnostics of biomolecules in the blood or cerebrospinal fluid will be shown with examples of immunoglobulin G and dopamine sensing.^[7] The exploitation of advanced iron oxide hybrids in catalysis will be illustrated with an example of the core-shell nanoarchitecture of magnetic nanoparticles decorated with noble metals acting as advanced magnetically separable catalysts or micro-mesoporous flower-like hematite morphologies serving as highly efficient heterogeneous Fenton catalysts.^[8]

The last part of the talk will be focused on the miscellaneous applications of carbon superstructures composed of various carbon allotropes and covalently functionalized graphene. In this context, the applicability of thiofluorographene for DNA sensing or graphene@carbon nanotube hybrid for inkjet printing technologies or highly conductive polymers will be discussed.^[9,10]

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Up-Converting Nanoparticles for Smart Traceability

N. Francolon¹, D. Boyer¹, R. Mahiou¹

¹ Université Clermont Auvergne, Institut de Chimie de Clermont-Ferrand, UMR 6296 CNRS / UBP / ENSCCF, 24 avenue des Landais, BP 80026, F-63171 AUBIERE

In the past few years, up-converting nanoparticles constituted of rare earth ions embedded in fluoride matrices have attracted much attention due to their outstanding optical properties for biomedical applications [1]. They can be used as nanosensors for bio-labelling by converting near-infrared into visible light. The NIR excitation (980 nm) allows deeper penetration in tissue and thus better diagnosis while being less invasive in comparison with UV sources. To this end, hexagonal NaYF₄:Yb,Er nanoparticles have been synthesized by thermolysis methods which consist in decomposing metallic trifluoroacetates at high temperature in organic solvents such as trioctylphosphine (TOPO) or oleic acid (OA). X-ray diffraction analysis was performed to control the phase purity while the diameter and size distribution of nanoparticles were evidenced by transmission electron microscopy and dynamic light scattering. Besides, optical properties upon NIR excitation were studied to determine the up-conversion efficiency. In order to disperse these nanoparticles either in polar or apolar solvent, depending on the final application, surface functionalization was achieved to provide hydrophobic and hydrophilic features. Finally recent results about NIR-visible converter films obtained by dispersing these fluoride nanoparticles in polymer matrices will be presented as a promising way to achieve a smart traceability in order to prevent counterfeits.

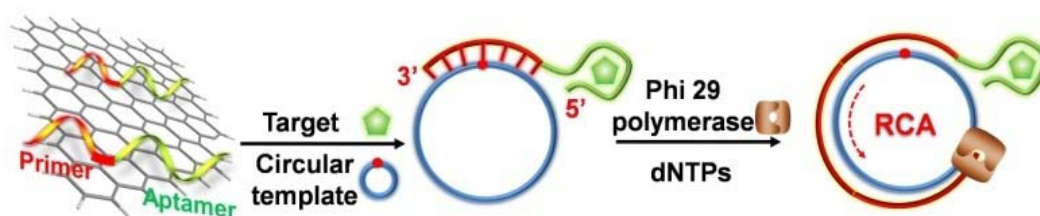
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A Biosensing Platform Based on Synergistic Release of DNA Probes from Reduced Graphene Oxide and Rolling Circle Amplification

Meng Liu,¹ Jinping Song,² Shaomin Shuang,² Chuan Dong,² Yingfu Li,¹ and John D. Brennan¹

1. Biointerfaces Institute, McMaster University, Hamilton, Ontario, L8S 4M1 Canada
2. Institute of Environmental Science, Shanxi University, Taiyuan, 030006 People's Republic of China

We report a versatile biosensing platform capable of achieving ultrasensitive detection of both small-molecule and macromolecular targets. The system features three components: reduced graphene oxide for its ability to adsorb single-stranded DNA molecules nonspecifically, DNA aptamers for their ability to bind reduced graphene oxide but undergo target-induced conformational changes that facilitate their release from the reduced graphene oxide surface, and rolling circle amplification (RCA) for its ability to amplify a primer-template recognition event into repetitive sequence units that can be easily detected. The key to the design is the tagging of a short primer to an aptamer sequence, which results in a small DNA probe that allows for both effective probe adsorption onto the reduced graphene oxide surface to mask the primer domain in the absence of the target, as well as efficient probe release in the presence of the target to make the primer available for template binding and RCA. We also made an observation that the circular template, which on its own does not cause a detectable level of probe release from the reduced graphene oxide, augments target-induced probe release. The synergistic release of DNA probes is interpreted to be a contributing factor for the high detection sensitivity. The broad utility of the platform is illustrated through engineering three different sensors that are capable of achieving ultrasensitive detection of a protein target, a DNA sequence and a small-molecule analyte.¹ Extension of this platform to produce paper-based biosensors will be described.



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Water Treatment by Various Methods – Advantages and Disadvantages

O. Solcova, L. Spacilova, M. Matejkova, P. Krystynik, M. Morozova

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

Nowadays, a great attention has been focused on water purification polluted by various compounds; organic as well inorganic contaminants. This study is focused on water treatment by application of three effective methods; electrocoagulation, sorption technique and photocatalytic oxidation.

Electrocoagulation is a method that utilizes electrochemical dissolution of electrode and simultaneous creation of small hydroxide particles (coagulants) in solutions. These small particles aggregate to larger particles (flocs) which can be described as highly porous aggregates created from many smaller particles. Flocs comprise oxides, hydroxides and oxohydroxides that have high absorption capacity and their high surface area enable pollutant adsorption. Therefore, electrocoagulation has been used for a wide range of pollutants removal.

Sorption methods are applicable for variety of contaminants, e.g. heavy metals as well as phenolic compounds which can be found in waste water generated from petroleum and petrochemical, pharmaceutical, plastic, rubber proofing, similarly as steel and phenol production industries. As sorbents usually active carbons, zeolites or special soils are applied.

Photocatalysis belongs to the Advanced Oxidation Processes (AOPs) and seems to a really promising technology for degradation of endocrine disrupting compounds (EDCs). This method is based on formation of the highly reactive species which can degrade even the most recalcitrant molecules. The most commonly used photocatalyst is titanium dioxide (TiO₂) which is applied in the form of powder or immobilized in a thin layer.

This study was focused on verification of these three methods including their combination on variety of polluted water which include not only simulated waste water but also the real polluted waste water from pharmaceutical and chemical industry.

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Coupling Photothermal Spectroscopy and Nanotechnology

M. Franko¹

¹University of Nova Gorica, Vipavska 13, SI-5000 Nova Gorica, Slovenia, mladen.franko@ung.si

Photothermal spectroscopy^[1] is based on the conversion of absorbed optical energy into heat and probing of consequent changes in temperature-dependent physical properties of samples. Such changes include changes in refractive index and density, internal pressure etc.. As such, photothermal spectroscopy provides information on optical (absorbance, energy band-gaps) and thermal properties (thermal conductivity, effusivity, diffusivity) of samples, and other related properties (e.g. charge carrier densities, sub-surface defects, porosity, surface roughness). On the other hand, photothermal spectroscopy can serve as an ultra-sensitive tool for chemical analysis of nL samples, where particular properties of nanomaterials offer an advantage for example in determination of metal ions, while nanoparticles can serve as chromophore labels or simply support material for immobilization of antibodies in immunoassays performed by lab-on-a-chip technology^[2, 3].

In this contribution, we will present some latest applications of thermal lens spectrometry (TLS) for determination of Ag based on on-line formation of nano-Ag particles^[4] as well as detection of biomarkers by thermal lens microscopy (TLM) in microfluidic systems^[5] following immobilization of antibodies on magnetic nanoparticles. In addition, capability of beam deflection spectroscopy (BDS) of determining energy band gaps and carrier lifetimes in semiconductor-based nanostructured materials will be demonstrated for titanomagnetite synthesized by atomic layer deposition to form an ultrathin (< 10 nm) overlayer ($\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$) grown on $\alpha\text{-Fe}_2\text{O}_3$ and $\varepsilon\text{-Fe}_2\text{O}_3$ columnar structures (80 – 600 nm) formed by chemical vapor deposition on Si(100) substrate^[6].

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Integrative Chemistry-based Rational Design of Advanced Porous Materials

Dedicated to Energy Conversion and Storage

Rénal Backov

CRPP-UPR CNRS 86, Université de Bordeaux,

115 Avenue Albert Schweitzer, 33600, Pessac France

Chemical sciences are on continuous evolution offering more and more complex synthetic strategies that rely on emerging inter- and trans-disciplinary action modes. In this context, beyond the ability of constructing advanced functional materials we demonstrate how the Integrative Chemistry¹ allows positioning chemical reactors within the geometric space. When it turns to energy dedicated advanced materials we will focus on oxide monoliths bearing hierarchical porosity. We will first show how through enzymatic engineering we can trigger biodiesel generation^{2,3} bearing unprecedented TON and TOF catalytic efficiency. Secondly when going from silica foams, used as hard templates, toward carbonaceous ones we will see how we can generate outstanding enzymatic biofuel cells,^{4,5} Li-ion⁶ and Li-S⁷⁻⁸ performing and stable battery electrodes. Beyond, we will see that it is possible to trigger hydrogen storage⁹ and reversibility when modified with gold/palladium nanoparticles¹⁰ based on Li(BH₄) confinements.

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Keywords: Energy conversion; Foams; Integrative chemistry; Hydrogen storage

Combining experimental and theoretical approaches for studying the sorption of vapours by Metal Organic Frameworks

P. Trens, D. Berthomieu, F. Di Renzo

Institut Charles Gerhardt, Ecole Nationale Supérieure de Chimie de Montpellier, Montpellier, 34296 cedex 5, France

MOFs is now a well known class of porous materials which has attracted an increasing interest, due to the tunability of the properties of these materials.[1] Compared to mineral zeolites or porous carbons, MOFs have specific features including the possibility to obtain flexible structures under stress or very high surface areas.[2] It is possible to choose the organic ligand for enhancing or disabling the interaction with a host. On the other hand, the inorganic centres may also be chosen to develop an interaction with a specific host. Indeed, if many MOFs have saturated inorganic centres, others have coordinatively unsaturated sites metal (CUS). This feature provides additional sites which may interact with host species. It is the case of Cu-BTC which possesses unsaturated copper centres even if very few studies were focused on the adsorption of ketones or aldehydes on Cu-BTC.[3] Sorbates having both a non polar hydrocarbon side and a polar carbonyl function clearly represent interesting candidates. We focused on acetone which is the most typical of these compounds. The isosteric heat of adsorption could be derived experimentally and was found to be -60 kJ.mol⁻¹. This value matches the theoretical data obtained by DFT-based methods at zero coverage. *In situ* DRIFT measurements allowed us to precisely describe the adsorption steps from zero coverage to saturation. Two main adsorption sites were determined for the adsorption of acetone. The small cavities were found to interact through van der Waals interaction with acetone while the

Cu(II) site was found to interact with the carbonyl function of acetone. Based on the *in situ* infrared experiments, it was demonstrated that the small cavities were first in interaction with acetone. DFT proved consistent with these findings by giving the energy of interaction in the different sites explored, but also by providing calculated infrared spectra of adsorbed acetone in Cu-BTC. Using acetone as a probe allowed showing that dispersive interactions with the pore sites of the Cu-BTC can be dominant among all other interactions (Figure 1).

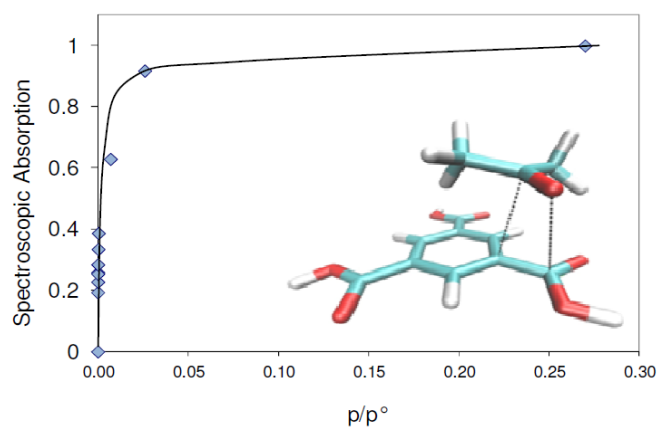


Figure 1. Spectroscopic isotherm of acetone adsorbed by Cu- BTC. Inset, DFT determination of the interaction between acetone and an organic ligand benzene dicarboxylate.

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Graphene nanoribbons in Li-ion batteries

K. Pirnat¹, J. Bitenc¹, I. Jerman¹, R. Dominko¹, B. Genorio²

¹National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, klemen.pirnat@ki.si

²Faculty of Chemistry and Chemical Technology, Večna pot 113, 1000 Ljubljana,
bostjan.genorio@gmail.com

Graphene nanoribbons (NR) can be easily prepared from multi walled carbon nanotubes (MWCNT) by unzipping with Potassium and further functionalized with desired functional groups ^[1]. They keep some desired properties from graphene (conductivity, mechanical strength, etc.) and by changing functional groups we can add some new additional properties. In our case NR were functionalized with protected hydroquinone groups which were subsequently deprotected. All materials were analyzed with TG-EGA, Raman, SEM and used without any additives (no binder or Carbon black) in Li-ion batteries as cathode materials using 1M LiPF₆/EC+DEC electrolyte. Results showed reversible redox activity at around 2.3-3.3 V against metallic Lithium and improved specific capacity compared to blank NR ^[2].

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Synthesis of Mesoporous Silica Nanoparticles with Controlled Architectures

A. Shimojima

Department of Applied Chemistry, Waseda University, 3-4-1 Ohkubo, Shinjuku-ku, Tokyo 169-8555, Japan

E-mail: Shimojima@waseda.jp

Mesoporous silica nanoparticles have attracted increasing attention because of their wide range of potential applications such as in catalysis, adsorption, drug delivery, and anti-reflective coatings.^[1-3] In addition to the fine control of their size, shape, and pore structures, incorporation of organic groups via Si–C bonds is important for functionalization and for tuning their properties. In this paper, our recent results on the synthesis of various types of mesoporous silica nanoparticles will be presented. For example, core/shell silica particles having different pore sizes in the core and the shell have been prepared by a re-growth method, i.e., by introducing additional silica source with or without pore expanding agents to induce the growth of porous shell on pre-synthesized cores (Fig. 1(a)).^[4] Hollow-type particles with different shell structures were also prepared by using hard templates such as Fe₂O₃ and SiO₂ nanoparticles (Figs. 1(b) and (c)).^[5,6] Most recently, a new class of mesoporous Janus nanoparticles has been prepared by adding phenyltriethoxysilane to a dispersion of colloidal mesostructured silica–surfactant composite nanoparticles. The nanoparticles possess an asymmetric structure, where a mesoporous silica nanosphere is capped with a hemispherical phenylsilsesquioxane shell (Fig. 1(d)).^[7] Such a design will lead to the creation of functional nanocarriers, nanocoatings, and complex assemblies.

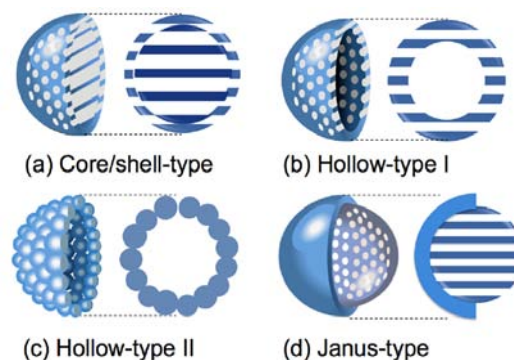


Fig. 1 Various types of mesoporous silica nanoparticles

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Nanostructured sol-gel coatings, preparation and application

D. Grosso, C. Boissière, M. Faustini, D. Ceratti, M. Boudot, R. Li, B. Louis

Laboratoire Chimie de la Matière Condensée de Paris, Group sol-gel chemistry and processing, UMR UPMC-CNRS 7574, Université Pierre et Marie Curie (Paris 6), Collège de France, 11, place Marcelin Berthelot, 75231 Paris. david.grosso@upmc.fr

It is known that nanostructured coatings with highly controlled mesoporosity can be achieved when combining chemical advanced strategies, such as self-assembly and sol-gel chemistry, together with liquid solution processing, such as dip-coating. It will be demonstrated that dip-coating is an extremely versatile tool to prepare thin nanostructured and mesoporous metal oxide films from liquid solutions and that it has been used for many decades without taking advantage of its whole potentiality. The present communication will focus on recent progresses related to this approach, mainly regarding preparation methods, novel materials, and unusual properties. It will be demonstrated that dip-coating is the ideal process to create lateral gradients of coating functions using acceleration modes, and can be easily combined with conventional “top-down” technologies, such as reactive ions etching or optical and nano imprint lithography, to construct even more complex morphologies with multi scales features and motifs. Novel materials, such as mesoporous piezoelectric epitaxial alpha-quartz, Pillar Planar Nano-channels for nano-fluidics, or ultra porous TiO₂ for photo-catalysis will be presented. Original and unusual properties of the latter mesoporous films, related to liquid natural capillary infiltration, giant wetting anisotropy, or hydro-alcoholic co-adsorption, will be presented. The usefulness of ellipsometric analytical techniques in determining thin films properties and characteristics will also be discussed all along the presentation.

Stimuli-responsive microarchitectures with peristaltic capabilities based on bilayered hybrid materials

Masahide Takahashi

Osaka Prefecture University (Sakai, Osaka 599-8531, Japan masa@photomater.com)

Multifunctional platforms based on microdevices are demanded to elaborate applied and basic sciences, for example biological insights into cells and tissues^[1]. Microactuators which drive and regulate micropumps and microvalves are crucial components for realizing these advanced platforms. We here demonstrate that surface architectures which exhibit morphological change and complex motion can be realized by hydrogel actuation on bilayered films. The surface architectures were designed by mimicking wrinkles in nature. These surface wrinkles were formed on a bilayered film of a crust top layer and an elastic bottom layer. As the bottom layer contracts (or the top layer swells), stress-driven instability is generated at the interface of layers. We designed a bilayered structure of a thermal-responsive hydrogel, poly(N-isopropylacrylamides) (PNIPAM), and hybrid siloxane. PNIPAM changes its dimension at a lower critical solution temperature (LCST), and thereby wrinkles of sub mm dimensions reversibly appear and disappear with changing external temperature. The quite large deformation ($\sim 40\%$) to temperature stimulus thanks to flexible PNIPAM hydrogel was demonstrated to realize nature-mimicking microstructures, such as folding and nested wrinkling structures. The aligned wrinkles were found to show a peristaltic motion with cooling, which conveys a microparticle whose dimension is comparable to the periodicity of the wrinkles. Particles are size-selectively transferred by the stimuli-responsive peristaltic motion. The present approach, in principle, can provide architectures which covers a diverse size range from a few nm to a few mm, over five orders of magnitude in length scales. The size diversity and solution processing used therein allow to fabricate nano/micro actuation systems.

