

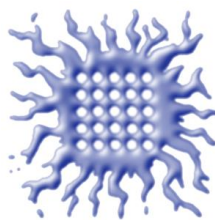


**European Cooperation
in Science and Technology**

**Workshop on Synthesis of advanced nano-and bio-colloidal
materials with highly active surfaces**

Joint Meeting of WG3 and WG4
COST Action CM1101
June 30-July 01, 2014
Belgrade, Serbia

Program and Abstracts



Vinča Institute of Nuclear Sciences

Organization

COST Action CM1101

Colloidal Aspects of Nanoscience for Innovative Processes and Materials

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WG 4 – Kinetic and catalytic aspects of nano-colloids and nano-structured surfaces, Leader: Dr

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Web-site: <http://costbg1101.elexcomm.com/#home>

Venue: University of Belgrade Rectorate Building, Studentski trg 1, Belgrade, Serbia

Program

| Monday, June 30, 2014 | | |
|-----------------------|--------------------------|---|
| 8.30-9.00 | Opening | |
| Session 1 | | |
| 9.00-9.40 | Thomas Hellweg | Smart core-shell microgels: synthesis and properties, P1 |
| 9.40-10.00 | Klaus von Haeften | Formation of colloidal nanoparticles by deposition of metal vapours onto liquid microjets, ST1 |
| 10.00-10.20 | Nadica Abazović | Tuning of reaction conditions in the synthesis of I-III-VI semiconductors, ST2 |
| 10.20-10.40 | Peter Lobotka | Nanocolloids prepared by vacuum sputtering of metals on an ionic liquid, ST3 |
| 10.40-11.10 | Coffee break | |
| Session 2 | | |
| 11.10-11.50 | Marc Koper | Electrochemistry of nanoparticles, P2 |
| 11.50-12.10 | Yolanda Piñeiro Redondo | Metallic quantum clusters, jellium model and applications, ST4 |
| 12.10-12.30 | Imre Dékány | Characterization of antibacterial silver and copper nanoparticles functionalized TiO ₂ composite photocatalysts, ST5 |
| 12.30-12.50 | Ger Koper | Carbon NanoNetworks for fuel cells, ST6 |
| 12.50-14.30 | Lunch | |
| Session 3 | | |
| 14.30-15.00 | Gordana Čirić-Marjanović | Progress in polyaniline composites with transition metal oxides, I1 |
| 15.00-15.20 | Marija Radoičić | Ferromagnetic polyaniline/TiO ₂ nanocomposites, ST7 |
| 15.20-15.40 | Pavol Kunzo | Electrophoretic deposition of nanoparticles synthesized in ionic liquids, ST8 |
| 15.40-16.00 | Katarzyna Kilan | Influence of different cations on properties of alginate containing multilayers for biomedical application, ST9 |
| 16.00-16.20 | Wuge H. Briscoe | Sustained frictional instabilities on nanostructured surfaces: <i>Stick-slip amplitude coefficient (SSAC)</i> , ST10 |
| 20.00 | Gala – Dinner | |

| Tuesday, July 01, 2014 | | |
|------------------------|-------------------------|--|
| Session 4 | | |
| 9.00-9.30 | Maja Radetić | Functionalization of textile materials with colloidal Ag and TiO ₂ nanoparticles, I2 |
| 9.30-9.50 | László Janovák | Development of photocatalyst/ polymer hybrid films for the inactivation of bacteria by visible light, ST11 |
| 9.50-10.10 | Jelena Krstić | Kinetic aspects of Ag ⁺ -ions releasing mechanism from nano-Ag/hydrogels synthesized by γ -irradiation, ST12 |
| 10.10-10.30 | Krzysztof Szczepanowicz | Targeted drug delivery system based on polyelectrolyte nanocapsules, ST13 |
| 10.30-11.00 | Coffee break | |
| 11.00-11.20 | Hector Torres Pierna | Liquid-Filled Capsules as Fast Responsive Photochromic Materials, ST14 |
| 11.20-11.40 | P. Alonso-Cristobal | Development of a DNA sensor based on upconversion nanoparticles and graphene oxide, ST15 |
| 11.40-12.00 | Georgia Pilkington | Dendritic nanofluids mediating surface forces, ST16 |
| 12.00-12.30 | Piotr Warszynski | Horizon2020, Closing |

PLENARY TALKS

P1**Presenting Author: Thomas Hellweg****E-mail: thomas.hellweg@uni-bielefeld.de****Smart core-shell microgels: synthesis and properties****T. Hellweg^a**^a*Bielefeld University, Faculty of Chemistry, Physical and Biophysical Chemistry, Universitätsstr. 25, 33615 Bielefeld, Germany*

Over the last decade smart microgels have been increasingly recognized as potential building blocks for photonic materials, catalytic carriers and sensors.[1] This applicability mainly comes from the fairly unlimited tuning possibilities of swelling properties as well as scattering properties of those particles.

This contribution presents some of our work related to core shell-structures microgels and elucidates the use of core-shell microgels with inorganic and also with organic cores. Inorganic nanoparticle cores inside a responsive polymer shell allow to make responsive colloidal crystals with a photonic band gap [2]. They are also interesting with respect to 2D assemblies which might exhibit plasmon coupling.

Moreover, a new system-class of *non* (*N*-isopropyl acrylamide)-based core-shell microgels that exhibit a linear thermoresponsive behavior in a temperature range between 25°C and 40°C will be presented. It is the combination of distinct materials in core and shell that gives these particles unique, reversible swelling behaviour.