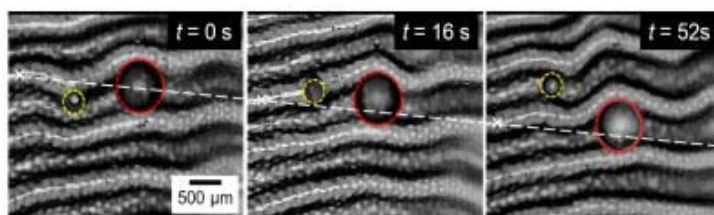


Figure Surface wrinkles on organosiloxane film, which show peristaltic motion along with cooling the substrate. Circles indicate the micro particles on the wrinkles; larger one (red) moves downward with the motion, but the smaller one (yellow) stays still.

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Core-shell nanoparticles designed for theranostics

M. Menard¹, D. Mertz¹, D. Felder-Flesch¹, F. Meyer², S. Begin¹

¹ Institut de Physique et Chimie des Matériaux de Strasbourg IPCMS UMR CNRS-Unistra-ECPM 7504
23 rue du loess BP 43 67034 Strasbourg cedex 2, France, sylvie.begin@ipcms.unistra.fr

² INSERM 1121, Faculté de Chirurgie Dentaire-Université de Strasbourg, 11 rue Humann, 67000
Strasbourg, fmeyer@unistra.fr

One of current challenges in materials for biomedicine is to develop theranostic nanoparticles (NPs) (i.e.) that include simultaneously therapeutic and diagnostic functions for image-guided therapy. Iron oxide nanoparticles (IO NPs) are widely investigated for theranostics because of their magnetic properties which allow cancer diagnosis through magnetic resonance imaging (MRI) and cancer therapy through hyperthermia which converts magnetic energy into local heating. To prevent IO NPs from aggregation in a physiological environment and ensure their biodistribution and bioelimination different types of organic or inorganic coatings are developed. Besides a lot of works are devoted to the design of coating ensuring also a local drug delivery.

In that context, we propose two concepts : The first approach developed in collaboration with the department of organic materials (DMO) (Dr. D. Felder) is to graft small dendrons at IO NPs surface. dendronized iron oxide nanoparticles have been designed as theranostic nano-objects : the dendritic coating has been shown to improve biodistribution, bioelimination (without captation by the RES) *in vivo* tumour targeting efficacy and to obtain better *in vivo* imaging properties. The size, morphology and composition of magnetic nanoparticles have been optimized to combine imaging by MRI and therapy by hyperthermia.

The second approach developed in collaboration with the INSERM U1121 unit in Strasbourg is to coat the IO NPs by a mesoporous silica shell containing antitumoral agents encapsulated in the pores by a thick human serum albumin (HSA) shell. This thick HSA shell ensures the biocompatibility of the NPs, avoids the leaking of drug from the pores and the destruction of this shell by proteases (present in lysosomes) allows drug release. The synthesis strategy described in **Figure 1** consists in building a thin silica shell with small pores (~3nm) around the superparamagnetic iron oxide nanoparticles (IO-MS) obtained by thermal decomposition and in loading by impregnation the antitumoral agent, doxorubicin (DOX), into the pores of the silica shell. Then HSA was deposited on the silica shell surface which was previously modified with isobutyramide (IBAM) binders. Finally incubation of the particles in proteases media allowed efficient HSA degradation and subsequent DOX release. These new theranostic hybrid nanoparticles are currently assessed in various biological studies (ca. cell viability/toxicity, cell uptake, intracellular behavior).

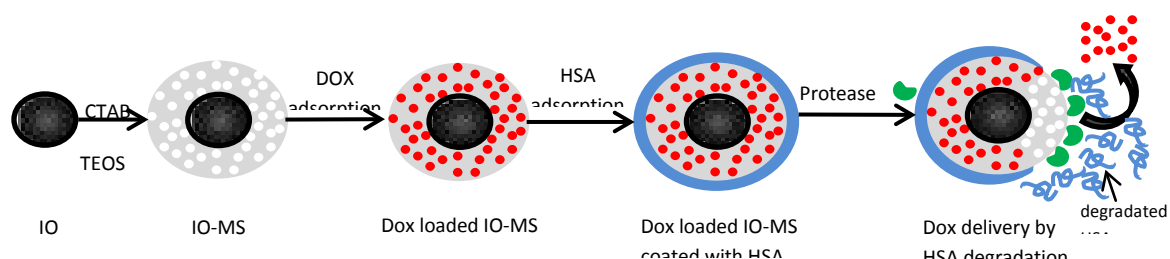


Figure 1. Scheme of IO-MS NPs particles synthesis loaded with DOX and the DOX delivery by HSA degradation in proteases media.

Click chemistry: a powerful tool for the functionalization of nanoparticles

X. Cattoën,^{1,2} A. Nouredine,¹ J. Croissant,¹ J.-O. Durand,¹ M. Wong Chi Man¹

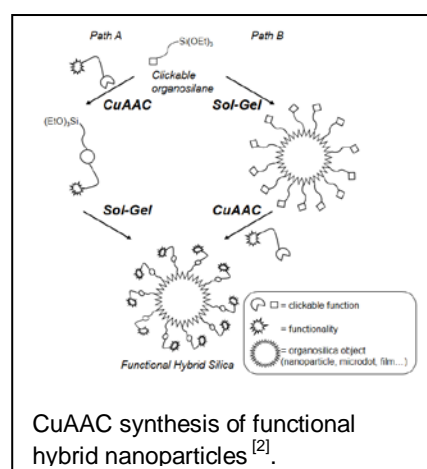
¹ Institut Charles Gerhardt, UMR5253 CNRS-UM2-ENSCM-UM1, Montpellier, FRANCE

² Institut Néel, UPR2940 CNRS-UJF, Grenoble, FRANCE

xavier.cattoen@neel.cnrs.fr

Hybrid silica nanoparticles are widely studied for application in nanomedicine, as imaging or therapeutic agents and drug carriers^[1]. The increasing complexity of their structure, with multiple appended functionalities such as imaging agents, targeting functions, antennas or PEG coatings results in the need of developing efficient functionalization strategies for such nanoparticles. The recent rise of the copper-catalyzed azide-alkyne cycloaddition *click* reaction (CuAAC) provides opportunities to improve the functionalization methodologies for hybrid nanoparticles, with a necessary control over the loading and spatial distribution of the organics^[2].

We will focus in this communication on the very rapid synthesis (5 min) of new organosilane precursors, with pending or bridging functionalities and that can be transformed into functional silsesquioxane nanoparticles^[3] for photodynamic therapy (Fig 1, path A)^[4]. We will also present the synthesis of mesoporous silica nanoparticles containing azide and/or alkyne functionalities for efficient post-functionalization with various functional (bio)molecules (Fig 1, path B). This enabled the formation of several light-activated nanomachines for drug delivery. In particular, we will describe the CuAAC-construction of nanomachines based on mesoporous silica nanoparticles bearing two communicating functionalities appended by CuAAC: a photoacid, and a pH-sensitive valve blocking the pore entrances. Upon light-activation the photoacids transfer protons to the supramolecular valves which then dissociate, enabling the release of the cargo^[5].



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Bridging the gap between solid state chemistry and nanoscale chemistry: from alloys to functional complex oxides

D. Portehault¹

¹Sorbonne Universités UPMC Univ Paris 06 - CNRS - Collège de France, UMR 7574 Chimie de la Matière Condensée de Paris Collège de France, 11 place Marcelin Berthelot, 75231 Paris Cedex 05, France, david.portehault@upmc.fr

Reactions between molecule-scale species enable cost effective synthesis of materials with controlled crystal, nano-, meso- and micro- structures. While such chemical pathways are intensively studied since three decades for nanostructured metals, chalcogenides and simple oxides, other compounds families were only scarcely, if ever, reported at the nanoscale. These systems show at the bulk scale mechanical, catalytic and electronic properties without equivalent among common compounds. The design of corresponding nanostructures could then modify or enhance existing properties, unveil new behaviors and novel processing possibilities. Therefore, how to overcome the current frontier of materials accessible at the nanoscale? We will highlight some recent breakthroughs in the design of functional nanomaterials with innovative elemental compositions, some being “exotic” to chemists. The discussed synthetic pathways rely on sol-gel chemistry or molecular reactions into inorganic molten salts towards mixed valence titanium oxides, so-called Magnéli phases, manganite perovskites, metal-boron alloys and boron-carbon-nitrogen covalent frameworks. For each compounds, we will show that electrical, electrocatalytic, thermoelectric or environmental remediation properties are deeply impacted by the nanoscale.

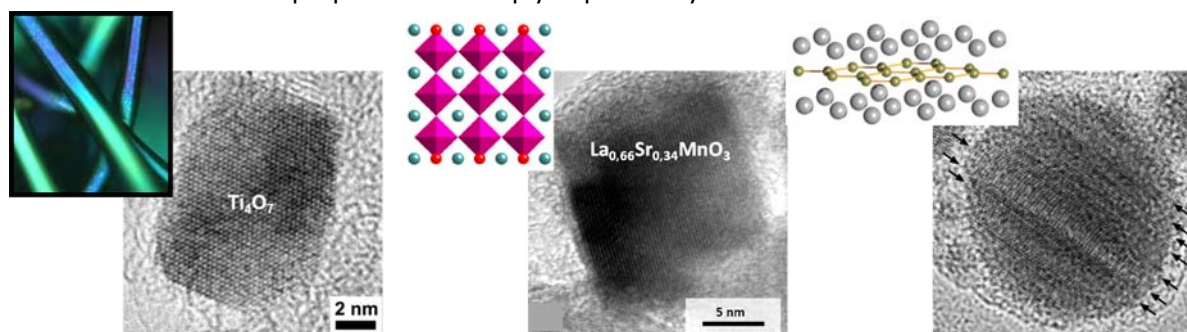


Figure. Examples of nanoparticles of Ti₄O₇ (insert: microfibers made by electrospinning), La_{0.66}Sr_{0.34}MnO₃ perovskite and NiB alloy (inserts: crystal structures)

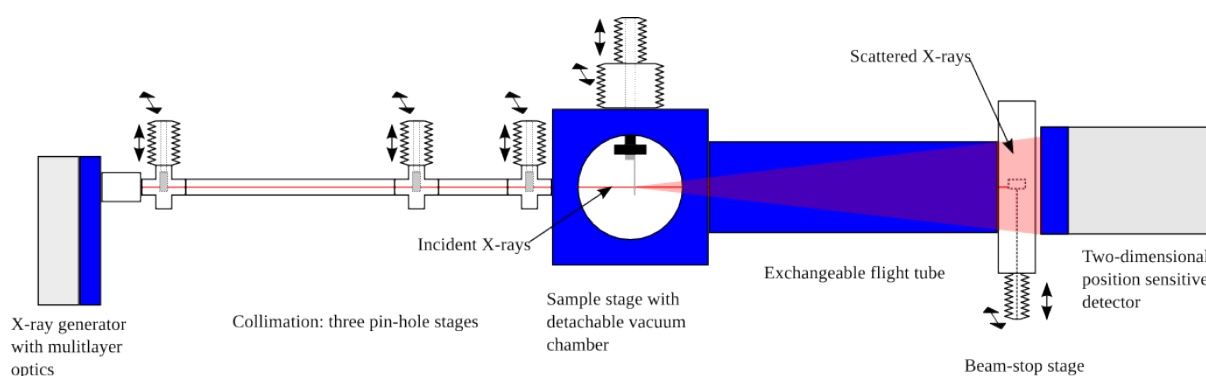
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Advantages of a new general purpose small-angle X-ray scattering laboratory instruments in characterization of nanomaterials

Wacha, Z. Varga and A. Bóta

Research Centre for Natural Sciences, Hungarian Academy of Sciences, Magyar Tudósok körútja
2, 1117 Budapest, Hungary

The details of a newly constructed small-angle X-ray scattering instrument are presented. The geometry of the instrument is highly customizable, enabling it to address vastly different experimental situations from academic research to industrial problems. The high degree of motorization and automation compared to conventional laboratory-scale SAXS instruments facilitates the alignment and daily use. Data reduction routines are incorporated in the instrument control software, yielding fully corrected and calibrated results promptly after the end of measurements. Optimization of the flux *versus* resolution balance can be done routinely for each measurement task. A wide, continuous range of $q = 4\pi\sin\Theta/\lambda$ can be reached, from below 0.02 nm^{-1} up to 30 nm^{-1} , corresponding to periodic distances of *ca* 350 nm down to 0.2 nm. Scattering curves are routinely calibrated into absolute units using a glassy carbon secondary standard. More information and recent developments can be found on the web page of the instrument at <http://credo.ttk.mta.hu>. A few representative results obtained from samples of different nano-research field are shown demonstrating the versatility and efficiency of the instrument.



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1D-confinement inside single-wall carbon nanotubes

J-L. Bantignies

² *Université Montpellier, Laboratoire Charles Coulomb UMR 5221, F-34095, Montpellier, France*

[*\(jean-louis.bantignies@um2.fr\)*](mailto:jean-louis.bantignies@um2.fr)

Confinement of molecules and atoms inside nano-containers (NaCons) provides a powerful strategy for creating original hybrid nanostructures and studying structures and chemical properties of individual molecules at the nanoscale. Carbon nanotubes (CNTs) used as NaCons offer different advantages: (1) CNTs are built of sp^2 carbon atoms held together by strong covalent bonds; (2) They are thermally stable (around 700 °C in air and up to 2800 °C in vacuum); (3) mechanically more robust (with tensile strength much higher than that of steel) than any other molecular or supramolecular NaCons; (4) Their hollow core has very low chemical reactivity. The nanotube diameter is the most important parameter in determining whether or not a molecule can be trapped inside a CNT. Once encapsulated, the behavior of the guest molecule is greatly affected by confinement.

We consider here Single-walled carbon nanotubes (SWNTs) having a one-dimensional hollow space of 0.4-2.0 nm that can encapsulate various molecules leading to hybrid nanotubes. Two examples will be reported, the first one concerning the encapsulation of Poly-iodides inside SWNTs; the second one related to the encapsulation of conducting oligomers into SWNTs.

We will firstly show that 1D-confinement of polyiodides (I_n) inside SWNTs lead to specific structural arrangement of iodine species as a function of the SWCNT diameters ^[1]. Evidence for long range one dimensional ordering of the iodine species is shown by X-ray and electron diffraction experiments independently of the tube diameter. Using X-ray absorption spectroscopy, we show that the confinement influences the local arrangement of the chains. Below a critical diameter ϕ_c of 1 nm, long linear I_n are evidenced leading to a weaker charge transfer than for nanotube diameter above ϕ_c . A shortening of the I_n is exhibited with the increase of the nanotube diameter leading to a more efficient charge transfer. This point reflects the 1D-confinement of the polyiodides inside the nanotubes.

Concerning the study on the confinement of conducting oligomers into SWNTs ^[2], we evidence by means of Raman spectroscopy and transmission electron microscopy that the supramolecular organizations of the confined oligothiophenes depend on the nanocontainer size. The Raman radial breathing mode frequency is shown to be monitored by both the number of confined molecules into a nanotube section and the competition between oligothiophene/oligothiophene and oligothiophene/tube wall interactions.

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Synthesis of magnetic and multifunctional nanocomposites based on the colloidal processing of nanoparticles

D. Makovec

Department for Materials Synthesis, Jožef Stefan Institute, Ljubljana, SI-1000, Slovenia.

Nanocomposites are multicomponent solid materials where at least one of the phases has at least one of its dimensions in the nano range. Because of this nanostructure, these materials frequently display unique properties. Such nanocomposites can be synthesised in different forms, i.e., bulk, films or (nano)particles, using the colloidal processing of nanoparticles in suspensions.

In the presentation, the synthesis of composite nanoparticles and some bulk nanocomposites will be discussed. First, the basic principles of the synthesis will be presented on model systems of nanoparticles, followed by some practical examples of the synthesis of magnetic and multifunctional nanocomposites, mainly those combining magnetic nanoparticles with nanoparticles or layers of other functional materials.

The composite nanoparticles can be synthesized by assembling two or more nanoparticles of different materials into a single nanoparticle. Different attractive interactions acting between the nanoparticles in the aqueous suspension can be applied for their controlled heteroaggregation. The interactions were studied on model suspensions of smaller carboxyl-functionalized maghemite nanoparticles (15 nm in size) and larger (80 nm) amino-functionalized silica nanoparticles. Electrostatic interactions between two types of nanoparticles displaying an opposite surface charge will be directly compared with the chemical interactions originating from the covalent bonding between the molecules at the surfaces of the nanoparticles.

Another method that can be used for the synthesis of composite nanoparticles is based on coating the core nanoparticles made of one material with a shell made of another material. The principles will be discussed in the case of coating silica-core nanoparticles with a magnetic shell of maghemite. The shell is formed by heterogeneous nucleation of the initial product of $\text{Fe}^{3+}/\text{Fe}^{2+}$ co-precipitation at the surfaces of the core nanoparticles. The method, which is based on close control of the supersaturation during the co-precipitation, was also applied for the synthesis of bi-magnetic, sandwich-type nanoparticles combining hard-magnetic hexaferrite core nanoplatelets with a soft-magnetic maghemite shell. Due to direct magnetic coupling, the energy product of the nanocomposite is greatly increased compared to that of the core nanoparticles.

The synthesis of bulk nanocomposites will also be presented with a focus on nanocomposites containing a high concentration of (magnetic) nanoparticles dispersed in a polymer matrix.

Enhancement of magnetic properties in Fe₃₋₆O₄@CoO core-shell nanoparticles exhibiting exchange bias coupling

Benoit. P. Pichon,¹ Walid Baaziz,¹ Xiaojie Liu,^{1,2} Yu Liu,¹ Mathias Dolci,¹ Dominique Bégin,² Sylvie Bégin-Colin¹

1 Institut de Physique et de Chimie des Matériaux de Strasbourg (IPCMS UMR CNRS 7504), 23 rue du Loess, BP 43, 67037, Strasbourg

2 Institut de chimie et procédés pour l'énergie, l'environnement et la santé (UMR 7515), 25 rue Becquerel, 67087 Strasbourg Cedex 2

Single magnetic domain nanoparticles are very promising for many advanced applications such as hyperthermia or magnetic storage media. Nevertheless, the miniaturization of devices which is correlated to the size reduction of nanoparticles usually results in the decrease of the magnetocrystalline anisotropy and in unblocked domains at room temperature, e.g. superparamagnetism. An alternative and very promising approach is heterostructures such as core-shell nanoparticles featured by exchange bias coupling between F(i)M and AFM phases. Although exchange bias has been well investigated during last years, the large panel of parameters which affect it still need to be investigated.