For the first part of this study we synthesized statistical copolymers from *N*-*n*-propylacrylamide (NNPAM) and *N*-isopropylmethacrylamide (NIPMAM) and study their behavior by means of scattering techniques [3]. Moreover, we have synthesized core-shell microgels from these monomers with differently cross-linked cores. This approach was inspired by the work of the Richtering group. [4] Photon correlation spectroscopy allowed us to study the temperature dependent swelling, which revealed a significant influence of the core properties on the overall core-shell behavior. A major finding of these experiments is that the swelling becomes linear dependent on temperature and the crosslinker content of the core is directly related to the linear response. The core-shell particles behave piezo-like and might have potential as actuators [5].

1) A. Fernandez-Nieves et al., *Microgel Suspensions*, (2011), Wiley VCH, Weinheim, Germany.

2) M. Kargel et al., *Adv. Func. Mater.*, **21** (2011) 4668.

3) B. Wedel, *Zeitschrift f. Physikal. Chem.*, **226** (2012) 737.

4) I. Berndt et al., *Macromolecules* **36** (2003) 8780.

5) M. Zeiser et al., *Polymer*, **53** (2012) 6096.

P2

Presenting Author: Marc Koper**E-mail: m.koper@chem.leidenuniv.nl**

Electrochemistry of nanoparticles

S.E.F.Kleijn,^a A.I.Yanson,^a P.Rodriguez,^{a,c} S.C.S.Lai,^b P.R.Unwin,^b M.T.M.Koper^a^a*Leiden Institute of Chemistry, Leiden University, PO Box 9502, 2300 RA, Leiden, The Netherlands*^b*Department of Chemistry, University of Warwick, UK*^c*School of Chemistry, University of Birmingham, UK*

This talk will discuss the electrochemistry and electrocatalysis of and at nanoparticles. The shape and size of nanoparticles profoundly influence the rate of electrochemical reactions and it will be discussed how this is related to the type of catalytically active sites available on the surface of the nanoparticle [1]. An electrochemical method for the preparation of size- and shape-controlled nanoparticles based on the phenomenon of cathodic corrosion will be illustrated [2]. These particles have a high activity for electrocatalysis. Finally, methods to characterize the electrochemistry of individual nanoparticles will be discussed [3].

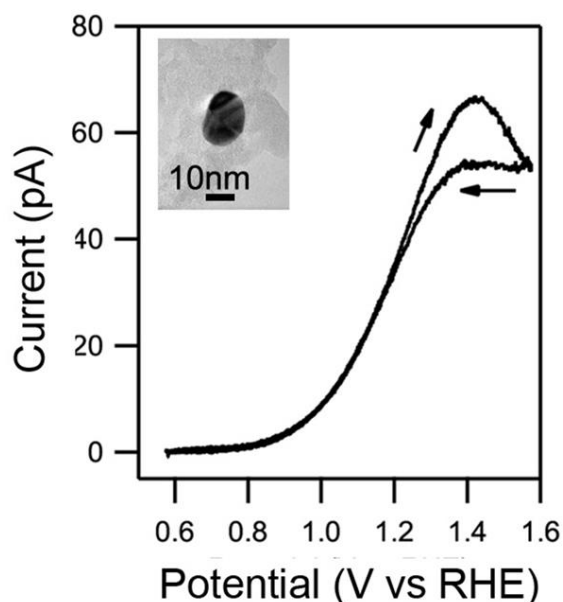


Fig.1 Electrochemistry of hydrazine oxidation at a single gold nanoparticle

- 1) M.T.M Koper, *Nanoscale*, **3** (2011) 2052.
- 2) A.I.Yanson, et al. *Angew.Chem.Int.Ed.*, **50** (2011) 6346.
- 3) S.E.F.Kleijn et al., *J.Am.Chem.Soc.* **134** (2012) 18558

INVITED TALKS

II

Presenting Author: Gordana Ćirić-Marjanović**E-mail: gordana@ffh.bg.ac.rs**

Progress in polyaniline composites with transition metal oxides

G. Ćirić-Marjanović*Faculty of Physical Chemistry, University of Belgrade, Serbia*

During the last three decades polyaniline (PANI) became the one of the most extensively studied conducting polymers due to its simple synthesis, low cost, high electrical conductivity, unique redox and acid-base properties, excellent environmental stability and numerous potential applications in many fields. Advanced applications are based on rapid development of the knowledge about PANI nanostructures in the 21th century. The preparation of PANI composites has attracted a great attention in recent years as the most reliable way to improve PANI processability as well as its functions and applicability.

This lecture presents an overview of recent advances in the preparation, characterization and applications of PANI composites with transition metal oxides such as TiO₂, ZnO, MnO₂, Fe₃O₄, FeO, Fe₂O₃, V₂O₅, Cr₂O₃, Cu₂O, CuO, Co₃O₄, NiO, ZnO, Y₂O₃, ZrO₂, Nb₂O₅, MoO₃, RuO₂, PdO, CdO, Ta₂O₅ and WO₃.

Special attention was paid to the preparation of PANI nanostructures (e.g., nanotubes, nanofibers) in the presence of transition metal oxide nanoparticles. PANI composites with transition metal oxides were successfully prepared by various techniques: the chemical/electrochemical oxidative polymerizations of aniline in the presence of corresponding transition metal oxide micro/submicro/nanostructures, reduction of transition metal compounds by PANI or by external reductants in the presence of PANI, formation of transition metal oxide particles by sol-gel method in the presence of PANI, mixing of PANI and transition metal oxide particles, chemical/electrochemical layer-by-layer technique, etc. The interfacial interactions between PANI and transition metal oxides still remain to be not well understood. Due to the synergistic action of PANI and transition metal oxides in many cases, PANI-transition metal oxide composites were found to show better performance in applications such as p-n heterojunctions, piezoresistive and magnetoresistive devices, electrochromic and photoelectrochemical devices, photovoltaic devices/solar cells, optoelectronic devices/UV detectors, catalysts, electrocatalysts, photocatalysts, photoelectrocatalysts, sensors, photoelectrochemical and microbial fuel cells, supercapacitors, electrode materials for rechargeable batteries, materials for corrosion protection and hydrogen storage, electromagnetic interference shielding/microwave absorption materials, adsorbents for pollutant removal, etc., than PANI and corresponding transition metal oxide alone.

I2

Presenting Author: Maja Radetić**E-mail: maja@tmf.bg.ac.rs**

Functionalization of textile materials with colloidal Ag and TiO₂ nanoparticles

M. Radetić,^a Z. Šaponjić,^b D. Marković,^c V. Lazić,^c M. Radoičić,^a V. Vodnik^b^aUniversity of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4, 11120 Belgrade, Serbia^bDepartment of Radiation Chemistry nad Physics, Vinča Institute of Nuclear Sciences, University of Belgrade, P.O. Box 522, Belgrade, Serbia^cUniversity of Belgrade, Innovation Center, Faculty of Technology and Metallurgy, Karnegijeva 4, 11120 Belgrade, Serbia

The functionalization of textile materials with metal and metal oxide nanoparticles gained much scientific attention over the last decade [1-2]. Textile nano-finishing could be a promising alternative to conventional finishing as the small amount of nanoparticles can impart specific properties to textile materials in different forms (fibers, yarns, fabrics). Ag nanoparticles were the most extensively investigated since they provide extraordinary antimicrobial properties against hundreds of various microorganisms (bacteria, fungi, viruses). On the other hand, photocatalytic activity, non-toxicity, high availability, biocompatibility, and low price make TiO₂ nanoparticles particularly attractive for manufacturing of different high value-added textile goods. Many efforts have been made to immobilize TiO₂ nanoparticles onto textile materials with an aim to fabricate goods with multifunctional properties such as UV protective, self-cleaning and antibacterial.

The impregnation of textile materials with colloidal Ag and TiO₂ nanoparticles is relatively simple by exhaustion method, but insufficient binding efficiency between certain fibers and nanoparticles imposes a problem related to stability and durability of nanocomposite systems during their exploitation. Therefore, recent studies were more oriented towards chemical and physico-chemical modification of fiber surfaces prior to impregnation with Ag and TiO₂ nanoparticles. Plasma treatment of textile surfaces at atmospheric pressure and low pressures ensures superficial chemical and morphological modification of fibers. Controlled plasma processing is limited to the thin surface layers of fibers, leaving the bulk properties unchanged. Hydrophilization of naturally hydrophobic fibers (PET, PA, PP) by plasma treatment is particularly important as fiber surfaces become more accessible for hydrophilic colloidal nanoparticles. In addition, desired functional groups on the fiber surface are introduced which improve binding efficiency of nanoparticles.

Taking into account the importance of environmental impact of novel technologies, potential environmental risks emerging from Ag and TiO₂ release during washing of textile materials became the focus of many recent studies [3].

1) M. Radetić, *J. Mater. Sci.*, **48** (2013) 5447.2) M. Radetić, *J. Photochem. Photobiol. C*, **16** (2013) 62.3) T.M. Benn et al., *Environ. Sci. Technol.* **42** (2008) 4133.

SESSION TALKS

ST1

Presenting Author: Klaus von Haefen

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Formation of colloidal nanoparticles by deposition of metal vapours onto liquid microjets

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Today, wet chemical synthesis is a mature method for the production of nanoparticles, often allowing for excellent control of size, structure and chemical composition. Limitations nevertheless exist: all starting materials need to be soluble; sometimes chemical waste is produced.

Recent developments such as plasma arc discharge and laser ablation in liquids address this issue. The idea behind these methods is to vaporise metals directly in liquids, which has the advantage that practically any metal or metal combinations become available. However, a disadvantage of plasma arc discharge and laser ablation in liquids is the required high concentration of energy within a small volume, resulting in comparatively violent vaporisation with insufficient control at the gas-liquid interface. Controlled vaporisation of metals requires vacuum, but vacuum and liquids cannot normally coexist.

As we show here, a much gentler method of introducing metal vapours into liquids exists via liquid microjets. Liquid microjets exhibit turbulent flow and do not freeze when operated in vacuum. We have shown that vaporisation of metals in vacuum near a microjet results in the deposition of metal atoms onto the liquid surface. The metal atoms enter the liquid, diffuse and - depending on the metal-solvent interaction - react with other metal atoms or the solvent molecules, resulting in the growth of nanoparticles (**Fig. 1 left**) [1].

In this paper, first results demonstrating control of the chemical state and the nanoparticle interaction are presented. We have investigated the growth of silicon and silver nanoparticles using liquid microjets composed of water, ethanol, isopropanol or mixtures thereof. Deposition times lasted typically a few minutes, yielding several millilitres of colloidal nanoparticle solution, which was then investigated using UV-Vis, FTIR, PL, XPS and AFM. Depending on the solvent composition, different oxidation states were observed in the XPS spectrum and in the FTIR spectrum. UV-Vis spectra of silver nanoparticles exhibit a plasmon resonance when ethanol microjets are used, indicating metallic behaviour. When using mixed water-ethanol solvents, the plasmon resonance was found to decrease in intensity when the water concentration increased. Silicon nanoparticles show fluorescence and exceptional stability in aqueous and alcoholic solvents on timescales of years; reversible solvent-exchange confirms this stability, showing distinct solvent-specific fluorescent bands. AFM images of nanoparticle films produced by dropcasting nanoparticle solution onto freshly cleaved highly-oriented pyrolytic graphite (HOPG) revealed exceptionally uniform coverage of the surface and height distributions with discrete steps of 1 nm (**Fig. 1 right**), also suggesting a similarly small size in solution. Repeated dropcasting was found to build multilayers in a Frank-van der Merwe growth mode. Alcohol molecules attached to the films were found to physisorb, showing an increased half-life of desorption compared to interaction with an uncoated substrate.