We report on a systematic study which consists in the modulation of the shell structure and of the AFM/FiM interface in order to study their influence on the exchange bias coupling. Fe₃₋₆O₄@CoO core-shell nanoparticles have been synthesized by a one-pot seed-mediated growth method based on the thermal decomposition of metal complexes at high temperature.[1] The shell structure and AFM/FiM interface are demonstrated to be strongly modulated by the synthetic conditions.[2] While exchange bias coupling is strongly influenced by the shell thickness, the AFM/FiM interface were intermixing of Co and Fe atoms takes place also enhances the magnetic properties. Furthermore, the exchange bias coupling is also investigated as function of dipolar interactions between nanoparticles which strength strongly affect the magnetic properties of nanoparticles.[3]

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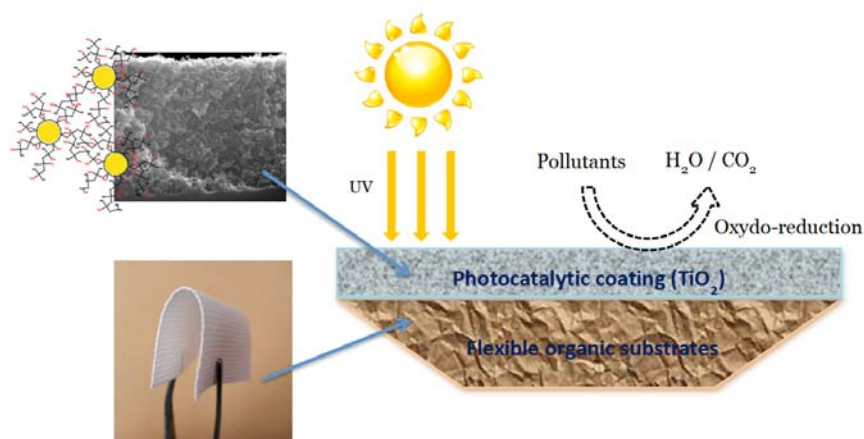
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Hybrid sol-gel composite materials with microstructuration for photocatalytic applications.

Stephane Parola

Laboratoire de Chimie, Ecole Normale Supérieure de Lyon, 46 allée d'Italie, 69364, Lyon, France.

Photocatalytic materials based on semiconductors are of interest for depollution and self-cleaning purposes. Most of the time, the photocatalyst is used as powder or coating on hard substrates such as silica glass. There is nowadays a strong interest to develop flexible coatings for application on organic substrates (polyurethane, polyester, polyvinylchloride, polymethylmetacrylate) related to textile or paper industry. In this work, photocatalytic porous coatings (micro-, meso- and macroporosity) were obtained by the dispersion of TiO₂ nanoparticles in sol-gel hybrid matrices.¹⁻³ The silica matrix was used as binder stabilizing the nanoparticles dispersion and as protective layer for the organic substrates. Organic groups are introduced into the matrix to induce the film flexibility and part of them is used to generate the final microstructuration allowing strong improvement of the photocatalytic properties. The film structuration and UV stability were fully characterized. The photocatalytic activity was evaluated through test with formic acid. Flexible efficient photoactive composites were obtained showing important capabilities for depollution (water and air) and self-cleaning applications. Finally the introduction of plasmonic nanostructures such as gold bypyramids,⁴ using specific surface modifications,⁵ allowed important modifications of the optical and photocatalytic properties of the final composites.



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Doped oxide powders and films through low temperature syntheses for applications in water purification and anti-corrosion

G. L.-M. Léonard¹, C. M. Malengreaux¹, S. Pirard¹, S. Remy¹, S. Douven¹, J. R. Bartlett², B. Heinrichs¹

¹Chemical Engineering - Nanomaterials, Catalysis, Electrochemistry, University of Liège, B6a, B-4000 Liège, Belgium

²Faculty of Science, Health, Education and Engineering, University of the Sunshine Coast, Maroondah DC, QLD 4558, Australia

An environmentally-friendly aqueous sol-gel process for producing undoped and metal cations-doped TiO₂ photocatalysts exhibiting a remarkably high photocatalytic activity without requiring any calcination step has been developed. Metal cations include Cu²⁺, Zn²⁺, Pb²⁺, Fe³⁺, La³⁺ and some combinations of the latter ones. The physicochemical properties of the catalysts were characterized by ICP-AES, XRD, UV-Vis spectroscopy and nitrogen adsorption-desorption.

Very interestingly, it has been found that the active crystalline phase is obtained without requiring any calcination step and all the different catalysts are composed of nanocrystallites of anatase with a size of 6–7 nm and a high specific surface area up to 300 m² g⁻¹. The effect of the NO₃:Ti(IV) mole ratio used to induce the peptisation reaction during the synthesis has been studied and the results revealed that this ratio can influence significantly the textural properties of the resulting catalyst.

A screening of the photocatalytic activity of the undoped, single-doped (with one type of cation) and co-doped (with two types of cations) photocatalysts has been performed by evaluating the degradation of 4-nitrophenol under UV-Visible light (330 nm < λ < 800 nm) using a custom-designed multisample photoreactor. The activity measured for the TiO₂-undoped catalyst was found to be five times higher than the activity measured for uncalcined TiO₂ catalysts produced by sol-gel methods in non-aqueous media. We propose that this important result is due to the particular nanocrystalline structure of the xerogels obtained. It has also been demonstrated that the presence of an adequate dopant in adequate amounts leads to an enhancement of the photocatalytic activity. The role of particular dopants in modulating the photocatalytic activity is discussed.

The aqueous sol-gel process developed in this study has been adapted to produce efficient photocatalytic thin films deposited on various substrates including glass, quartz and steel. As a first example, the possibility of producing undoped and Zn²⁺-doped films deposited on glass and presenting a higher activity than commercial photocatalytic coatings without requiring any calcination step has been demonstrated. A second example concerns the production of TiO₂ thin films doped with multiwall carbon nanotubes and deposited on 316L stainless steel to protect it against corrosion. It has been shown that the anti-corrosive property of TiO₂ due to the photogenerated electrons, but also to a simple barrier effect, is reinforced by the introduction of carbon nanotubes which reduce the corrosion potential and current.

Advanced heat storage materials for integrated storage solutions

Nataša Zabukovec Logar

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

University of Nova Gorica, Vipavska 13, 5000 Nova Gorica, Slovenia

Thermal energy storage is becoming a crucial technology in enabling more efficient use of fossil fuels and the use of renewable energy. Development of new generation heat storage systems that would enable efficient utilization of low-temperature solar energy or waste heat for heating and cooling applications is in the focus of recent research activities. Thermochemical heat storage (TCS), which utilise the reversible chemical and physical sorption of gases in solids enables long-term low-temperature heat storage. The development of materials was so far focused on the optimized synthesis to achieve high storage capacities. However, the development of the reservoirs with current state-of-the-art materials showed that the list of criteria that we followed for materials properties is incomplete. Namely, the constraints in the system (available pressure and temperature limits, heat and mass transfer) significantly affect the dynamics of the process of storage; i.e. processes of adsorption/desorption can last from a few tens of minutes to a few days. Despite the fact that some materials show remarkable results for heat storage in the laboratory testing regarding the maximum storage density, the dynamics of the process is in most of the known cases inadequate for effective use. In the lecture, the optimisation of nanoporous materials by considering the dynamics of the process in the storages will be presented. The focus will be on the equilibrium studies of the adsorption-desorption processes in selected systems.

Towards efficient removal of contaminants from households grey waste water: Photocatalytic ozonation process

M. Kete^{*} and U. Lavrenčič Štangar

University of Nova Gorica (Vipavska 13, 5000 Nova Gorica, Slovenia; e-mail: urska.lavrencic@ung.si)

^{*}present address: Geida d.o.o. (Letališka 33, 1000 Ljubljana, Slovenia; e-mail: marko@geida.si)

Domestic in-house specific water demand in industrialised countries approximates 100-150 L/p/d (liters per capita per day), of which 60-75% is transformed into grey water, which is less polluted fraction of waste waters released from households ^[1,2]. Part of total household water consumption (7 – 24%) is used for clothes washing. Even if this waste water contains surfactants, textile dyes and other contaminants, represents a source of water, which could be reused in households after appropriate treatment ^[3,4]. Photocatalytic properties of titanium(IV) oxide (TiO₂) in anatase form can be used for various purposes, including photocatalytic purification ^[5,6,7,8] and disinfection of waste water ^[9]. This advanced oxidation process (AOP) is still confronted by different technological issues like: (I) its slow degradation of organic pollutants, especially in higher concentrations, and (II) its implementation in terms of use of photocatalyst in photocatalytic reactor (suspended or immobilized). Reactors with fixed phase photocatalyst seem to be preferred due to some advantages, one of them is the avoidance of photocatalyst filtration. To avoid leaching and exfoliation of the fixed phase, an immobilization procedure leading to a good adhesion of a catalyst to a substrate is crucial. This was successfully achieved by immobilization of commercial TiO₂ (P25, P90, PC500 and P25+PC500) by a "sol suspension" procedure ^[10,11].

For the purpose of simulated grey water treatment, special compact reactor was designed and developed. With (I) utilization of custom made Al₂O₃ porous reticulated monolith foams as TiO₂ carriers, offering high photocatalytically active surface (Figure 1A) and (II) placement of irradiation source (lamps) inside the reactor (Figure 1B), significant reduction in reactor dimensions in comparison to old prototype reactor was achieved. To increase process efficiency TiO₂ photocatalysis was coupled with ozonation, which is excellent electron scavenger. The result of the two processes is combined synergistic process, known as photocatalytic ozonation process (PH-OZ) ^[7,8,12,13], which normally occurs in neutral and acidic pH ^[14].

With degradation of LAS+PBIS and Reactive blue 19 (RB 19) as representatives of surfactants and textile dyes respectively, commonly found in household grey waste water, and phenol as trace contaminant, an evaluation of PH-OZ and photocatalytic processes in old prototype and compact reactor has been performed. From this research of LAS+PBIS, phenol and RB 19 degradation in two reactors it can be concluded that RB 19 and phenol are easily degradable in particular due to small and simpler molecule (phenol) and low stability in presence of ozone (RB 19). On the other hand LAS and PBIS are more resistant, so that PH-OZ process is actually not much more efficient in comparison to photocatalysis. The series of experiments in compact reactor was conducted at neutral-acidic pH,

since it was shown in prototype reactor that alkaline pH negatively influences both PH-OZ and photocatalysis. Synergistic effect of PH-OZ was generally much more expressed in mineralization reactions, but was in case of LAS+PBIS mineralization still minimal. Nevertheless TOC half lives in compact reactor are despite higher concentrations of pollutants much shorter (13 – 43 min) in comparison to prototype, which looks promising in case of using the similar reactor in reality. The work was concluded by performing the experiment with simulated waste water, which was prepared by using all four model pollutants (RB19, phenol, LAS and PBIS) present in tap water. The experiment (Figure 1C) showed that PH-OZ process is due to its higher cleaning capacity more suitable for treating waste waters with higher loading of organic pollutants and therefore represents more realistic application. The mineralization process half-life has been, degradation of LAS and PBIS mixture in the same reactor.

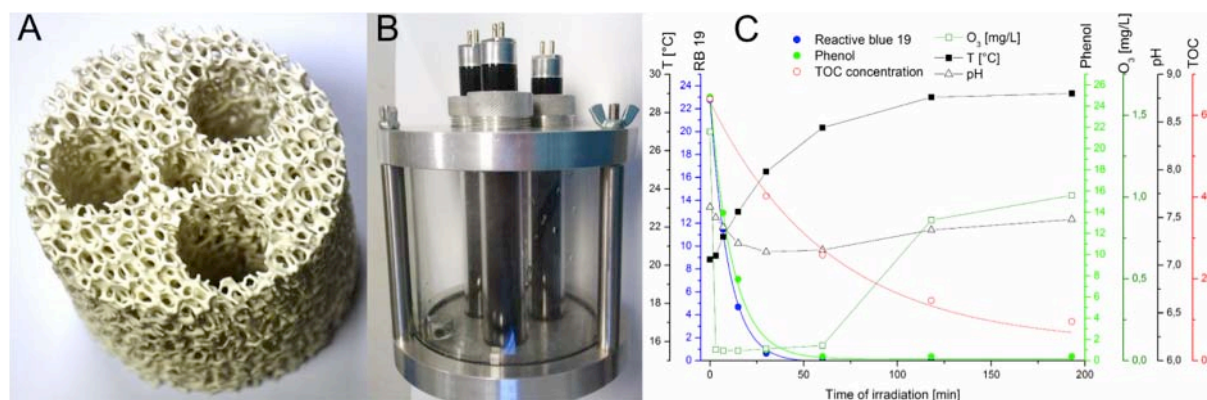


Figure 1. Custom made Al₂O₃ porous reticulated monoliths (A), compact reactor without inserted monoliths (B) and degradation/mineralization curves of LAS, PBIS, RB19 and phenol by PH-OZ process in compact reactor (C).

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Preparation of ferrite-based exchange-coupled hard/soft magnetic nanocomposites

**Petra Jenuš^{1,*}, Martin Topole¹, Paul McGuinness¹, Marian Stingaciu², Mogens Christensen²,
Spomenka Kobe¹, Kristina Žužek Rožman¹**

¹ Department for nanostructured materials, Jožef Stefan Institute, Ljubljana, Slovenia

² Center for Materials Crystallography, Department of Chemistry and iNANO, Aarhus University
Langelandsgade 140, DK-8000 Aarhus C, Denmark.

[*petra.jenus@ijs.si](mailto:petra.jenus@ijs.si)

Exchange-coupled hard/soft magnetic nanocomposites have gained a lot of interest in recent years due to enhanced magnetic properties when compared to the pure phase material. In this study we will present synthesis, densification, microstructural analysis and magnetic characterization of ferrite-based exchange-coupled nanocomposites.

Ferrite-based hard/soft magnetic nanocomposites were prepared by wet-chemistry which was followed by spark plasma sintering (SPS). Conditions during SPS process (sintering temperature, time and applied pressure) were examined and will be discussed in detail. The microstructural analysis and magnetic properties of nanocomposites were evaluated and the evolution of maximum energy product, BH_{\max} , with SPS conditions was monitored. Using SPS for the compaction of ferrite-based nanocomposites, nanoparticles growth was prevented and with that the size of soft magnetic phase remained within the limits for the effective exchange-coupling. The indication on the presence of later in prepared nanocomposites are the shape of hysteresis loops of nanocomposites after SPS and an increase in BH_{\max} of nanocomposites when compared to the hard magnetic single phase material.

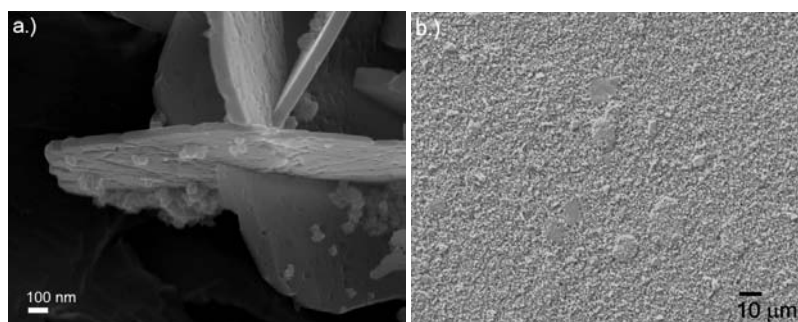


Figure1: SEM image of dried $\text{SrFe}_{12}\text{O}_{19}/\text{CoFe}_2\text{O}_4$ nanocomposite before a.), and after densification with spark plasma sintering b.).

Acknowledgments:

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Solution processing Transition Metal Oxides and Graphene for Printed Organic Solar Cells

Monica Lira Cantu

Transition metal oxides (TMOs), from the simplest binary oxides to the more complex oxide compounds, are a class of materials with great variety of functional properties. These span from insulating, semiconducting or metallic behavior, to ferroelectricity, magnetism, magnetoresistance or superconductivity, among many more. TMOs are now regularly applied in many printed electronic and optoelectronic devices such as thin film photovoltaics (TFPVs), field effect (FETs) and thin film transistors (TFTs), light emitting diodes (LEDs), among many others. In this work we will present a brief overview about the application of oxide semiconductors (from binary oxides or graphene oxide to more complex semiconductors) in different photovoltaic devices and a description of the current work developed in our laboratory. We will show the synthesis of TMOs, their optimization as “green ink” and their application in photovoltaic devices at laboratory and the scale up applying printing processes.

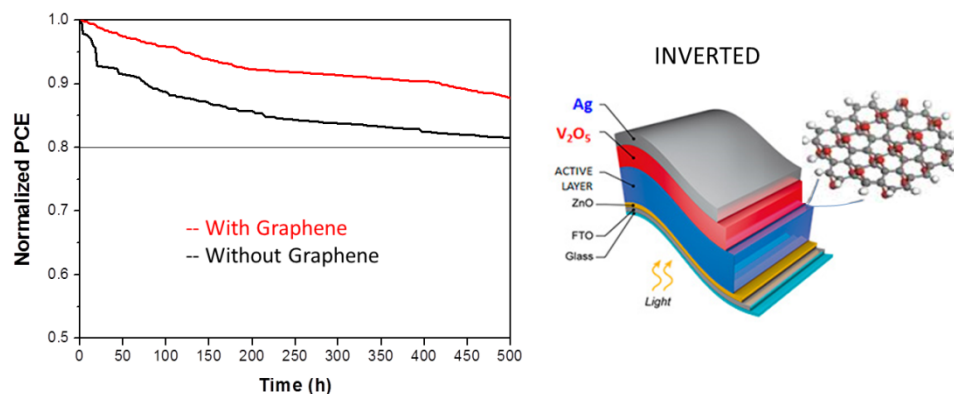


Figure 1. Initial 500 h outdoor testing of Organic solar cells applying GO as interlayer between the Hole transport oxide layer (V_2O_5) and the active layer (P3HT:PCBM). All layers were applied by solution processing in air.

Latent heat storage by silica nanoparticles-coated polymer beads containing organic phase change materials

Tivadar Feczko^{a,b*}, Bence Németh^b, László Trifa, Daniel Horák^c

^aInstitute of Materials and Environmental Chemistry, Research Centre for Natural Sciences,
Hungarian Academy of Sciences, Magyar tudósok körútja 2., 1117, Budapest, Hungary

^bResearch Institute of Chemical and Process Engineering, Faculty of Information Technology,
University of Pannonia, Egyetem u. 10, H-8200 Veszprém, Hungary

^cInstitute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2,
16206 Prague 6, Czech Republic

* E-mail: tivadar.feczko@gmail.com, phone: +36-88-623508, fax: +36-88-624038

Thermal energy storage has received more and more attention during the past decades due to the endeavour of energy saving. Latent heat storage is one of the most efficient ways of thermal energy storing. The main benefits of latent heat storage compared with that of sensible heat are the much higher storage density accompanying with a smaller temperature difference between storing and releasing heat. Phase change materials (PCMs) are used for latent heat storage. Most promising applications of PCMs are waste heat recovery systems, solar heating systems, building energy conservation systems and air-conditioning systems. Most of the organic PCMs are non-corrosive and chemically inert, stable, recyclable and compatible with numerous building materials. They have desirable cohesion, a high latent heat per unit weight, low vapour pressure, no supercooling, and offer congruent melting and self-nucleation. They have disadvantages such as low thermal conductivities, flammability and high changes in volume during phase change. In order to overcome these problems, their microencapsulation can be an efficient tool.

Macroporous sorbent beads were prepared by the AIBN-initiated suspension radical polymerization of glycidyl methacrylate and ethylene dimethacrylate monomers in the presence of an inert porogen. The microspheres were loaded with cetyl alcohol, stearic acid and paraffin PCMs, respectively. After PCM loading, the particles were dispersed in aqueous [(2-hydroxypropyl)methyl]cellulose solution and coated with silica (SiO₂) nanoparticles using trimethoxy(methyl)silane hydrolysate to yield PCM-PGMA/PEDMA&Me-SiO₂ hybrid particles. The size distribution of the particles was measured by laser diffraction method. Their morphology was investigated by scanning and transmission electron microscopy. The PCM content was determined after the extraction of the microcomposites. The specific surface area of the microspheres was determined by nitrogen adsorption technique and the pore volume was determined from cyclohexane or 1-chlorododecane regain using centrifugation method. Thermogravimetric analyses were performed, while the energy storing capacity of the

microcapsules was monitored by differential scanning calorimetry. Accelerated thermal cycling tests were carried out to determine the thermal reliability of the microencapsulated PCMs. PCM content of the microcapsules ranged from 43 % to 75 %. The microcapsules with high PCM content showed correspondingly high latent heat storage capacity, furthermore, there was no significant enthalpy change observed after 1000 thermal cycles indicating no leakage of the PCM from the microcomposites.

Acknowledgement

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Molecularly Imprinted Nanoparticles for Advanced Biomimetic Assays

Boris Mizaikoff

University of Ulm, Institute of Analytical and Bioanalytical Chemistry, 89081 Ulm, Germany
boris.mizaikoff@uni-ulm.de

Biomimetic recognition utilizing molecularly imprinted polymers (MIPs) has proven its potential by providing synthetic receptors for numerous analytical applications including liquid chromatography, solid phase extraction, biomimetic assays, and sensor systems. The inherent advantages of synthetic receptors and functionalized membranes in contrast to biochemical/biological recognition and immobilization schemes include their robustness, synthetic versatility, and potentially lower costs. In principle, molecularly imprinted/templated materials are an ideal molecular capturing matrix tailorable for selective recognition or immobilization of a wide range of molecules. However, tailoring synthetic recognition elements to a target analyte requires thorough analysis and fundamental understanding of the governing molecular processes during the imprinting procedure, with the ultimate goal of rationally designing and predicting optimized synthesis pathways leading to molecular capture, recognition, and biomimetic assay matrices with superior control on their physical geometry and molecular selectivity.

Fundamental understanding of the involved processes via analysis of the governing interactions at a molecular level providing complex stoichiometries, binding affinities, and facilitating pre-screening of optimized functional monomers and component ratios provides the basis for molecular dynamics simulations enabling modeling of the interactions of template molecules with functional monomers and cross-linkers in explicit solvent. While it is anticipated that molecular templating based on rational synthetic design will significantly reduce the number of trial & error experiments currently required, it is evident that the complexity of simulating the generation of molecular imprints still requires extensive efforts toward rational design of next-generation synthetic receptors. Of particular interest is the development of biomimetic recognition schemes for selectively binding proteins and large biomolecules, e.g., for usage in biomimetic assay applications. Recent developments on this new frontier in molecular imprinting based on protein-selective nanoparticles will be highlighted with selected examples and novel routes toward tailoring polymeric receptors for biomolecular recognition facilitating innovative strategies in advanced assay technology.

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Nanoparticle-based nanohybrid materials for biomedical applications

K. Katagiri¹

¹ Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University (1-4-1 Kagamiyama, Higashi-Hiroshima 739-8527, Japan. E-mail: kktgr@hiroshima-u.ac.jp)

Inorganic nanoparticles (NPs) possess a number of features which are advantageous for application in the biomedical field. In recognition of such potentials, a number of researches have been carried out to develop NPs as imaging/contrast agents, carriers for targeted drug and gene delivery, hyperthermia agents, etc. In this study, novel smart NP-based nanohybrid materials for biomedical applications have been developed. We have firstly developed hybrids consisting of polysaccharide nanogels and iron oxide NPs. These nanohybrids were exploited as MRI contrast-enhancement agents. In addition, the ability of these nanohybrids for the agents of magnetic hyperthermia therapy was also confirmed. Next, nanohybrids for photodynamic therapy via near infrared (NIR) irradiation have been developed. Photodynamic therapy (PDT) is a medical treatment for cancers using photosensitive agents. The near infrared (NIR) window is known as the optical tissue penetration window, in which biological tissues have the minimal light absorption. Therefore, development of photosensitizers which can generate singlet oxygen by NIR irradiation is one of the important targets of researches of PDT. Here, nanohybrid clusters formed with lipid-coated photon upconverting nanoparticles (UCNPs) incorporating C₇₀ fullerene have been developed. UCNPs have the ability to convert NIR light to visible photons, which can activate C₇₀ incorporated into lipid membrane via resonance energy transfer, generating cytotoxic singlet oxygen. The energy transfer from UCNPs to C₇₀ is confirmed from upconversion luminescence spectra (Fig. 1). Formation of singlet oxygen was determined by 9,10-anthracenediyl-bis(methylene)dimalonic acid (ABDA). The amount of ABDA decreases exponentially with NIR irradiation time when incubated with nanohybrid particles. This observation illustrates that singlet oxygen could be generated only from the cooperation of UCNPs and C₇₀ via an efficient energy transfer process.

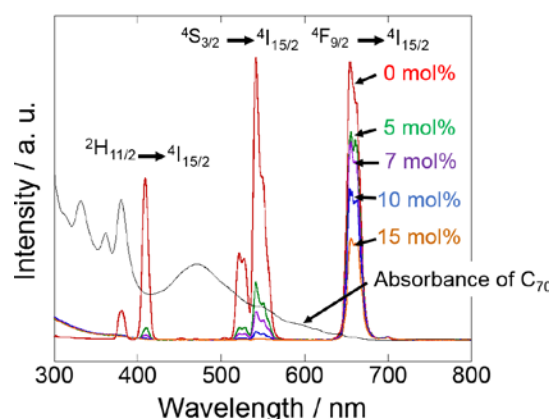


Fig. 1. Emission spectra of aqueous dispersions of nanohybrid clusters before and after incorporation of C₇₀. C₇₀ concentrations are 0, 5, 7, 10, and 15 mol% for the amount of lipid molecules in the dispersions. λ_{ex} = 980

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New insight into the colloidal behavior of suspensions with nanoparticles

H. Hofmann¹ and V. Bernau²

¹ Powder Technology Laboratory, Station 12 Ecole Polytechnique Fédérale de Lausanne, 1015
Lausanne, Switzerland; heinrich.hofmann@epfl.ch

² Powder Technology Laboratory, Station 12 Ecole Polytechnique Fédérale de Lausanne, 1015
Lausanne, Switzerland; vianney.bernau@epfl.ch

Nanomaterials are often used in the form of nanoparticles, for example in cosmetics, for surface coatings (paints) or for medical applications in form of drug delivery systems. For all the mentioned applications, nanoparticles are used in one or the other step of manufacturing as suspensions. This includes synthesis, formulation, application and also tests regarding their behavior in human and environment (toxicity tests). It is interestingly to note that only little work exists investigating in detail the colloidal stability of nanoparticles in aqueous or more complex solutions even it is well known that the well-established DLVO theory is not valid if the radius of the particles is < than 10 times the double layer thickness^[1].

In order to quantify the “to be expected” colloidal stability of the particles, the first approach is to apply the well-known DLVO-theory. When the magnitude of the energy barrier corresponding to the maximum of the sum of both van der Waals and electrostatic force is larger than the Brownian kinetic energy of the two particles moving towards each other, the particles trajectories will be efficiently modified leading to a prevention of aggregation. Applying this to “real” nanoparticle systems, we observe a domain where neither DLVO nor the spherical Poisson-Boltzmann equation solution satisfactorily describes the simulated ionic polarization structure. Furthermore, it appears that in that given range of conditions, taking into account non-zero ion radii, as well as specific Coulombic ion-ion interactions is crucial to the organization of the electrostatic double layer near the surface. A previously unknown limit of validity for the applicability of a mean field approach to the description of electrostatic forces could be identified. It is not clear how this new estimation of the ion distribution finally will affect the electrostatic interaction energy between particles, as current models do not take into consideration the modified slope of potential drop. However, the final effect will probably be a lower electrostatic long range interaction, and a larger short range interaction. It is the author’s opinion that this effect results in a higher stabilization against aggregation than predicted by the method mentioned above, and that the interaction of the strongly bound counter-ions near the surface may act as a quasi-steric energy barrier. Still, this view is expressed for the case where no supplementary, non DLVO effects are considered. The impact of our new results on the colloidal suspension and their application will be discussed.

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Hierarchically Structured Assembly of 2D Nanosheets for Tailored Artificial Materials

Minoru Osada¹

¹ International Center for Materials Nanoarchitectonics, National Institute for Materials Science

(1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan. E-mail: osada.minoru@nims.go.jp)

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Hierarchical self-assembly is a ubiquitous process in nature where it underlies the formation of complex biological structures. Over the past decades, scientists have aspired to exploit biomimetic approaches to create new artificial materials with hierarchical structures and tailored properties. However, *de-novo* design of such hierarchical structured materials is still a major challenge. In this talk, we provide new design principles for tailoring artificial materials using hierarchically structured assembly of 2D oxide nanosheets [1-3]. This strategy has been driven by the recent developments of well-defined 2D building blocks such as graphene and various inorganic nanosheets (oxides, hydroxides, chalcogenides). In designing artificial materials with novel functionalities, we focus on 2D oxide nanosheets (such as $\text{Ti}_{1-\delta}\text{O}_2$, $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$, MnO_2 , perovskites), which are obtained by delaminating a layered compound into its single layers through soft-chemical procedures. These oxide nanosheets have distinct differences and advantages compared with graphene because of their potential to be used as insulators, semiconductors, and even conductors, depending on their composition and structures. Oxide nanosheets also have remarkable potential as building blocks for tailoring fusion materials combined with a range of foreign materials such as organic molecules, gels, polymers, and inorganic and metal nanoparticles. Sophisticated functionalities can be designed through the selection of nanosheets and combining materials, and precise control over their arrangement at the molecular scale. We present a perspective on the advantages offered by nanosheet architectures for various applications in optoelectronics, spinelectronics, energy and environment technologies.

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Using van der Waals force for gripping nano/micro sized objects

R. Šafarič, D. Lukman, B. Bratina

Faculty of electrical engineering and computer science, University of Maribor (Smetanova 17, 2000

Maribor Slovenia, e-mail: riko.safaric@um.si)

The presented research work touches upon the research area of assembly nano-manipulation, especially the practical development of a reliable gripper able to grip, transfer, and actively release nano to micro-sized objects. In particular, the active release of nano/micro objects from a gripper has proved to be problematic in already-developed nano-manipulator systems, over recent decade (nano-soldering, nano-welding, dielectrophoresis, gluing, sintering, chemical bonding, etc [1]). The presented results demonstrate how one-finger gripper using variable Van der Waals forces is capable of gripping, transferring, and actively releasing different geometrical nano/micro objects (of sizes from 700 nm to 50 μm), made using different materials with the processes of gripping or releasing being done within a few seconds. An approach is used that changes the interaction areas between the object, the gripper, and the support surface. It was discovered, in our opinion, the most suitable approach of gripping/releasing procedure regarding costs, the time of gripping/releasing, the wide-range of objects' materials and the independence of the object's geometry. In fact, a combination of top-down and a self-assembling technique was used to create a variable geometry for the gripper's tip (from apex diameter 50 nm to any other type of geometry which would partly incorporate a nano to micro-sized object).

The well-known physical effect of H_2O deposition/sublimation was used under the so-called triple point in the pressure/temperature diagram (6 mbar, 0°C) [2]. According to this effect, the deposition of H_2O crystal starts if the pressure of the H_2O vapor around the tip is lower than 6 mbar and the temperature of the gripper's tip is less than 0°C , and vice versa, so if the temperature is a slightly increased then the H_2O crystal sublimate into vapor. If the pressure is higher, then the H_2O crystal layer is thicker around the tip (in the same deposition time and temperature). The thicker layer of the H_2O crystal is needed for larger objects gripping, and vice versa. Typical times for gripping and releasing are 5 s and 3 s, respectively.

A nanomanipulator system, the hardware for pressure and temperature control [3] are used to manipulate the object with a resolution of 61 nm, to change the pressure from 0.01 mbar to 1 bar and change the temperature from -50°C to 25°C . Fig. 1 shows images of the complete gripping/releasing procedure for moving an SiO_2 sphere-shaped object of approx. diameter 20 μm from a SiO_2 support surface on the top of an object of approx. diameter 10 μm and vice versa.

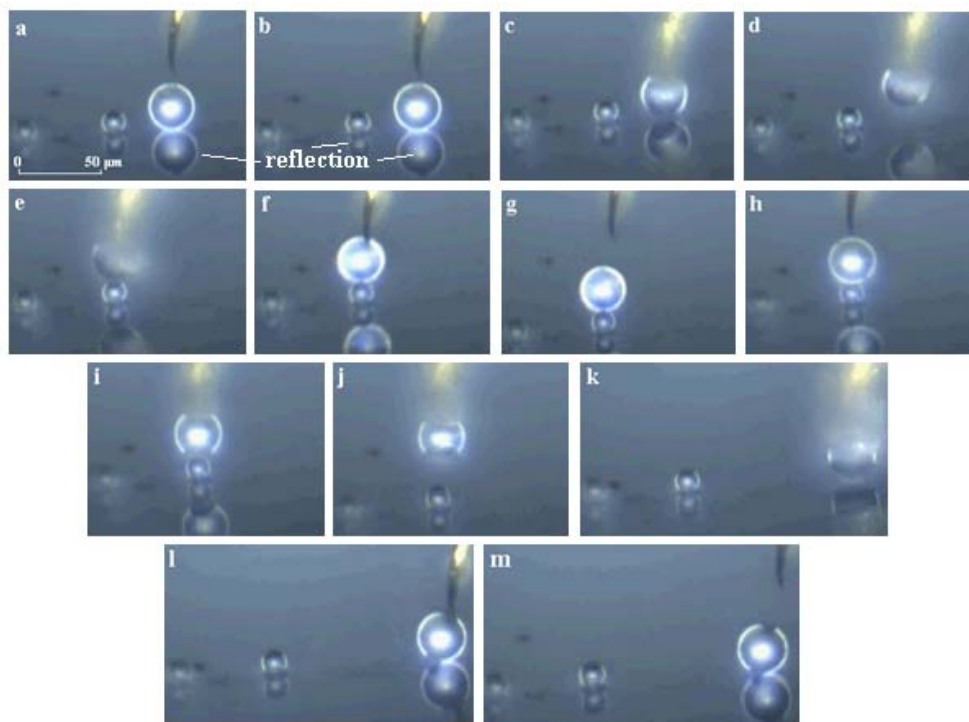


Fig. 3: Images of gripping/releasing procedures (starting position (a) closing the tip (b), gripping - deposition (c), lifting the gripped object (d), moving the object to the top of another object (e), releasing – sublimation (f), tip lifting (g), closing tip again (h), gripping – deposition (i), lifting the gripped object from the top of another object (j), moving the object to the support surface again (k), releasing – sublimation (l), tip lifting (m).

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Making the Hospital a Safer Place by the Sonochemical Coating of the Textiles by Antibacterial Nanoparticles

Aharon Gedanken

Sonochemistry is an excellent technique to coat functional nanomaterials on various substrates, and imparting new properties to the substrates. After a short demonstration of coating NPs on ceramics and stainless steel, I'll present the coating of textiles such as polyester, cotton, nylon, and nonwoven. In all cases a homogeneous coating of NPs was achieved. Silver is known for generations as antibacterial, and indeed the Ag NPs have killed the gram-negative E. Coli (strain 1313) as well as the gram-positive Staphylococcus aureus (strain 195) bacteria very efficiently¹. Lately, since the FDA shows less enthusiasm towards nanoAg we have moved to NPs of ZnO, CuO and MgO as antibacterial agents. They were coated on the above-mentioned fabrics and showed excellent antibacterial properties. The coated textiles were examined for the changes in the mechanical strength of the fabric. A special attention was dedicated to the question whether the NPs are leaching off the fabric when washed repeatedly. The coated ZnO NPs on cotton underwent 65 washing cycles at 92 °C in water in a Hospital washing machine, no NPs were found in the washing solution and the antibacterial behavior was maintained. Recently, an experiment was conducted at PIGOROV Hospital in Sofia, Bulgaria in which one operation room was equipped with antibacterial textiles, namely, bed sheets, pajamas, pillow cover, and bed cover. 22 Patients in this operation room were probed for bacterial infections. Their infection level was compared with 17 control patient that were using regular textiles. The results are demonstrating that a lower infection level is observed for those patient exposed to the antibacterial textiles.

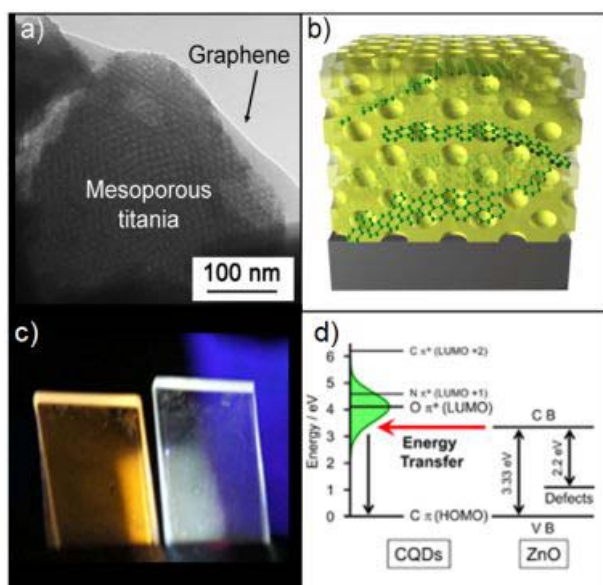
Coating of Catheters with the above mentioned NPs were performed and the coated catheters were inserted in rabbits. Results showed that the urine of the rabbits was not contaminated with bacteria and the growth of biofilm on the Catheters is avoided.