Our results are relevant for application of novel nanoparticles in drug delivery, the production of conducting inks for printed electronics applications, bio-chemical sensing and opto-electronics.

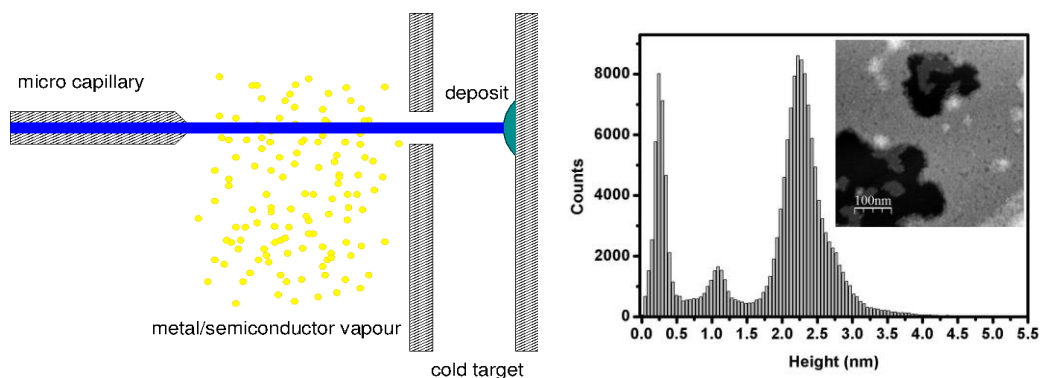


Fig. 1 Left: schematic of experiment. Right: AFM image and height distribution of nanoparticle film.

ST2**Presenting Author: Nadica Abazović****E-mail: kiki@vinca.rs****Tuning of reaction conditions in synthesis of I-III-VI semiconductors****M. Carević,^a N. Abazović,^a M. Čomor^a**^a*Laboratory for Radiation Chemistry and Physics, Vinča Institute of Nuclear Sciences, University of Belgrade, P.O. Box 522, Belgrade, Serbia*

Ternary I-II-VI semiconductors are extensively studied group of compounds being quite promising candidates for photovoltaic and photocatalytic applications. Among them, $\text{AgInS}_2/\text{Se}_2$ and $\text{CuInS}_2/\text{Se}_2$ are especially interesting due to their band-gap energies that lie in visible spectral range. Finding a proper approach for their synthesis is a challenge. Every step in synthesis, choice of proper precursors, solvents and surfactants, estimation of suitable reaction conditions and later, assembly of these materials in solar cells or in their implementation in photocatalytic processes, is very important and can add additional percent at the account of quantum efficiency or photocatalytic activity.

Our method- of- choice was always solvothermal hot-injection method, since it gives wide field for variation of different factors during synthesis of desired semiconductor. Additionally, as this method is widely used for synthesis of II-VI semiconductors, a lot of knowledge acquired during studies of these systems can be used in planning synthesis of I-II-VI semiconductors.

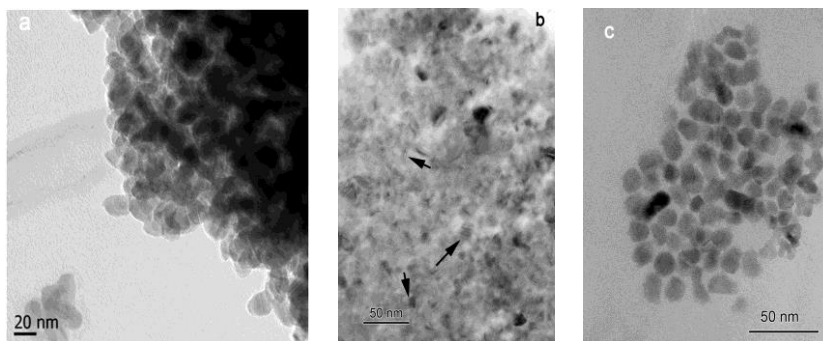


Fig. 1 TEM images of AgInSe_2 nanocrystals synthesized in presence of a) 1-octadecene, b) TOP and c) oleylamine [1]

Here we will give a short overview of our synthetic approaches and knowledge that we have gained during last few years. Special accent will be put at influence of anion precursor and reaction media on shape, size and crystal phase of obtained semiconductor nanocrystals.

- 1) N. Abazović et al., *J. Nanopart. Res.*, **14** (2012) 810.

Acknowledgements

This work is supported by COST Action CM1101.

ST3**Presenting Author: Peter Lobotka****E-mail: eleklobo@savba.sk****Nanocolloids prepared by vacuum sputtering of metals on an ionic liquid****P. Lobotka,^a I. Vávra,^a P. Kunzo,^a G. Radnóczy,^b M. Mičušík^c**^a*Institute of Electrical Engineering, Slovak Academy of Sciences, Dúbravská cesta 9, SK-84104 Bratislava, Slovakia*^b*MFA KFKI Budapest, Hungary*^c*Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, SK-84104 Bratislava, Slovakia*

Torimoto et al. published in 2006 [1] an interesting method of preparation of gold nanoparticles by magnetron sputtering of gold on an ionic liquid (IL). The nanoparticles prepared in this “microelectronic” way using IL as a “liquid substrate”, have very low size dispersion, very high purity, their average size can be tailored by selection of a proper ionic liquid, etc.

We used this progressive method for preparation of nickel, permalloy or Ag-Cu nanoparticles in various ionic liquids. The presence of nanoparticles in the nanocolloids was evidenced by localized surface plasmon resonance (LSPR) that is clearly visible as a peak in UV-vis spectra (Fig. 1). As revealed by TEM, the nanoparticles are faceted and the average size is about 10, 12, and 40 nm (Ni, Ni-Fe, Ag-Cu, respectively). In Figure 2, the nickel nanoparticles are depicted.

We assume, the purity of the nanoparticles is practically the same as that of sputtered target (e.g. 99.99%), which is not the case when the nanoparticles are prepared by heating or irradiation of a mixture of a salt and IL. This can be considered as one of the advantages of this method. Other advantages are: (i) long-term stability. For example, Ni-nanocolloid lasted for two years before the coagulation started. This makes the nanocolloid marketable. (ii) using rf magnetron sputtering it is possible to prepare composite nanoparticles from oxides, nitrides, etc., (iii) the nanoparticles are faceted which makes them attractive for catalysis.

The feasibility of upscaling will be shortly discussed.

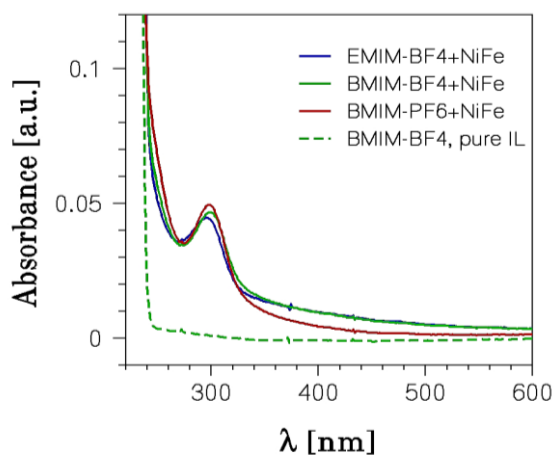


Fig. 1 UV-vis spectra of the nanocolloids containing Ni-Fe nanoparticles. For comparison, the spectrum of pure IL [BMIM]-[BF₄] is shown.

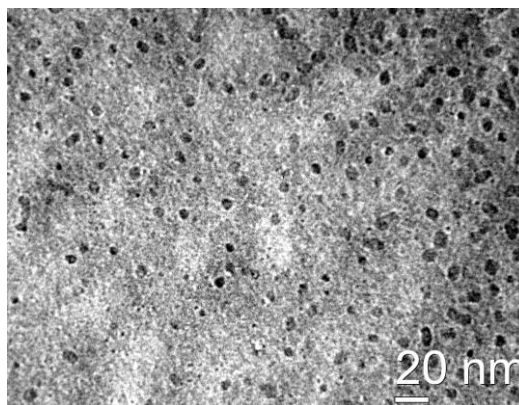


Fig. 2 TEM micrograph of Ni nanoparticles prepared by magnetron sputtering of nickel on [BMIM]-[PF₆] ionic liquid.

1) T. Torimoto et al., *Appl. Phys Lett.*, **89** (2006) 243117.

Acknowledgements

We acknowledge the financial support of the project APVV 593-11.

ST4

Presenting Author: Yolanda Piñeiro Redondo

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Metallic quantum clusters, jellium model and applications

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Subnanometric metallic clusters or atomic quantum clusters (AQC), formed by two to hundreds of atoms, with stable compositions and dimensions below 1-2 nm, stand at the cross-point between fundamental quantum mechanics and classical physics responses.

The combination of their reduced dimensions, which allows them to operate at the same scale of biological objects, together with their unexpected physical properties, provides the possibility to design a plethora of new solutions in different fields as biomedicine, energy or electronics.

Quantum confinement is in the origin of AQC's unexpected physicochemical properties that are critically dependent on their precise number of atoms which allows to tailor physical responses only by controlling the AQC's size. Therefore, a profound knowledge of this strongly-size dependent physics, is not only an appealing challenge from the theoretical point of view but also desirable from the point of view of a reliable technological exploitation.

With this aim, several theoretical approaches with different degrees of detail in the description of the AQC's many-body problem, as ab initio or density functional theories, are under development to obtain precise details of the electronic structure for clusters up to 20 atoms [1]. However, a simple jellium approach based on a 3-dimensional symmetric harmonic oscillator (H.O.) has been able to reproduce the main trends of the size dependent properties of metal QCLs as abundance numbers, shell structure or size dependence of band gap.

In this work experimental results of very small Au, Ag, and Cu-QCLs (2 to 20 atoms) [2,3] will be presented showing, molecular-like absorption bands, photoluminescence, and size dependent HOMO-LUMO gap at the Fermi level compared to theoretical predictions of the H.O. jellium model.