Graphene nanostructures in self-assembled mesoporous films: towards the design of highly performing nanocomposites

L. Malfatti¹

¹Laboratorio di Scienza dei Materiali e Nanotecnologie, CR-INSTN, Università di Sassari, Palazzo Pou Solid, Piazza Duomo 6, 07041 Alghero (SS)

Incorporation of graphene and carbon quantum dots in sol-gel films enables a number of innovative applications with the possibility of tuning the functional properties of the nanocomposite. The direct addition of graphene colloidal solution into highly acidic sols, for instance, is an effective method to insert graphene with low amount of defects into highly ordered siliceous and non-siliceous hybrid organic-inorganic films. The incorporation into optically transparent and durable materials, such as silica, is of particular interest for the development of functional coatings exploiting the optical linear and non-linear properties of graphene, such as optical limiting devices. A similar chemical approach can be applied to the fabrication of nanocomposite films with an organized mesoporous structure,



such as nano-crystalline mesoporous titania containing physically exfoliated graphene with enhanced photocatalytic activity (Figure 1a and b).^[1] Moreover, the graphene-silica nanocomposites can be used as mesoporous matrices for nucleation of metal nanoparticle bearing plasmonic properties. The films show the so-called Graphene-mediated Surface-Enhanced Raman Scattering (G-SERS).^[2] Optical properties can be also imparted to porous films made by carbon quantum dots embedded into ZnO matrixes. The nanocomposites enable the tuning of the photoluminescence in a wide visible wavelength range. Considering the down-converting property and broad emission,

implementation of these materials into functional optical devices, such as UV shielding windows and phosphors for lighting, can be foreseen.

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Inkjet-printed mesoporous silica dots as biosensors for cancer diagnosis and therapy

A. Nouredine¹, J. Graffion¹, O. De Los Cobos¹, R. Trihan¹, M. Lejeune¹, F. Rossignol¹, L. Micallef², H. Akil², F. Lalloué², X. Cattoën³, M. Wong Chi Man⁴, J.O. Durand⁵, C. Sanchez⁶

¹ European Center of Ceramics, SPCTS- 12 rue Atlantis 87068 Limoges, France.

achraf.nouredine@unilim.fr, julien.graffion@unilim.fr, olivia.de-los-cobos@unilim.fr, romain.trihan@etu.unilim.fr, martine.lejeune@unilim.fr, fabrice.rossignol@unilim.fr

² Faculty of Pharmacy, EA 3842- University of Limoges, 2 rue du Dr Marcland 87025 Limoges, France.

ludovic.micallef@unilim.fr, hussein.akil@unilim.fr, fabrice.lalloue@unilim.fr

³ Néel Institute, MatONLP- UPR 2940 CNRS/UJF- 25 rue des Martyrs 38042 Grenoble Cedex 9, France.

xavier.cattoen@neel.cnrs.fr

⁴ Charles Gerhardt Montpellier Institute, AM₂N- ENSCM 12 rue de l'Ecole Normale 34296 Montpellier, France.

michel.wong-chi-man@enscm.fr

⁵ Charles Gerhardt Montpellier Institute, CMOS-UM2, place Eugène Bataillon 34095 Montpellier Cedex 5, France.

durand@um2.fr

⁶ University of Pierre and Marie Curie, LCMCP Collège de France, 11 place Marcelin Berthelot 75005 Paris, France.

clement.sanchez@upmc.fr

In this communication, we present an innovative approach for detection and treatment of cancers ^[1,2]. We use the flexibility and the resolution of the inkjet printing process combined to Evaporation-Induced Self-Assembly (EISA) to elaborate simple devices made of mesoporous silica microdots arrays functionalized by click chemistry. Bio-receptors labeled with appropriate fluorophores are then anchored to the surface of the mesoporous silica, so that conformation change occurs when bio-receptors interact with the tumor cells' biomarker of interest reducing the distance between fluorophores and inducing Fluorescence Resonance Energy Transfer (FRET). Once the tumor is detected, the mesoporous silica dots can be derivatized by photosensitizers in order to produce singlet oxygen and induce cancer cell apoptosis. Currently, work is ongoing to transpose this concept to a more developed and applied device for non-invasive clinical tests.

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Patterned surface modification of ultra-thin PDMS films with polysaccharides for advanced biomedical sensoric devices

Matej Bračič¹, Tamilselvan Mohan², Rupert Kargl¹, Lidija Fras Zemljič¹, Karin Stana Kleinschek¹

¹ Institute for the Engineering and Design of Materials, University of Maribor, Smetanova 17, 2000 Maribor, Slovenia (matej.bracic@um.si, rupert.kargl@um.si, lidija.fras@um.si, karin.stana@um.si)

² Institute of Chemistry, University of Graz, Heinrichstraße 28, AT 8010 Graz, Austria
(tamilselvan.mohan@uni-graz.at)

In this work, polydimethylsiloxane (PDMS) ultrathin films are prepared on glass, silicon wafers, and gold covered quartz crystals by a simple and fast spin coating method, and patterned with the natural biopolymer cellulose via lithography methods. Two surface patterning methods are developed to create coatings of the hydrophilic polymer cellulose, regenerated from trimethylsilyl cellulose (TMSC) on the PDMS thin films. In both methods a metal mask is used to spatially separate the cellulose pads from the PDMS. The conversion of hydrophobic TMSC into hydrophilic cellulose coatings is confirmed by wettability and fluorescence measurements. The developed structures are highly transparent and stable both in aqueous solutions (pH 4-9) and in organic solvents. The surface and physicochemical properties of the patterned polymer films are characterized using quartz crystal microbalance with dissipation (QCM-D), ellipsometry, atomic force microscope (AFM), contact angle and fluorescent scanning. The cellulose pads can be further functionalised with cationic polysaccharides¹ or single stranded DNA² with the aim to specifically bind and detect proteins and DNA molecules.

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Nanostructured mixtures of mixed oxides derived from layered double hydroxides reconstructed in $\text{Ga}_2(\text{SO}_4)_3$ and $\text{In}(\text{C}_2\text{H}_3\text{O}_2)_3$ aqueous solutions for efficient UV and solar-driven photocatalysis

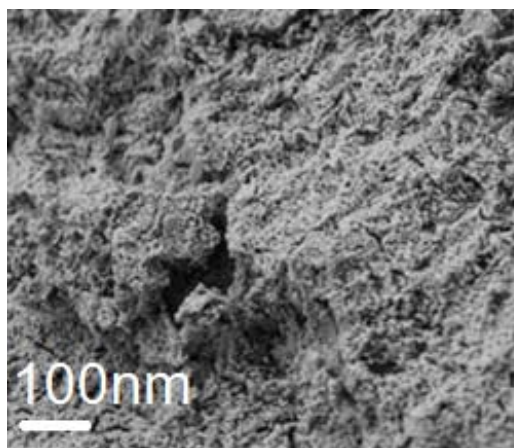
E. F. Grosu¹, L. E. Dartu², E. M. Seftel³ and G. Carja¹

¹ Department of Chemical Engineering, Faculty of Chemical Engineering and Environmental Protection, Technical University "Gh. Asachi" of Iasi, Bd. Mangeron no.71, Iasi 700554, Romania, e-mail: carja@uaic.ro

² Department of Preclinical Disciplines, Faculty of Medical Dentistry, Apollonia University of Iasi, Muzicii Street, no. 2, Iasi, Romania, e-mail: laura_ekaa@yahoo.com

³ Laboratory of Adsorption and Catalysis, Department of Chemistry, University of Antwerpen (CDE), Universiteitsplein 1, 2610 Wilrijk, Antwerpen, Belgium, e-mail: elena.seftel@uantwerpen.be

Layered double hydroxides (LDHs) are a class of anionic clays represented by the general formula $[\text{M(II)}_1-x\text{M(III)}_x(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$ [1]. Zinc-galium (ZnGaLDH) and zinc-aluminium (ZnAlLDH) clay matrices are



The SEM image of $\text{Ga}_2\text{O}_3/\text{ZnO}/\text{ZnGa}_2\text{O}_4$.

members of layered double hydroxides group, containing Zn^{2+} , Ga^{3+} and Al^{3+} as M(II) and M(III) cations of the brucite-like layers. Calcination of ZnAlLDH and ZnGaLDH destroys the layered clay structure and gives rise to mixtures of mixed oxides of $\text{ZnO}/\text{ZnAl}_2\text{O}_4$ and $\text{ZnO}/\text{ZnGa}_2\text{O}_4$, respectively. The concept of Zn containing LDHs semiconductors was very recently introduced by Garcia group reporting the behaviour of Me(III) and/or Me(IV) partially substituted zinc containing LDHs as zinc oxide semiconductors doped with the tri- or tetravalent metal ions [2]. We have enlarged the concept of ZnLDHs based semiconductors by describing novel nanoarchitectonics of the self-assemblies of nanoparticles of metal oxides (MexOyNP) and LDHs [1, 3]. MexOyNP/LDHs self-

assemblies were fabricated by exploiting the manifestation of the LDHs structural memory effect in the aqueous solutions of Me(III), Me(IV) inorganic salts. We present here the nanosized mixtures of mixed oxides obtained after the thermal treatment of ZnLDHs and ZnGaLDHs - reconstructed in $\text{Ga}_2(\text{SO}_4)_3$ and $\text{In}(\text{C}_2\text{H}_3\text{O}_2)_3$ aqueous solutions, as novel photoresponsive formulations under UV and solar irradiation. X-ray diffraction (XRD), energy dispersive X-ray (EDX) mapping, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM –inset Figure), and UV-Vis analysis were adopted to investigate the structure, surface, morphology and photoresponsive properties of the nanostructured mixtures of mixed oxides derived from the reconstructed ZnAlLDH and/or ZnGaLDH. The efficiency of the novel photocatalysts were tested for phenol degradation from aqueous solutions.

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Structural properties of novel zeolite-modified cellulose nanofibril composites, and their potential applications

Madhuri Lakhane^{1,2}, Rajendra Khairnar², Megha Mahabole², Vanja Kokol^{1*}

¹ Institute of Engineering Materials and Design, University of Maribor, Slovenia

² School of Physical Sciences, Swami Ramanand Teerth Marathwada University, Nanded (MS), India

[*vanja.kokol@um.si](mailto:vanja.kokol@um.si)

Zeolites are microporous crystalline aluminosilicates with uniform pore size, chemically and thermally stable. They possess permanently negative charge which is composed by exchangeable cations to balance the framework structure. Due to their unique properties they are widely used in adsorption, and separation of gases, ion-exchange, catalysis, and sensing. As biocompatible and bioactive they can be also applied in biomedical applications like antitumor, drug-carrier, hemostatic material etc.

Based on green and safe nanotechnology which is the requirement for today and the future, the aim of this study was to develop new bio-based and nano-structured film-forming materials by using nanocellulose fibrils (CNFs), being another biorenewable and biodegradable material, and differently formulated nano-zeolites. Their nano-scale dimensions and ability to form a strong entangled nanoporous network have been studied by dispersing zeolite into the CNF matrix using different approaches and conditions. The films have been characterised by various analytical techniques like FTIR, X-RD, TG/DSC, BET, SEM and AFM analysis, and evaluated relate to the water and selected solvent stability. These results reveals that the prepared green nanocomposite films can have prospective and high-added value applications like gas adsorption, separation and sensing, oxygen-impermeable packaging, water and solvent filtration membranes.

Keywords: zeolite, cellulose nanofibrils, FTIR, X-RD, TG/DSC, BET, SEM, AFM, applications.

Synthesis of core-shell nanoparticles to capture radioactive cesium

C. Mansas¹, X. Deschanel¹, A. Grandjean², J. Causse¹

¹ ICSM, UMR 5257, CEA-CNRS-UM2-ENSCM, BP17171, 30207 Bagnols-sur-Cèze

(clementine.mansas@cea.fr; xavier.deschanel@cea.fr; jeremy.causse@cea.fr)

² CEA Marcoule, DTCD/SPDE/LPSD, BP17171, 30207 Bagnols-sur-Cèze

(agnes.grandjean@cea.fr)

After the incident of Fukushima-Daiichi in 2011, a large amount of aqueous effluents was contaminated with radioactive elements, such as Cesium. A sorption process of radioelements on inorganic solids, as silica monoliths, has been already described to capture radioactive cesium and to anchor it on solid phase ^[1]. Inorganic materials were therefore functionalized with copper hexacyanoferrate nanoparticles ($K_2CuFe(CN)_6$) that are well known to be highly cesium selective. However, these materials do not allow Cs optimal sorption because of strong aggregation of PBA nanoparticles.

Therefore, the aim of this study is to propose a solution to fix that aggregation using core-shell nanoparticles. In this case, the core is made of PBA with a protecting porous silica shell all around. Two main synthetic routes were first tested: an inverse microemulsion ^[2] to control the size of the particles on one hand and a more direct aqueous phase synthesis ^[3] on the other hand. Nanoparticles formed were characterized using FTIR-ATR, DRX, SAXS and TEM. Both synthetic routes need high control of the charges located at the surface of PBA nanoparticles and silica species to allow the shaping of the expected nanomaterial.

First results obtained with inverse microemulsion way will be discussed in this presentation.

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Electrospun nanofibrous CMC/PEO as a part of an effective pain relieving wound dressing

T. Maver¹, U. Maver², M. Kurečič^{1,3}, D. M. Smrke⁴ and K. Stana Kleinschek¹

¹ University of Maribor, Faculty of Mechanical Engineering, Laboratory for Characterisation and Processing of Polymers, Smetanova 17, SI-2000 Maribor, Slovenia (tina.maver@um.si, manja.kurecic@um.si, karin.stana@um.si)

² University of Maribor, Faculty of Medicine, Laboratory of Pharmacology and Toxicology and Institute for Palliative Medicine and Care, Taborska ulica 8, SI-2000 Maribor, Slovenia (uros.maver@um.si)

³ Centre of Excellency PoliMaT, Tehnološki park 24, SI-1000, Ljubljana, Slovenia (manja.kurecic@um.si)

⁴ University Medical Centre Ljubljana, Zaloška cesta 2, SI-1000, Ljubljana, Slovenia (uros.maver@um.si)

Electrospinning is a modern technique, enabling development of matrices with nanometer sized fibers with similar features and morphologies to the extracellular matrix. Such materials are therefore believed to stimulate cell proliferation and encourage wound healing. Electrospun matrices have also been shown to provide a high-surface area and micro-porosity, making them ideal for loading of drugs or other biomolecules ^[1].

Based on the desired properties of electrospun fibers and the awareness of the negative effects of pain on wound healing ^[2, 3], we combined specially designed electrospun nanofibers and two pain-relieving drugs. To achieve a fast (acute) reduction of pain, which is often caused by the wound treatment (dressing exchange etc.), a local anesthetic - lidocaine with fast beginning of action, was used. The second included drug was added to provide a long lasting pain relief. For this purpose a nonsteroidal anti-inflammatory drug (NSAID) diclofenac was used.

We studied the possibility to influence the drug release by using different techniques of drug incorporation into the prepared carrier materials.

Acknowledgement

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Facile one-pot synthesis of copper hexacyanoferrate functionalized silica monoliths for the selective uptake of ^{137}Cs

A. Sommer-Marquez¹, N. Talha¹, Agnès Grandjean^{1,2}, Yves Barré², Xavier Deschanel¹
and Jérémy Causse*¹

¹ICSM, CEA-UM2-ENSCM-CNRS, CEA Marcoule, Bat.426, 30207 Bagnols sur Cèze, France

²DTCD/SPDE/LPSD, CEA Marcoule, Bat.56, 30207 Bagnols sur Cèze, France

The goal of this study was to develop a facile synthetic route for the preparation of monolithic materials devoted to the decontamination of radioactive effluents. Here, the targeted radionuclide, ^{137}Cs , is one of the most problematic elements of the nuclear cycle. Radioactive ^{137}Cs is also widely present in contaminated liquid effluents from the Fukushima nuclear plant accident following the tsunami which occurred on March, 11th 2011 making ^{137}Cs extraction a topical issue. Hexacyanoferrate (HCF) compounds containing potassium in the lattice structures are quite efficient in the uptake of Cs ions; the exchange mechanism being the insertion of Cs ions into the structure, while K ions are concurrently released into the solution. These coordination polymers (HCF) are very selective towards Cs ions with regard to Na ions. However, due to their low mechanical hardness and their fine powder form leading to a slow filtration rate as well as a clogging problem, only small volumes of effluent can be treated. For this reason, the use of the bulk compound in column process decontamination cannot be considered, while monolithic materials with hierarchical porosity can. Our group is now studying metal hexacyanoferrate based nanomaterials for nuclear decontamination purposes for several years ^[1,2]. In the present work, the synthetic route uses high internal phase emulsion (HIPE) as a template to prepare hexacyanoferrate nanoparticle (NP) functionalized silica monoliths with various loading levels from 0.2%wt to 5.1%wt^[3]. Not only are these monoliths macroporous, and therefore usable in a continuous process, but the novel functionalizing route used here has allowed for high incorporation of the HCF nanoparticles into the monolith structure. Sorption experiments on ^{137}Cs have shown that these monoliths are very selective of this radionuclide despite the presence of huge concentration of competitive sodium ions in the contaminated solution. The coefficient distribution values reached with these monoliths are very high; above 1.10^5 ml/g for the monoliths with the highest content of nanoparticles. Besides, TEM experiments show that HCF nanoparticles are aggregated in the monoliths and that accessibility to these nanoparticles is allowed by the porosity of the silica walls.

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Periodic mesoporous organosilicas for drug delivery and metal adsorption

Chang-Sik Ha

Department of Polymer Science and Engineering, Pusan National University, Busan 609—735, Korea

E-mail: csha@pnu.edu

A novel class of organic–inorganic nanocomposites known as periodic mesoporous organosilicas (PMOs) has been introduced in 1999. The organic functional groups in the frameworks of these solids allow tuning of the surface properties and modification of the bulk properties of the material. In PMOs, the organic groups are located within the channel walls as bridges between the Si centers ($((R'O)_3Si-R-Si(OR')_3$ (R' = methyl or ethyl, R = the bridged organic groups)). Organic–inorganic hybrid materials can be synthesized by hydrolysis and condensation reactions of bridged organosilica precursors via the self-assembly process of a structure-directing agent, corresponding to a similar process for the preparation of mesoporous silica materials. In the pioneering study of PMOs, the materials were synthesized using single bridged silane as the framework composition. In later studies, two or multiorganosilane precursors were used to obtain PMOs with multifunctional or advanced functionality. Many works reported their different functionalities, morphology and applications of PMOs, such as catalysis, drug delivery, sensing, optics, electronic devices, environmental applications (gas sensing and gas adsorption), biomolecule adsorption and chromatography, and so on.

In this presentation, I will touch on the advanced applications of PMOs such as drug delivery and metal adsorption systems mainly based on our own works that have been done in recent years.^[1-5]

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Cooperative Physical and Chemical Interactions for the Sol-Gel Processing of Organised Films and Nanoparticles

John Bartlett

Faculty of Science, Health, Education and Engineering, University of the Sunshine Coast,
Maroochydore, QLD, Australia

This presentation will explore the use of self-assembly and cooperative physical and chemical interactions for controlling the structural evolution of organised nanohybrid films and nanoparticles via sol-gel processing. The underlying physical and chemical processes will be illustrated through a number of examples.

In the first series of examples, the production of thin films of self-structured silsesquioxane nanohybrids by spin coating, through the sol-gel hydrolysis and condensation of bridged organosilanes bearing self-assembling urea groups, will be described. The resulting nanostructures are shown to be dependent on the type of catalyst used (nucleophilic or acidic), and are further modulated by varying the deposition conditions. FTIR studies revealed the presence of highly organized structures due to strong hydrogen bonding between urea groups and hydrophobic interactions between long alkylene chains. The preferential orientation of the urea cross-links parallel to the substrate is shown using polarized FTIR experiments. A mechanistic model is described to explain such long-range structuring under far-from-equilibrium conditions.

In the second series, a new approach for producing metal oxide nanoparticles via sol-gel processing in reverse micelles is explored, in which the chemical and physical properties of the polar aqueous core of the reverse micelles are modulated by the inclusion of a second polar co-solvent. The co-solvents were selected for their capacity to solubilise compounds with low water solubility (suitable for the encapsulation of species such as oncology drugs) and included DMSO, DMF, EG, n-PrOH, DMA and NMP. A broad range of processing conditions are elucidated that are suitable for preparing nanoparticles with dimensions of 50 nm to 500 nm. In contrast, only a relatively narrow range of processing conditions were suitable for preparing nanoparticles in the absence of the co-solvents, highlighting the key role of the co-solvent in modulating the properties of the polar core of the reverse micelles. A mechanism is described that links the interactions between the various reactive sites on the polar head group of the surfactant and the co-solvent to the nucleation and growth of the nanoparticles. The use of this strategy for encapsulating drugs with low water solubility such as 3-hydroxyquinolinone derivatives, for potential applications in oncology drug delivery will be discussed.

Polysaccharide materials for biomedical applications

R. Kargl¹, M. Kurečič¹, U. Maver², T. Mohan^{1,3}, S. Spirk^{1,4}, V. Ribitsch³, and K. Stana-Kleinschek¹

¹Faculty of Mechanical Engineering, Laboratory for Characterization and Processing of Polymers, University of Maribor, Smetanova 17, 2000 Maribor, Slovenia; E-mail: karin.stana@um.si, rupert.kargl@um.si

²Medical Faculty, University of Maribor, Taborska ulica 8, 2000 Maribor, Slovenia, 2000 Maribor, Slovenia, uros.maver@um.si

³Institut für Chemie, Karl-Franzens-Universität Graz, Heinrichstrasse 28/III, 8010 Graz, Austria, mohan.tamilselvan@uni-graz.at

⁴University of Technology Graz, Institute for Chemistry and Technology of Materials, Stremayrgasse 9, 8010 Graz, Austria, stefan.spirk@tugraz.at

Polysaccharides (PS) as materials have a huge potential to be applied in advanced biomedical applications. For many of their functions surface properties and the interaction at the materials' interfaces are crucial. By having a detailed understanding of wetting, adsorption/desorption, adhesion and morphology, PS materials with desired surface properties can be created. Well defined thin films of PS are one platform that can be used to elucidate these surface phenomena^[1]. Knowledge obtained from basic studies on thin films can then be transferred to the development of functional materials. Characterization of their defined composition is performed with modern surface analytical methods such as a quartz-crystal microbalance, surface plasmon resonance, and X-ray photoelectron spectroscopy. As an example, these films can further be surface structured and serve as a basis for functional layers in optical sensors for the detection of DNA and proteins^[2]. The biological efficacy of many charged polysaccharides can also be exploited in the coating of metal (nano-) particles on modern wound dressings, having antimicrobial properties. Electrospinning of PS with incorporated functional ingredients presents another possibility to develop functional wound dressings that are super-absorbing and analgesic^[3]. Different PS spinning formulations and PS wound dressings were studied with respect to surface properties, biocompatibility, bioactivity, wettability, and morphology. In this presentation an overview on the current achievements in the fields of polysaccharide materials research will be given.

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Point-of-care photonic nanobiosensors for global health diagnostics: Challenges and opportunities

L. M. Lechuga

Nanobiosensors and Bioanalytical Applications Group.
Institut Català de Nanociència i Nanotecnologia (ICN2). CSIC and CIBER-BBN. Barcelona, Spain
Laura.lechuga@cin2.es

Modern healthcare is demanding novel diagnostic tools that could enable quick, accurate, reliable, and cost-effective results so that appropriate treatments can be implemented in time, leading to improved clinical outcome. Such hand-held point-of-care (POC) devices, able to deliver an instant diagnostics of our health status at home, at doctor's office, at bed side or at resource-limited settings, could become a reality soon thanks to the last advances in nanobiosensors, lab-on-a-chip, wireless and smart-phone technologies which promise to surpass the existing challenges, opening the door to a global health access.

The driving force of our research is to achieve such ultrasensitive platforms for POC label-free analysis using nanophotonic technologies and custom-designed biofunctionalization protocols, accomplishing the requirements of disposability and portability. We are using innovative designs of nanophotonic biosensors based on plasmonic nanostructures or silicon photonics technology (heteromodal nanointerferometers) and full microfluidics lab-on-chip integration^[1,2].

We have demonstrated the suitability of our photonic nanobiosensors for the clinical diagnostics, with extremely sensitivity and selectivity and directly using untreated human samples, as for the evaluation of allergy reactions in blood serum, the detection of infectious microorganisms (at few cfu/mL) in human ascetic fluids, the early detection of colorectal cancer through the presence of autoantibodies in patients serum or the detection of microRNA biomarkers related to cancer progression in urine or serum, among others^[3,4].

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Metal oxide clusters as models for metal oxide nanoparticles

U. Schubert

Institute of Materials Chemistry, TU Wien, Getreidemarkt 9, 1060 Wien, Austria.

E-mail: Ulrich.Schubert@tuwien.ac.at

Protecting ligands play an important role for stabilization, dispersibility, functionalization, etc. of nanoparticles. Phenomena related to the ligands, however, are not easily investigated. Molecular clusters can be considered small nanoparticles and have the advantage that they are much easier to study because of their clearly defined size, shape and metal coordination, and because the methods of molecular chemistry can be applied. This will be exemplified mainly for carboxylato-stabilized metal oxide clusters ^[1].

The following issues will be addressed in the talk:

- Ligand dynamics (movement of the ligands on the cluster surface)
- Ligand exchange reactions (including preparation of mixed-ligand clusters)
- Conflicting results on cluster degradation/rearrangement upon ligand exchange
- Can information on cluster growth (depending on the ligand sphere) be gained from structural studies?

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Elimination of Pt Organic Compounds from Groundwater

B. Papežová, M. Matějková, F. Kaštánek, O. Šolcová

Institute of Chemical Process Fundamentals of the ASCR, v. v. i., Rozvojová 135, 165 02 Prague 6;

Phone: +420 220 279 280, e-mail: papezova@icpf.cas.cz

Pt compounds (Cisplatin, Carboplatin and Oxaliplatin) have been usually used as medicaments for the cancer therapy. During the therapy Pt compounds are excreted from the human body into the hospital waste water. These toxic Pt compounds cannot be removed from the waste water by the common sewage treatment, thus they could accumulate in the natural water sources. Therefore, the hospital waste water requires the special waste water treatment. Nevertheless, this treatment is not so easy and various decontamination techniques have been applied to remove or at least reduce these compounds from the waste water.

This study is focused on the total elimination of Pt compounds from contaminated water by the sorption technique. Zeolite (Clinoptilolite, Bentonite Braňany), special soil (Lufa) and active carbon (Supersorbon) have been tested as sorbents for Pt elimination. These sorbents were selected based on their textural properties. For testing three concentrations of the model contaminants were prepared.

The experiments were performed in the batch reactor during the continuous shaking. The experiments were carried out for 24 h and the amount of Pt was determined by ICP-MS technique.

Activity of four various sorbents (Supersorbon Bentonite, Clinoptilolite and Lufa) were tested for the model solutions of Cisplatin, Carboplatin and Oxaliplatin. Supersorbon was evaluated as the most active sorbent and the mild sorption activity revealed also Bentonite. Their efficiency was verified on the real waste water from hospital.

Acknowledgement

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Mo₆S₃I₆ NANOWIRES – NANOBODY® BASED CAFFEINE BIOSENSOR

**Tinkara MASTNAK¹, Peter M. MIHAILOVIĆ³, Matevž KORENČ², Gregor GUNČAR²,
Aleksandra LOBNIK¹, Dragan MIHAILOVIĆ³**

¹University of Maribor, Faculty of Mechanical Engineering, Maribor, Slovenija

²University of Ljubljana, Faculty of Chemistry and Chemical Tehnology, Ljubljana, Slovenija

³Jožef Stefan Institute, Ljubljana, Slovenija

Molybdenum-chalcogenide-halide nanowires (NWs), composed of molybdenum (Mo), sulfur (S), and iodine (I) in the form of Mo₆S₃I₆ (MoSI) are a class of quasi-one-dimensional objects. They act as molecular-scale connectors to bind thiolated proteins and are capable of forming covalent bonds with a gold surface or with thiol groups of large molecules. Their biosensing application relies on MoSI nanowires as a substrate for antibody immobilization for electrochemical sensing of proteins.

Most antibodies are composed of two longer »heavy« and two shorter »light« chains. Both chains contribute to the antigen-binding site. In addition to these conventional antibodies, camels, llamas and cartilaginous fish also produce antibodies composed only of heavy chains. Unlike conventional antibodies, the antigen binding site of these unusual heavy chain antibodies is formed by a modified single domain, known as hypervariable binding domain, designated VHH. These domains are small, well soluble and can be easily produced as recombinant proteins in bacteria, yeast, and animal or plant cells. VHHs derived from camels or llamas commercially called Nanobodies®. Due to their versatility they are increasingly used for therapeutic purposes and in the technology of biosensors.

Caffeine (1,3,7-trimethylxanthine) is a stable alkaloid found in various plants such as coffee and cocoa beans, tea leaves, guarana berries and the kola nut, and thus has a long history of human consumption. While being a stimulant to the central nervous system, it can have some adverse effects on health. For this reason its efficient measurement is relevant and the development of a sensitive, rapid and cost effective method for monitoring caffeine is greatly needed.

In this preliminary study we have successfully developed a caffeine biosensor for quick, easy and accurate caffeine detection. The sensor consists of a carbon electrode and a film made of Mo₆S₃I₆ nanowires with immobilized anti-caffeine Nanobodies®. The response is measured by differential pulse voltammetry. Our further research is focused on optimization of an array of parameters for the biosensor and improved yield of anti-caffeine Nanobodies® production

Removal of Pb(II) and Cr(III) ions from aqueous solutions by applying amino functionalized nanoparticles

M. Bauman¹, A. Košak², S. Krajnc³, G. Petek³, J. Volmajer Valh³, S. Vajnhandl³, A. Lobnik^{1,2}
maja.bauman@ios.si

¹IOS, Institute of Environmental Protection and Sensors, Ltd., Beloruska 7, SI-2000 Maribor, Slovenia

²University of Maribor, Faculty of Mechanical Engineering, Centre of Sensor Technology, Smetanova 17, SI-2000 Maribor, Slovenia

³University of Maribor, Faculty of Mechanical Engineering, Smetanova 17, SI-2000 Maribor, Slovenia

Recently, different functionalized SiO₂ nanoparticles based on tetraethoxysilane (TEOS) are developed as sorbent material, since showing potential for selective removal of heavy metal ions from aqueous solutions and wastewaters.^[1,2] Precursors, such as 3-(Trimethoxysilyl)-propyl]diethylenetriamine (DETA) in 3-(Aminopropyl)trimethoxysilane (APTMS) are promising to synthesize more selective SiO₂ particles since varying in number of alkoxy (-Si(OR)₃) groups, length of aliphatic (hydrophobic) chains and numbers of amino (-NH₂) functional groups. In order to obtain the specific functionality of new adsorbent material as "filtration media" or additional surface layer on filtration membranes, determination of controlled synthesis conditions, size, distribution and morphology, is essential.^[3,4]

In this study surface functionalized SiO₂ (DETA, APTMS, TEOS:DETA and TEOS:APTMS) nanoparticles were synthesized in one-pot solution according to Stöber method.^[3] Experiments were focused in testing the synthesis conditions and adsorption efficiency using Pb(NO₃)₂ and Cr(NO₃)₃·9H₂O salt solution at constant concentration [HM]_{ion}]=100 mg/L. Adsorption rate (R in %) was calculated based on the results of AAS spectroscopy analytics of heavy metal ions in supernatant and initial solution. Prepared and surface functionalized SiO₂ nanoparticles were characterized using FT-IR/Raman spectroscopy, specific surface area and porosimetry (BET), TEM microscopy and zeta potential.

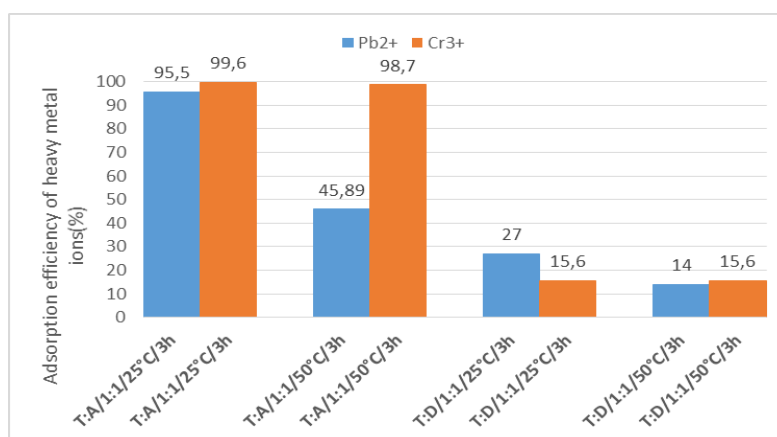


Figure 1: Adsorption efficiency of Pb²⁺ and Cr³⁺ on TEOS:APTMS and TEOS:DETA nanoparticles.

Acknowledgement:

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An efficient approach for heavy metal ions removal using thiol functional cobalt ferrite nanoparticles

Branka Viltužnik¹, Aljoša Košak², Aleksandra Lobnik²

¹Institute for Environmental Protection and Sensors, Beloruska 7, SI-2000 Maribor, Slovenia

²University of Maribor, Faculty of Mechanical Engineering, Centre for Sensor Technology, Smetanova 17, SI-2000 Maribor, Slovenia

branka.viltuznik@ios.si

Cobalt-ferrite nanoparticles prepared via co-precipitation method were functionalized with tetraethyl orthosilicate (TEOS) and 3-mercaptopropyl trimethoxysilane (MPTMS) with purpose of cleaning waste water contaminated with heavy metal ions. The influence of the different experimental parameters (reaction time, react concentration and different TEOS:MPTMS ration) on the coating cobalt-ferrite nanoparticles with a thin layer of silica and after functionalized with thiol group was systematically studied. Silanes adsorb to the particle surface with alkoxy ($\text{Si}(\text{OR})_4$) groups at one end, while functional substituents ($-\text{SH}$) at the opposite end stay extended into surrounding aqueous medium and chemically interact with heavy metal contaminants. Functionalized cobalt-ferrite nanoparticles were characterizing using IR spectroscopy, X-ray diffraction (XRD), transmission electron microscopy/high-resolution transmission electron microscopy (TEM/HRTEM) and energy-dispersive X-ray spectroscopy (EDXS).

The synthesized cobalt-ferrite nanoparticles and functionalized with TEOS or/and MPTMS were used for treating the wastewater contaminated with heavy metal ions, such as Pb^{2+} and Hg^{2+} . Effect of treatment has been demonstrated using atomic absorption spectroscopy (AAS).

Under the experimental conditions used, the thiol functionalized cobalt ferrite magnetic nanoparticles displayed high efficiency for Pb^{2+} and Hg^{2+} ions (96 and 98 %) removal. Therefore thiol functionalized CoFe_2O_4 nanoparticles show great potential for the removal of Pb^{2+} and Hg^{2+} ions from water, via magnetic separation. Desorption experiments for Pb^{2+} ions by using 0.1 M HCl show that the thiol functionalized CoFe_2O_4 magnetic nanoparticles could be reused without significant losses of their initial properties even after third adsorption-desorption cycles, while for Hg^{2+} ions desorption the results are not so satisfying.

Application of sol-gel prepared phenyl-modified silica coatings for the stone protection and evaluation of sol-gel chemistry on the wettability and surface modification

M. Ramezani¹, M. R. Vaezi¹ and A. Kazemzadeh²

¹Division of Nanotechnology and Advanced Materials, Materials and Energy Research Center, Karaj, Iran (m.ramezani@merc.ac.ir and m_r_vaezi@merc.ac.ir)

²Division of Semiconductors, Materials and Energy Research Center, Karaj, Iran
(a-kazemzadeh@merc.ac.ir)

In recent years, acceleration in the rate of stone decay is observed. Stone located outdoors is exposed to the effects of natural weathering. Stone degradation mechanisms are controlled by several factors. Among them, condensed water is one of the main factors for the weathering and decay of stone and stone based monuments. Water can cause stone deterioration through cycles of freezing and thawing inside the pores of the stone or by intra porous crystallization of the salts transferred by water from the environment ^[1,2]. In this study, to protect the stone from water, hydrophobic silica coatings were prepared via sol-gel method from tetraethoxysilane (TEOS) as a precursor and phenyltriethoxysilane (PhTES) as a modifying agent. The water repellent silica films were characterized by atomic force microscopy (AFM), fourier transform infrared spectroscopy (FT-IR), contact angle measurement (CA) and field emission scanning electron microscopy (FE-SEM) images. A static water contact angle was obtained as high as 142° with particle size of 42 nm on the stone substrate. Also, we investigated the influence of the other sol-gel reaction parameters, such as catalyst, solvent and water content on the morphology and wettability of the silica films. The results revealed that by altering the molar ratio of NH₄OH, EtOH and H₂O, hydrophobic properties of the silica coatings on the stone substrate were obtained from 86° to 146°.

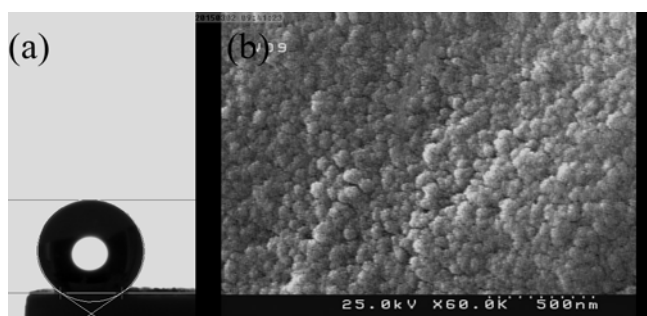


Fig. 1. (a) Contact angle and (b) FE-SEM images of hydrophobic silica film on the stone substrate.