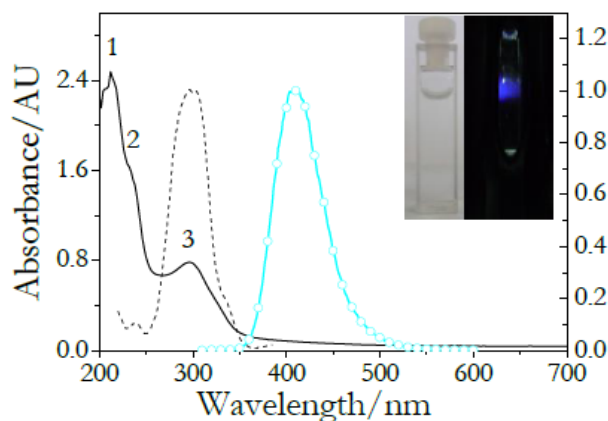


Fig. 1 UV-vis absorption (continuous black line) and luminescence spectrum of Cu-CLs/H₂O, with excitation (dotted line) at 296 (nm) and emission (continuous blue) at 400(nm) (inset shows the blue emission of the CLs)

Compared to QDs, noble metal clusters are highly attractive for bioimaging and biolabeling, due to their lower toxicity, ultra small size and tunable performances [4]. Color emissions in all the UV-Vis-IR range can be achieved by varying the atom metal (Au, Ag, Cu), their size, N, or the ligands, where quantum yields (QY) have been reported to rise up to 70% for small Au₅, [4].

- 1) M. Brack, *Rev. Mod. Phys.*, **65** (1993) 677.
- 2) B.Santiago González, et al., *Nanoletters*, **10** (2010) 4217.
- 3) N.Vilar-Vidal et al., *J. Am. Chem. Soc.* **114** (2010) 15924.
- 4) J. Zheng et al., *Phys. Rev. Lett.* **93** (2004) 077402.

ST5**Presenting Author: Imre Dékány****E-mail: i.dekany@chem.u-szeged.hu****Characterization of antibacterial silver and copper nanoparticles functionalized TiO₂ composite photocatalysts****I. Dékány,^{a,b} L. Janovák,^a S. Tallósy,^a Á. Deák,^a J. Ménesi,^a M. Sztakó,^a Á. Juhász,^c N. Buzás^c**^a Department of Physical Chemistry and Materials Sciences, University of Szeged, H-6720, Szeged, Rerrich B. Square 1., Hungary^bSupramolecular and Nanostructured Materials Research Group of Hungarian Academy of Sciences, H-6720, Szeged, Dóm square 8., Hungary^cNanocolltech Ltd H-6722 Szeged, Gogol u 9/B, Hungary

Plasmonic metal nanodots on TiO₂ photocatalyst nanoparticles has been widely used to extend the light absorption to the visible region [1-5]. Therefore, visible light irradiation combined with the noble metals (Ag, Au) and Cu functionalized photocatalyst is expected to make a significant contribution to the development of the self-cleaning and self-sterilizing surfaces. An alternative method for eliminating bacterial strains that have become resistant to certain antibiotics (e.g. *Staphylococcus aureus*) may be the application of photocatalyst nanoparticles [1-2]. Most of alternative methods are ineffective to inactivate antibiotic resistant bacterial strains, so photocatalyst nanoparticles as antibacterial application have achieved a great scientific interest world-wide.

AgNPs and CuNPs modified TiO₂ photocatalysts were synthesised. The amounts of Cu, Ag and Cu/Ag loading were varied between 0.01 and 0.5 wt.% with respect to the TiO₂. Surface modification of TiO₂ by addition of Ag and Cu NPs resulted in broad absorbance peaks in the Vis range at 455 nm and 565 nm for Ag and Cu, respectively. Photooxidation of ethanol vapour on catalyst films was examined by a gas chromatograph using ethanol as test molecule. The functionalized TiO₂ photocatalysts showed significantly increased photocatalytic degradation rates of ethanol using Vis-light rich light source (characteristic emission peak at 435 nm) with an emitted light intensity of 1.26×10^{-6} einstein/s. This is due to the increased charge carrier separation and delayed recombination due to the presence of noble metal nanoparticles on the surface of TiO₂.

The Cu, Ag and Cu/Ag functionalized photocatalysts that, in addition to being photochemically active, also possess antibacterial activity [1-2, 4]. The antimicrobial effect on the surface was proved with microbiological investigations with the modified standard ISO 27447:2009 method. The functionalized photocatalysts could kill 99.9% of the investigated *Staphylococcus aureus* bacteria after 90-120 minutes of illumination with LED-light source ($\lambda = 405$ nm). The microbiological measurements were supported with fluorescence microscopy and fluorimetric measurements.

Noble metal functionalized titania/ hydroxyapatite (HAP) nanocomposite were also synthesised. The use of inorganic and cheap HAP as additives in titania-based composites was therefore attempted to promote the recruitment of microorganisms for subsequent photocatalytic inactivation.

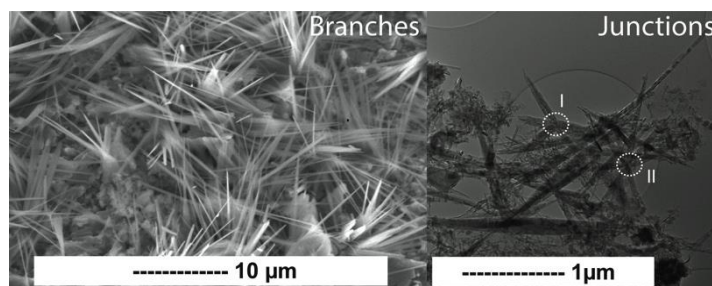
- 1) Sz. P. Tallósy et al., *J. Adv. Oxidation Techn.* **17** (1) (2014) 9.
- 2) Sz. P. Tallósy et al., *Environ. Sci. and Pollut. Research*, (2014), DOI 10.1007/s11356-014-2568-6
- 3) Á. Veres et al., *Colloid Polymer Sci.*, (2013), DOI 10.1007/s00396-013-3063-1.
- 4) Á. Veres et al., *J. Adv. Oxidation Techn.*, **15** (2012) 205.
- 5) Á. Veres et al., *Catalysis Today* **181** (2012) 156.