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Polyvinyl alcohol (PVA) coated superparamagnetic maghemite ($\gamma\text{Fe}_2\text{O}_3$) nanoparticles for applications in biomedicine

M. Hriberšek¹, A. Košak^{2,3*}, A. Lobnik^{2,3}, J. Stergar⁴, I. Ban⁵

¹Il. gimnazija Maribor, Trg Miloša Zidanška 1, SI-2000 Maribor, Slovenia

²University of Maribor, Faculty for Mechanical Engineering, Smetanova 17, SI-2000 Maribor, Slovenia

³Institute for Environmental Protection and Sensors, Beloruska 7, SI-2000 Maribor, Slovenia

⁴University of Maribor, Faculty of Medicine, Taborska 8, SI-2000 Maribor, Slovenia

⁵University of Maribor, Faculty for Chemistry and Chemical Engineering, Smetanova 17, SI-2000 Maribor, Slovenia

(mojca.hribersek@druga.si; aljosa.kosak@siol.net*)

Nanotechnology is one of the very prospective fields in science, especially in connection with biomedical applications. The main aim of our work was to establish suitable conditions for producing polyvinyl alcohol (PVA) coated superparamagnetic maghemite ($\gamma\text{Fe}_2\text{O}_3$) nanoparticles that could be used in biomedical applications.

Maghemite ($\gamma\text{Fe}_2\text{O}_3$) nanoparticles were initially synthesized using the coprecipitation technique and then coated with tetramethylammonium hydroxide (TMAH) molecules in order to obtain a stable aqueous colloidal dispersion of $\gamma\text{Fe}_2\text{O}_3$ nanoparticles. The content of the $\gamma\text{Fe}_2\text{O}_3$ nanoparticles in the final colloid varied from 0.41 wt% to 1.51 wt%. The $\gamma\text{Fe}_2\text{O}_3$ nanoparticles were additionally coated with PVA molecules which differed in molecular weights: from 30.000-51.000 g/mol for PVA-1 through 89.000-98.000 g/mol for PVA-2 to 146.000-186.000 g/mol for PVA-3. The reaction time and temperature varied from 20 min to 90 min and from 80 °C to 90 °C, respectively.

The synthesized powders were characterized by the X-ray diffractometry (XRD) which confirmed the formation of a spinel maghemite ($\gamma\text{Fe}_2\text{O}_3$) nanoparticles with the particle size distribution of around 10 ± 1 nm. Transmission electron microscopy (TEM) indicated mono-dispersed and spherical morphology of the prepared $\gamma\text{Fe}_2\text{O}_3$ product, coated with a thin layer of PVA molecules. Infrared spectroscopy (FTIR) was used to confirm the binding of TMAH and PVA molecules onto the surface of the $\gamma\text{Fe}_2\text{O}_3$ nanoparticles. Electrokinetic potential (ζ) of the prepared PVA-coated $\gamma\text{Fe}_2\text{O}_3$ nanoparticles in aqueous solutions was measured using laser Doppler electrophoresis (ZetasizerNano). Analysis showed that the final colloidal solutions were stable for all the prepared samples and had a negatively charged surface in a wide pH range (> 2.5). Differential scanning calorimetry (DSC) measurements performed under oxidative atmosphere were used to determine the thermal transitions of the PVA molecules. We determined that PVA-coated $\gamma\text{Fe}_2\text{O}_3$ nanoparticles were thermally stable up to 200 °C, whereupon thermal changes of PVA molecules started. The magnetic properties of the prepared PVA-coated $\gamma\text{Fe}_2\text{O}_3$ nanoparticles were also measured using a vibrating sample magnetometer (VSM). Magnetizing curves confirmed the superparamagnetic

characters of the PVA-coated $\gamma\text{Fe}_2\text{O}_3$ nanoparticles, presenting a basis for their potential usage in biomedicine.

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Magnetic nanoparticle with surface modification for biomedical utilization – chemical route and sol-gel method

E. Puscasu¹, L. Sacarescu², N. Lupu³, G. Oanca¹, M. Balasoiu^{4,5} and D. Creanga¹

¹ “Alexandru Ioan Cuza” Univ., Physics Faculty, 11 Blvd. Carol I, 700506, Iasi, Romania, mdor@uaic.ro

² “Petru Poni” Institute of Macromolecular Chemistry, Iasi, Romania, livius@icmpp.ro

³ National Institute of Research and Development for Technical Physics, Blvd. Prof. Dr. doc. D. Mangeron 47, Iași 700050, Romania, nicole@phys-iasi.ro

⁴ Joint Institute for Nuclear Research, Dubna, 141980, Moscow Region, Russian Federation

⁵ Horia Hulubei Institute of Physics and Nuclear Engineering, Bucuresti, Romania
balasoiuaria@yahoo.com

Magnetic nanoparticles (MNP) are already known as suitable vectors of drug and biomolecules to target organs and tissues. Metallic cores as well as surface modification could be carried out by various techniques like chemical route and sol-gel method [1]. Iron oxide magnetic cores were chosen in our study for their biocompatibility and good magnetic properties; their stabilization in water was carried out with organic

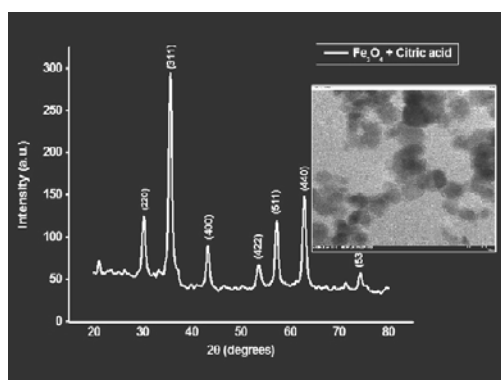


Fig. 1. TEM and XRD results

molecules while further surface modification was done with silica coating that confers further biomolecule grafting affinity. Microstructural and magnetic properties were investigated by standard methods evidencing sub-micron size, good crystallinity, and magnetization capacity (Fig. 1). Comparative analysis was done regarding the electrostatic stabilization provided by first capping layer and steric stabilization related to the second coating layer; benefits and disadvantages of chemical coprecipitation and sol-gel method were emphasized.

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Heavy metals adsorption from diluted aqueous solution by mesoporous silica with different functional groups for functionalization of UF polymeric membrane

Sliesarenko V.¹, Bauman M.², Košak A.^{2,3}, Lobnik A.^{2,3}, Dudarko O.¹, Zub Yu¹

sliesarenko@isc.gov.ua

¹Chuiko Institute of Surface Chemistry, NAS of Ukraine, 17 General Naumov Str, Kyiv 03164, Ukraine

²Institute for Environmental Protection and Sensors, IOS Ltd, Beloruska 7, Maribor 2000, Slovenia

³University of Maribor, Faculty for Mechanical Engineering, Smetanova 17, Maribor 2000, Slovenia

Membrane technology is extremely effective in the field of water and gas purification and also promising to solve environmental pollution problems caused by heavy metals ^[1,2]. However, polymeric UF membranes are not selective to these ions. Therefore, the idea of this research was to create an additional functional layer on the PVDF UF membrane surface that can selectively retain heavy metals ions, while maintaining the productivity (flux) as in the nonmodified membrane. For this mesoporous silica containing functional groups, such as: $-\text{N}(\text{CH}_3)_3\text{Cl}$; $-\text{NH}_2$; $-\text{NHCH}_2\text{CH}_2\text{NH}_2$; $-\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$; $-\text{SH}$; $-\text{PO}(\text{OH})_2$; $-\text{COOH}$ was synthesized by template method ^[3-5]. The presence of functional groups was confirmed by IR spectroscopy. In this work, the application of functional mesoporous silica was focused for UF membrane coating and treatment of wastewater containing 100 mg/L of $\text{Cr}(\text{NO}_3)_3$, $\text{Cd}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$ salt, and removal efficiency analyzed by AAS spectroscopy. The results in Fig.1 show that ammonium groups have no potential for heavy metals removal ($\leq 5\%$), which can be attributed to acidifying synthesis conditions. The best results were observed for the samples with phosphonic ($-\text{PO}(\text{OH})_2$) groups, which enable adsorption $> 50\%$. High removal was also observed for the mercapto ($-\text{SH}$) groups with respect to cadmium $\text{Cd}(\text{II})$, about 39%.

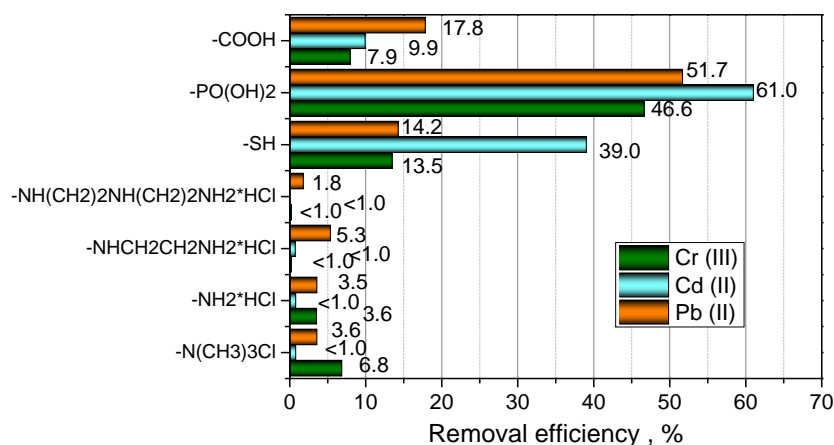


Fig. 1. Removal of heavy metal ions by mesoporous silica with different functional groups.

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New surface engineered TiO₂-MWCNT nanocomposites with diverse functionalities

Mojca Božič^a, Irena Ban^b, Darinka Fakin^a, Karin Stana-Kleinschek^a

^a University of Maribor, Institute for Engineering Materials and Design, Smetanova ulica 17, SI-2000 Maribor, Slovenia, Email: mojca.bozic@um.si

^b University of Maribor, Faculty of Chemistry and Chemical Engineering, Smetanova ulica 17, SI-2000

Photocatalytic reactions on the surface of TiO₂ involve not only photo-excited holes and electrons, but also oxidatively or reductively generated reactive oxygen species (ROS) such as $\cdot\text{OH}$, $\text{O}_2^{\cdot-}$ and H_2O_2 even in the absence of specific irradiation with UV light. Their behaviour has not yet been fully understood. When ROS desorbs from the TiO₂ surface and diffuse into the gas or aqueous phase, their toxicity is questionable. ROS may cause, if produced in excess, oxidative stress or may act as signalling molecules for the immune system. One example is TiO₂ powder used in sunscreen formulations, where free radicals generated under sunlight irradiation are responsible for toxic effects. In order to limit the transportation of ROS from the TiO₂ surfaces into the gas phase, in this contribution we present new photoactive TiO₂-MWCNT nanocomposites with antioxidant modified surfaces, which can capture ROS species. The TiO₂-MWCNT nanocomposites were surface functionalized by using laccase as catalyst to attaching gallic acid polymerized molecules on the nanocomposite surface. Structure and surface functionalization was investigated by X-ray, infrared and UV-vis diffuse reflectance spectroscopy analysis. The antioxidant activity was analyzed using 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) and photocatalytic activity toward the liquid-phase degradation of methylene blue in aqueous solution under both UV and visible light irradiation.

Solution parameters affecting electrospinning of bio-based nano-fibrous mats

Z. Persin¹, M. Kurecic^{1,3}, M. Ravber², K. Stana Kleinschek¹, S. Hribernik¹, Ž. Knez² and M. Škerget²

¹University of Maribor, Faculty of Mechanical Engineering, Laboratory for Characterization and Processing of Polymers, Smetanova 17, SI-2000 Maribor, Slovenia; zdenka.persin@um.si; manja.kurecic@um.si; silvo.hribernik@um.si; karin.stana@um.si

²University of Maribor, Faculty of Chemistry and Chemical Engineering, Smetanova 17, SI-2000 Maribor, Slovenia; matej.ravber@um.si; zeljko.knez@um.si; mojca.skerget@um.si

³Centre of Excellence for Polymer Materials and Technologies, PoliMaT, Tehnološki park 24, SI-1000 Ljubljana, Slovenia; manja.kurecic@um.si

Electrospinning is a process that exploits electrostatic forces for formation of nanofibers with diameter ranging from few tens to hundreds of nanometers. Since the polymer solution, composed of natural and/or synthetic polymers, is exposed to electric field during the electrospinning process, the formation of nanofibers is affected by environmental and operational condition as well as parameters of the prepared polymer solution. The composition of spinning solution greatly influences the solutions' viscosity, conductivity and surface tension and plays a major role in fiber formation.

The spinning solution, used in our study, was composed of polysaccharides (carboxymethyl cellulose and alginic acid sodium salt), olive leaf extract and calcium chloride (PS solution), mixed in different ratios with polyethylene oxide (PEO solution). The morphology of formed fibers, depending on distance between the electrodes and the volume ratio of natural content within the spinning solution, was evaluated using Scanning Electron Microscopy. The presence of active components was determined by High Performance Liquid Chromatography, while the antioxidative activity was detected using the free radical scavenging activity by DPPH. The antimicrobial testing was performed under dynamic conditions using AATCC 100:1999 standard. A noticeable viscosity decrease and conductivity increase by higher PS content (i.e. PS: PEO) 40:60; 50:50; 60:40) used in spinning solution, was obtained. The added olive leaf extract slightly increase the conductivity, while the most effect was noticed as decrease in surface tension. In both cases (solution with and without extract) the formation of uniform nanofibers was noticed when the distance between the electrodes increased from 15 up to 17 cm. The chromatographs confirm the presence of hydroxytyrosol and oleuropein resulting in antioxidative inhibition and reduction on *E. coli* and *S. aureus*. The results obtained within this study predict the optimum operational parameters as well as spinning solution composition and volume ratio for creating bio-based mats with finest fiber diameter.

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Metal ion doping TiO₂ layers prepared by sol-gel technique

M. Morozova¹, P. Dragounova¹, P. Dytrych¹, U. Ragonnaud², O. Solcova¹

¹ Institute of Chemical Process Fundamentals of the ASCR, v. v. i., Rozvojova 135, 165 02 Prague 6,
Czech Republic

² Institut Universitaire de Technologie, 14 allée Jean Monnet, TSA 41114, 86073 Poitiers Cedex 9,
France

Titanium dioxide (TiO₂) is a versatile material that finds utilization in many various applications. It is still considered to be a very promising semiconductor widely used in the field of water or air purification due to its excellent photo-induced properties. The ability of the electron-hole pair generation is important property of photoactive material. This property can be improved by doping process, e.g. transition metal ion doping belongs to the various methods used for increasing the semiconductor photo-activity. Transition metal ions might easily be incorporated with the crystal lattice of TiO₂.

Titanium dioxide doped by Fe, Ce or Zr ions is able to the efficient sunlight absorption and thereby increase the photo-induced activity of TiO₂. Besides that, the metal ion doping leads to structural modifications in the TiO₂ crystallographic lattice which opens up the possibility of changing the electron structure. Generally, Fe ions could enhance hydrogen production effectively and possess an important effect in photocatalytical process; Ce ions create a large number of oxygen vacancies and Zr ions affect the surface defects.

The sol-gel technique is commonly used for the nanoscaled metal oxides thin layers preparation. Metal-doped TiO₂ thin layers were prepared by the sol-gel technique controlled in the reverse micellar environment. In this case the chemical process of hydrolysis and polycondensation takes place in the core of reverse micelles. This provides the uniform particle size in layers. Prepared TiO₂ layers were deposited on a substrate by the dip-coating method and then the organic matter was removed by calcination. The surface properties of the calcined layers were determined by Raman spectroscopy, SEM, UV-Vis analyses and by XPS. The photo-induced properties of nanoparticulate TiO₂ layers were studied by electrochemical measurements combined with UV irradiation.

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Single particle ICP-MS: A powerful tool for sizing and quantification of TiO₂NPs in environmental water samples

Janja Vidmar^{1,2}, Radmila Milačič^{1,2}, Janez Ščančar^{1,2}

¹ Department of Environmental Sciences, Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia

² Jožef Stefan International Postgraduate School, Jamova 39, 1000 Ljubljana, Slovenia

As a consequence of their widespread use, titanium dioxide nanoparticles (TiO₂NPs) have been released into the environment where they can act as stressors towards biota. For the assessment of the environmental impact of these NPs it is important to quantitatively determine their concentration and size distribution in different water samples. In the present work, a new analytical approach was applied for the determination of concentration and size distribution of TiO₂NPs in anatase and rutile dispersed in river water samples by the use of single particle inductively coupled plasma mass spectrometry (SP-ICP-MS). This technique requires minimal sample preparation, offers superior sensitivity, and enables also simultaneous characterization of analyte in nanoscale and dissolved forms. Suspensions of TiO₂NPs were sufficiently diluted (ng L⁻¹ level) and short integration times (10 ms) used in order to measure the intensity of single particle as a single pulse. Under such conditions, the frequency of pulses was proportional to the number concentration of NPs and the number of counts of each pulse was related to the NP size [1].

Sizing and simultaneous quantification of TiO₂NPs and dissolved Ti form in environmental waters was performed on river water sample collected at Sava River (Litija, Slovenia) during the first sampling campaign of the EU 7th FW funded GLOBAQUA project [2] in September 2014. The concentrations of nanoscale Ti (below the LOD_{NP}) and dissolved Ti (0.588 ± 0.022 ng Ti mL⁻¹) were determined in river water by SP-ICP-MS. To evaluate the influence of sample matrix on the determination of TiO₂NPs mass concentration and their size, river water was spiked with different concentrations of nanoscale rutile and anatase. Good recoveries, defined as the ratio between the determined and expected TiNPs mass concentrations, were obtained, while the diameters of TiO₂NPs in the river water sample (128 and 44 nm for rutile and anatase, respectively) were slightly higher than those provided by the manufacturer (< 100 and < 25 nm for rutile and anatase, respectively). It was demonstrated that the SP-ICP-MS procedure developed can be applied in sizing and quantification of TiNPs in environmental water samples.

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Low-temperature TiO₂/ZrO₂/SiO₂ photoactive thin films on glass

N. Vodišek and U. Lavrenčič Štanger

Laboratory for Environmental Research, University of Nova Gorica (Vipavska 13, Rožna Dolina, 5000

Nova Gorica, nives.vodisek@ung.si)

Photocatalytic properties of nanosized TiO₂ are well-known and investigated. With adding another semiconductor or metal, functional properties of thin films can be improved. Addition of zirconia improves, among some other properties ^[1], the mechanical quality of resulting thin films, which is especially evident upon aging of the samples.

Mixture of titanium isopropoxide (TTIP), zirconium tetrabutoxide (ZTB) and ethanol was hydrolysed in acidified water (HClO₄). Acid acts as a peptizing agent and stabilizes the sol. White amorphous TiO₂ and ZrO₂ are formed and refluxed for 48 hours. During this process, crystallization and deaggregation take place and that leads to stable TiO₂-ZrO₂ sol ^[2]. For better adhesion and homogeneity of thin films, silica binder was added and it contains tetraethoxysilane (TEOS), Levasil, 1-propanol and HCl ^[3]. Different properties of resulting samples are related to different concentration of Zr. Four solutions were prepared with various molar ratios between Ti and Zr: i) 100:0; ii) 10:1; iii) 5:1 and iv) 20:1. For applying thin films on glass substrates dip-coating technique was used. After deposition films were heat treated in the furnace at 150°C.