Acknowledgements

This research was financed by the TÁMOP 4.2.2.A-11/1/KONV-2012-0047, as well as by the MTA-SZTE Supramolecular and Nanostructured Materials Research Group and by the Hungarian National Office of Research and Technology (NKTH) under contract no. TECH-09-A2-2009-0129 (NANOSTER).

ST6**Presenting Author: Ger Koper****E-mail: g.j.m.koper@tudelft.nl****Carbon NanoNetworks for fuel cells****Emanuela Negro and Ger Koper***Department of Chemical Engineering, Technical University of Delft, the Netherlands*

We developed a novel carbon material (see Figure 1) that consists of networked carbon nanostructures. We report on the synthesis of carbon nano-networks (CNNs) consisting of branches that are chemically bonded into junctions and of which the dimensions can – to a certain extent – be controlled. The synthesis involves three phases: the formation of a carbon catalyst network from a dense microemulsion in which catalyst nanoparticles have been synthesized directly, the growth of branches from a carbon containing gas, and the subsequent annealing. The influence of a variety of process conditions was studied. CNNs show attractive properties for catalysis of fuel cells such as high specific surface area, high electrical conductivity, great oxidation resistance, surface defects increasing the material ability to disperse in solution and to simplify integration into polymer matrices. In order to test their performance as a fuel cell catalyst support, CNNs were functionalized with either Pt or non-noble metal Fe-N/C catalyst. Functionalized CNNs were either deposited with spraying or blading or directly grown on on the electrode support. Activity for Oxygen Reduction Reaction and durability to potential cycling or potential holding was tested and benchmarked with commercial catalyst and Carbon Nano-Tubes, CNTs. We demonstrate that CNNs can be successfully used as a more durable support compared to commercially used carbon supports while their performance is comparable to that of CNTs. Since CNN mass production is expected to be cheaper than for CNTs because of the simplicity of the synthesis route, we conclude that CNNs are a promising material for the fuel cell market.

**Fig. 1** Carbon NanoNetworks.

ST7

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Ferromagnetic polyaniline/TiO₂ nanocompositesM. Radoičić^a, Z. Šaponjić^a, G. Ćirić-Marjanović^b^aVinča Institute of Nuclear Sciences, University of Belgrade, P.O. Box 522, Belgrade, Serbia^bFaculty of Physical Chemistry, University of Belgrade, Belgrade 11158, Serbia

Magnetic properties of polyaniline (PANI) and its derivatives have been extensively studied because they can provide important data on charge-carrying species and unpaired spins. It has been found that the magnetic susceptibility of doped PANI is strongly influenced by the manner of polymer preparation (e.g., doping level, dopant type), and measuring conditions (temperature, applied magnetic field) [1]. There are a lot of studies of magnetic properties of PANI, but the articles reporting the ferromagnetic behavior of PANI and its nanocomposites are scarce [2]. Magnetic properties of PANI/TiO₂ nanocomposites have not yet been extensively examined [3]. The goal of the present work was to investigate the magnetic properties of novel PANI/TiO₂ nanocomposites, along with their characterization by various techniques to obtain information on their molecular and crystalline structure, morphology, and electrical conductivity.

Novel ferromagnetic polyaniline PANI/ TiO₂ nanocomposites were synthesized by the oxidative polymerization of aniline with ammonium peroxydisulfate in an aqueous medium, in the presence of colloidal TiO₂ nanoparticles (d ~ 4.5 nm), without added acid [4]. The morphological, magnetic, structural, and optical properties of the PANI/TiO₂ nanocomposites prepared at initial aniline/TiO₂ mole ratios 80, 40, and 20 were studied by scanning electron microscopy, superconducting quantum interference device, FTIR, Raman, and UV-Vis spectroscopies. The electrical conductivity of synthesized composites was at semiconducting level, ~10⁻³ Scm⁻¹.

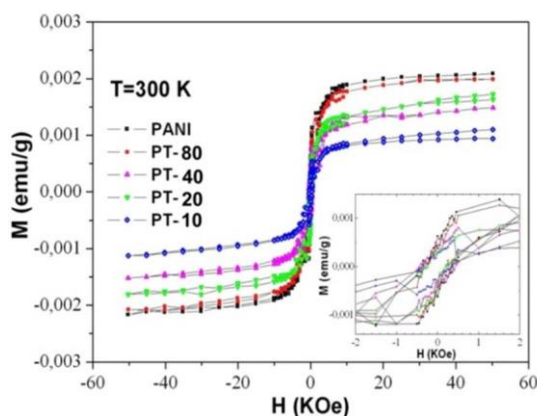


Fig. 1. The magnetic field dependence of magnetization after diamagnetic correction at 300 K for the pure PANI and PANI/TiO₂ nanocomposite samples

Ferromagnetic response for pure PANI and PANI/TiO₂ nanocomposites are shown in Fig.1. The room temperature ferromagnetic response with coercive field of $H_c \sim 300$ Oe and the remanent magnetization of $M_r \sim 4.35 \times 10^{-24}$ emu/g was detected in all investigated samples.

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ST8**Presenting Author: Pavol Kunzo****E-mail: pavol.kunzo@savba.sk****Electrophoretic deposition of nanoparticles synthesized in ionic liquids****P. Kunzo,^a P. Lobotka,^a E. Kováčová,^a V. Šmatko,^a I. Vávra^a**^a*Institute of Electrical Engineering, Slovak Academy of Sciences, Dúbravská cesta 9, 841 04 Bratislava, Slovakia*

Synthesis and stabilisation of nanocolloids possessing long-term stability is an emerging application of ionic liquids (ILs). ILs have been recognized as a suitable medium for preparation of colloidal nanoparticles by sputter deposition of materials in vacuum [1,2]. The current problem for many practical applications is how to deposit the nanoparticles on a proper substrate (battery electrode, sensor surface etc.) and to remove the IL.