Photocatalytic activity was measured with two methods: i) determination of degradation ratio of methyl stearate with measuring the contact angle and ii) degradation of terephthalic acid to hydroxyterephthalic acid measured by spectrofluorometer ^[3]. UV-Vis transmittance measurements, photoinduced superhydrophilicity and SEM analyses were also performed on the samples.

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Nanocolloids from polysaccharide and alkaline nanoparticles – application in cultural heritage preservation

T. Mohan^{1,*}, L. Amornkitbamrung¹, M. Bračič², S. Hribernik², T. Palani¹, R. Kargl², K. Stana-Kleinshek², V. Ribitsch¹

¹Institute of chemistry, University of Graz, Heinrichstrasse 28, Graz 8010, Austria. E-mail: tamilselvan.mohan@uni-graz.at

²Institute for engineering materials and design, university of Maribor, Smetanova Ulica 17, 2000 Maribor, Slovenia

The deterioration of cellulose-based items such as papers, books and other written documents over time has been a serious problem for libraries and conservators around the world. A main cause of deterioration is the acidity generated upon natural aging. The acids accelerate the hydrolytic scission of cellulose and result in the yellowing and reduction of mechanical strength of paper. In this contribution, we present a method for the simultaneous deacidification and strengthening of aged historical wood pulp (HWP) paper using nanocolloids prepared from an organo soluble polysaccharide derivative and an alkaline nanoparticles^[1]. Colloidal dispersions of alkaline nanoparticles (Mg(OH)₂, size: ca. 150 nm) stabilized by trimethylsilyl cellulose (TMSC) in hexamethyldisiloxane (HMDSO) are employed for coating of HWP paper. The influence of the polymer shell on the particles size and morphology, and the stability of the dispersion is examined in detail. The influence of the treatment on the pH, the alkaline reserve and the mechanical strength of the coated paper is investigated. Infrared spectroscopy confirms the irreversible deposition of alkaline nanoparticles and polymers on the paper. The surfaces are evenly coated and the nanoparticles penetrate also into the inner fiber structure of the paper as confirmed by electron microscopy and contact angle measurement. The long term effect of treatment is investigated by artificial aging. This process is versatile and can be extended to other kinds of cellulose-based materials such as wooden artefacts.

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Decontamination of Transformer Oils by Nanoporous Sorbents

M. Matejkova, B. Papezova, F. Kastanek, O. Solcova

Institute of Chemical Process Fundamentals of the CAS, v.v.i., Rozvojova 135/02, 16500, Prague 6,
Czech Republic

Sulphur compounds occur as contaminants in oils used in power transformers which may cause failure in oil insulated power apparatus due to deposition of copper sulphide on the conductors and in the insulation paper. Therefore, it is necessary to find an effective way to decontaminate such oils to prevent failures of power transformers. Even now, contamination of oil-filled transformers and cleaning oils used to wash auxiliary equipment is still a problem. The sulphur compounds tend to react with the copper windings, forming harmful by-products such as Cu_2S . Dibenzyl disulphide (DBDS) has been found to be the leading corrosive sulphur compound in the insulation oil.

Three types of sorbents (two natural Bentonites from different locations and one activated alumina) were applied for purification of two different oils. All used sorbents were comprehensively characterized by Nitrogen physical adsorption, Mercury porosimetry and Helium pycnometry. The structure of activated alumina was additionally described by XRD analysis. Sulphur compounds were determined by GC-SCD and DBDS by GC-EC.

The sorption experiments were performed in the filled column (length 450 mm, inner diameter 28 mm) in the same conditions and the sorption capacities of each sorbents were compared. The volume ratio of oils to the sorbents was 1.5:1.

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**Luminescent water/ethanol - soluble lanthanide complex with
possible applications on “bio-sensors”**

**Nuša Hojnik¹ Matjaž Kristl¹, Gregor Ferk¹, Amalija Golobič², Matejka Turel³, Zvonko
Jagličič⁴,
Miha Drofenik^{1,5}**

¹University of Maribor, Faculty of Chemistry and Chemical Engineering, Smetanova 17, SI-2000
Maribor, Slovenia

(e-mail: nusa.hojnik@gmail.com)

²University of Ljubljana, Faculty of Chemistry and Chemical Technology, Večna pot 113, SI-1001
Ljubljana, Slovenia

³Institute for Environmental Protection and Sensors, Beloruska 7, SI-2000 Maribor

⁴Institute of Mathematics, Physics and Mechanics, Jadranska 19, SI-1000 Ljubljana, Slovenia

⁵Jozef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia

Over the last few years the interest in lanthanide chelates as light emitting materials for photonic applications, such as light emitting diodes (LED) optical fibres and biomarkers, has increased remarkably^{1,2}. Due to their unique luminescent properties the lanthanide complexes may be applied as a molecular probe for generating image or monitoring the change in intracellular pH, due to the changes in the emission intensity caused by the protonation or deprotonation of the ligand coordinated to the emitting ion³.

In order to obtain complexes with high quantum efficiencies, it is necessary to choose organic molecules with pronounced internal conversion, efficient energy transfer from the ligand to the metal ion, and an efficient luminescent ion.

In this work, europium(III) and terbium(III) ions were complexed with 2-aminobenzothiazole and 2,6-pyridinedicarboxylic acid, resulting in a water/ethanol soluble and highly luminescent complexes. The luminescent spectra of the obtained complexes are shown in Figure 1.

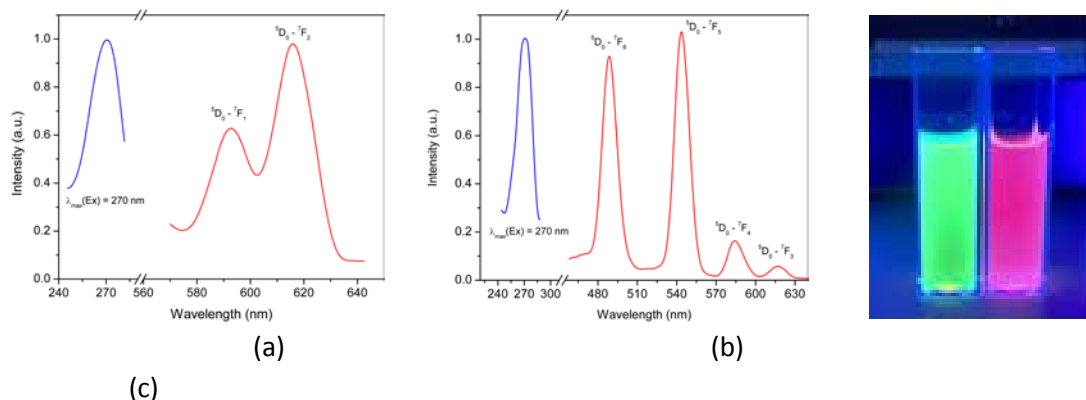


Fig.1: Excitation and emission spectra of europium (a) and terbium (b) trivalent complex with 2,6-pyridinedicarboxylic acid and 2-aminobenzothiazol as ligands. (c) water/ethanol solution of the europium(III) and terbium(III) complex under UV light.

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Nanoparticles formed by amphiphilic 1,4-dihydropyridine derivatives

M. Rucinskis, K. Pajuste, M. Gosteva, A. Sobolev, B. Cekavicus, Kl. Pajuste, B. Vigante, A. Plotniece

Latvian Institute of Organic Synthesis (Aizkraukles str. 21, Riga, LV-1006, Latvia, rucinskis@osi.lv)

Cationic derivatives that possess self-assembling properties and are able to form liposomes in aqueous solutions have received widespread attention in gene delivery.^[1] Polyfunctional pyridinium derivatives on the 1,4-dihydropyridine (1,4-DHP) scaffold possess self-assembling properties. 1,4-DHP **1** (Fig. 1) forms liposomes and efficiently acts as gene delivery agent.^[2,3] The influence of lipids head-groups on transfection activity^[4] and properties of formed liposomes^[5] were studied.

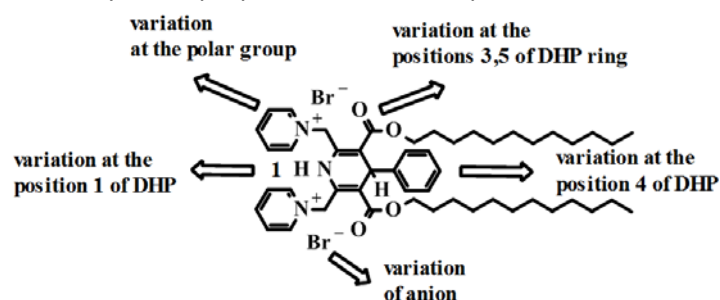


Figure 1. Variety of the family of cationic amphiphiles on the 1,4-DHP core.

The aim of this study is modification of the substituents of 1,4-DHP **1** at the positions from one to six (Fig. 1) for clarification of the relationships between biological activity and physical-chemical properties of self-assembling 1,4-DHPs: for individual compounds and their formed nanoaggregates. Novel group of self-assembling amphiphiles with various substituents of 1,4-DHP core were synthesised. All studied 1,4-DHP amphiphiles were found to possess self-assembling properties, such as formation of nanoparticles. DLS measurements of nanoaggregates of synthesized amphiphiles were performed and it was found that studied amphiphiles had mean diameter 90-350 nm, mean zeta-potential 49-64 mV.

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Synthesis, structural characterization and catalytic activity of a novel Cu^{II} (Sal-Ala)/CuAILDH hybrid material

Mihaela Mureşeanu^{1*}, Magda Puşcaşu², Gabriela Cârlă^{2*}

¹ Faculty of Chemistry, University of Craiova, 107 I Calea Bucureşti, 200478, Craiova, Romania (* email: mihaela_mure@yahoo.com)

² Faculty of Chemical Engineering and Environmental Protection, Technical University of Iasi, 71 D. Mangeron, Iasi, Romania (* email: carja@uaic.ro)

The design of heterogeneous oxidation catalysts by molecular control of active species and their uniform distribution into a controlled environment can allow fine-tuning of material in order to improve its reactivity, selectivity and potential applications ^[1]. The clay-based heterogeneous catalysis have many practical and potential applications in green and sustainable chemistry ^[2] since clay minerals provide distinct nanometer-scaled layers and interlayers for engineering them as active catalysts.

We present in this work the facile synthesis of a novel hybrid material based on the Cu^{II}(Sal-Ala) complex (Sal-Ala represents Schiff base ligand made up of salicylaldehyde with alanine amino acid) immobilized on the Cu-Al-layered double hydroxide (CuAILDH) support. Powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR), diffuse reflectance UV-vis spectroscopy (DRUV) and thermogravimetric analysis (TGA) were used to investigate the physical-chemical properties of the studied catalysts. The cyclohexene oxidation by H₂O₂ and the superoxide dismutase (SOD) activity were demonstrated both for the hybrid catalyst and for the CuAILDH support. Interesting is that the support itself present an important catalytic activity that was improved for both tested reactions after complex immobilization. The influence of the copper chemical state in the active site and its microenvironment on the catalytic performance of the synthesized catalysts were discussed.

The oxidative and biomimetic SOD activities of this new catalyst was superior to other catalytic systems. In addition, an oxidation system that uses H₂O₂ in conjunction with cheap, relatively non-toxic heterogeneous catalysts is potentially viable for large scale production of inexpensive products and for specialized applications in industry and research.

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Synthesis, evaluation, and release studies of NIPA nanoparticles presumed for temperature controlled drug delivery

Monika Gasztych¹, Julija Volmajer Valh², Agnieszka Gola¹, Witold Musiał¹

¹Wrocław Medical University, Faculty of Pharmacy, Department of Physical Chemistry, Borowska 211, 50-556 Wrocław, Poland, witold.musial@umed.wroc.pl

² University of Maribor, Faculty of Mechanical Engineering, Institute of Engineering Materials and Design, Laboratory for Chemistry and Environmental Protection, Smetanova 17, 2000 Maribor, Slovenia, julija.volmajer@uni-mb.si

Introduction: N-isopropyl acrylamide (NIPA) derivatives are widely researched due to unique feature: sharp and reversible volume phase transition at 32°C, corresponding well to physiological value, i.e. for targeted or controlled drug release^[1,2]. The hydrodynamic diameter of nanomolecules influences the possibility of practical application of the particles to selected human organs and tissues. Application of kinetic methods taken from pharmaceutical praxis, used for evaluation of release rate constants, and half-release times, enable prediction of potential applicative field of the NIPA nanoparticles.

The aim of the work was to evaluate the influence of selected co-monomers used in the synthesis of NIPA co-polymers on the release rate and on the potential applicative field of the NIPA co-polymers.

Methods: Nanospheric derivatives of NIPA were produced by surfactant free precipitation polymerization (SFPP). The composition and morphology were confirmed by IR, NMR and SEM. HD was measured by DLS method. Evaluation of the release kinetics of model biologically active substances – nonsteroidal antiinflammatory drugs (NSAIDs), was performed according to the modified pharmacopoeial standards, included in European Pharmacopoeia and in United States Pharmacopoeia. The release rate constants, as well as the half-release times, due to the zero-order and first order kinetics were calculated, and statistically compared.

Results and discussion: Due to IR assay, vinyl group were identified in the NIPA monomer at 808, 664, 3104 and 3030 cm⁻¹ and disappeared from the spectra after SFPP. ¹H NMR spectra proved implementation of used co-monomers into polymer. Hydrodynamic diameters were in the range between 400 and 800 nm, and possessed characteristic volume phase transition temperature. The assessed release rate constants were between 4,64 x 10⁻⁴ h⁻¹, and 5,84 x 10⁻⁴ h⁻¹, depending on the type of co-monomer, and temperature of acceptor medium in the release experiments. In most of the cases the release kinetics was congenial to the first order kinetics, as it is presented on the Fig. 1

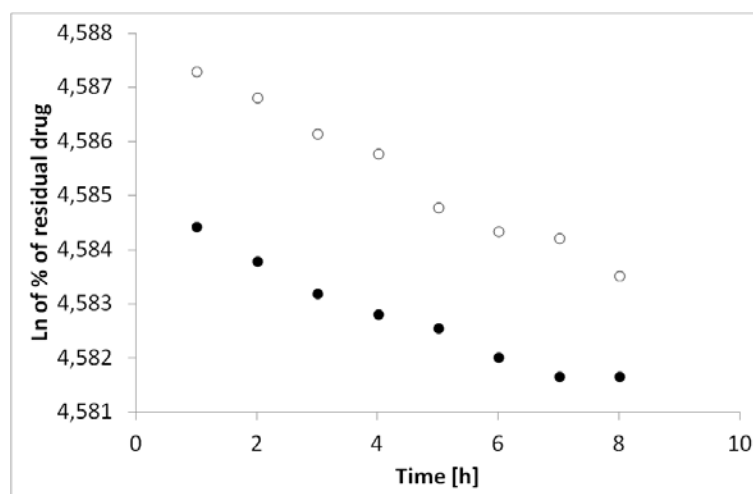


Fig. 1. The kinetics of release of the model NSAID at various temperatures. The white circles (o) represent release kinetics at the temperature over VPPT, whereas the black dots represent the release kinetics at the temperature maintained below VPTT.

Conclusions: The release experiments, performed parallel with spectral methods, and DLS measurements, enabled evaluation of nanoparticles prepared by SFPP. The synthesized nanoparticles have potential for application as drug carriers applied in targeted and controlled drug delivery formulations.

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Determination of biogenic-amines using functionalized silica particles

P. Nedeljko¹, M. Turel¹, A. Kosak^{1,2}, A. Lobnik^{1,2},

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

(polonca.nedeljko@ios.si)

² University of Maribor, Faculty of Mechanical Engineering, Centre for Sensor Technology, Smetanova 17, 2000 Maribor, Slovenia (aleksandra.lobnik@um.si)

Biogenic amines (BAs) are classified as mono- or poly-amines according to their amine content ^[1]. They can be formed and degraded as a result of normal metabolic activity in animals, plants, microorganisms and humans and are usually produced by the decarboxylation of free amino acids. Development of materials for sensor applications has become one of the most important areas of interest and research in recent decades. Hybrid nanomaterials based on silica (SiO₂) 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 ^[2]. In the preparation of the hybrid silica materials, functionalization of the surfaces of silica particles with hydroxyl, amino, thiol, carboxyl groups, etc., is often the first step in their various applications ^[3].

In this study, we report on the fluorimetric method for the determination of biogenic amines based on 3-mercaptopropyltrimethoxysilane (MPTMS) functionalized silica particles (SH-SiO₂) in combination with indicator dye o-phthaldialdehyde (OPA). Obtained nanoparticles were characterized using infrared spectroscopy (FT-IR), transmission and scanning electron microscopy (TEM/SEM), zeta potential, particle size distribution and potentiometric titration.

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Rhodamine 6G incorporated silica particles as potential hard templates for preparation of hollow spheres

M. Lakić¹, A. Košak^{*1,2}, A. Lobnik^{1,2}

¹University of Maribor, Faculty of Mechanical Engineering, Centre of Sensor Technology,
Smetanova ulica 17, SI-2000 Maribor, Slovenia

²Institute for Environmental Protection and Sensors, IOS, Beloruska 7, SI-2000 Maribor, Slovenia
(lakic.marijana@gmail.com; aljosa.kosak@siol.net * (Corresponding author))

Hollow spherical microstructures and nanostructures, have recently attracted attention due to their internal hollow space that 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, 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. One of the most commonly used hard templates are monodispersed silica particles due to their narrow size distribution, ready availability in a relatively large amounts and in wide range of sizes, and also simplicity of their synthesis^[2]. Incorporation of fluorescent dye rhodamine 6G (R6G) in silica templates gives traceability to particles and opportunity of using this particles in biomedical applications.

In this study, we present synthesis of monodisperse silica particles with incorporated fluorescent dye R6G as hard templates for preparation of hollow spheres. Monodispersed silica (SiO₂) particles were prepared using the Stöber method, which was based on the hydrolysis and condensation of a tetraethoxysilane (TEOS) precursor in the presence of ammonia within a mixture of alcoholic/R6G water solution. We tested three different concentrations of R6G (aq) – 0,05M, 0,1M and 0,15M. Product obtained after the synthesis, was subsequently centrifuged and washed with distilled water and each supernatant was measured by UV/VIS spectroscopy in order to find out the effect of washing - dye leaching. Final Rhodamine 6G incorporated solid SiO₂ product was dried and characterized using fluorescent microscopy, Fourier transform infrared spectroscopy (FTIR), and specific surface area measurements (BET).

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