Colloidal nanoparticles (Ni, Ag-Cu, and Ni-Fe; 12 to 50 nm in size) were produced by magnetron sputtering of metals onto the surface of imidazolium-based ILs. Although no surfactants were added, the colloids did not show any agglomeration of the nanoparticles (it is believed that nanoparticles are stabilized by supramolecular ionic network of IL and its electrosteric interactions with nanoparticles).

We used electrophoretic deposition (EPD) to immobilise the nanoparticles on the surface of thin film of polyaniline (PAni). PAni is a conducting polymer with significant application potential in gas sensors [3]. Catalytic properties of the nanoparticles can effectively modify the selectivity of the sensor. EPD is based on the application of electric potential between the two electrodes (PAni film and Pt counter electrode) immersed in a colloidal suspension of charged nanoparticles. Nanoparticles move toward the oppositely charged electrode where they are eventually deposited [4]. Pulsed potential was used to overcome the ion shielding of the electric field and electrochemical effects. Application of voltage pulses (2-4 V in amplitude and ~1 s in pulse duration) prevents the ions from accumulation within the electrostatic double layers at the electrodes. Colloidal solutions were diluted with methanol to reduce their viscosity and enhance the electrophoretic mobility of nanoparticles.

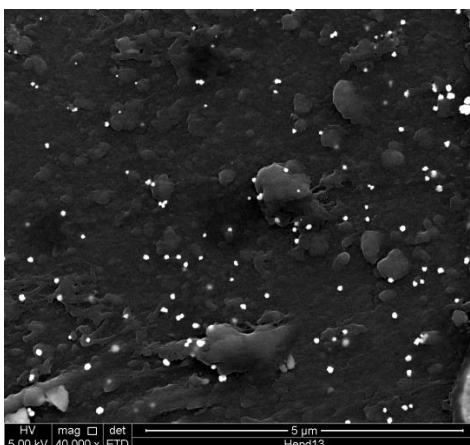


Fig. 1 SEM view of the surface of PAni film with Ni-Fe nanoparticles deposited by EPD.

We successfully deposited the nanoparticles from 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMIM Tf₂N) and BMIM hexafluorophosphate (BMIM PF₆) ionic liquids onto the surface of thin-film PAni electrode. The first deposits were observed after 5 min with anodic polarization of the PAni electrode. However, no deposits were obtained under the cathodic polarization, nor symmetrical AC voltage. This supports the assumption that the nanoparticles in the ionic liquid are coated by anions.

Nanoparticles immobilized at the PAni film were studied by the means of SEM, EDS and FTIR. Gas sensing properties of pristine and nanoparticle-decorated thin PAni films were measured by their exposure to the gaseous ammonia. We found enhanced ammonia sensitivity of PAni film decorated with Ag-Cu nanoparticles, which is the effect of their catalytic activity.

The authors acknowledge the financial support provided by the APVV grant agency under the grant APVV-0593-11.

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ST9

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Influence of different cations on properties of alginate containing multilayers for biomedical application

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The rapid development of medicine induces growing interest in the new ways of drug administration, especially as, so called, drug delivery systems. The most promising of those are systems in form of nanocapsules. They increase bioavailability of some medicines, which direct application have not been so far suitable for therapies. Potent therapeutics have often some essential drawbacks – they are toxic, relatively non-stable or poorly soluble in water [1]. To overcome these disadvantages some ‘tailor made’ nanocarriers could be prepared. One of the most useful methods for the preparation of polymeric carriers is the layer-by-layer (LBL) assembly [2], which involves sequential adsorption of polycations and polyanions on a charged template.

Aim of our work was to characterize properties of ultrathin polymeric multilayers composed of sodium alginate (ALG) and poly-L-arginine (PLArg) which can be further utilized as functional membranes of nanocapsules. ALG, in the presence of some divalent ions, can crosslink to form hydrogels [3], and we utilize this phenomenon to tailor properties of ALG-PLArg multilayers. During formation multilayers were contacted with different salts solutions (e.g. NaCl, CaCl₂, BaCl₂, MgCl₂). Multilayer films’ buildup was followed in-situ in the flow cell with quartz crystal microbalance. The mass/thickness of the films were calculated with viscoelastic model (Q-Tools3, Q-sense) and compared with the ellipsometric thickness in dry state (EP3 Nanofilm). The permeability of selected systems was examined by means of electrochemical techniques (cyclic voltammetry, impedance spectroscopy).

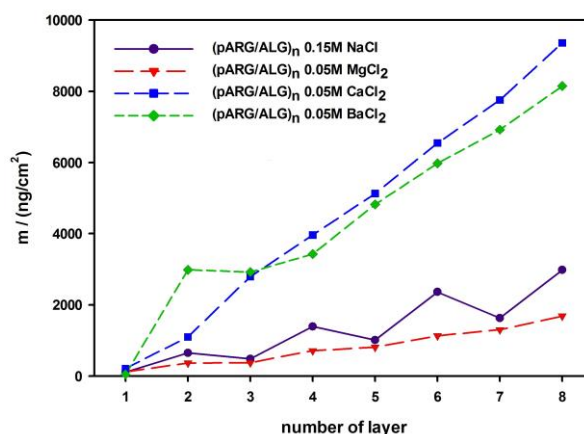


Fig. 1 The dependence of the QCM-D determined mass of multilayer films of the increasing number of layers on the type of salt the in rinsing solution.

We observed a strong dependence of mass/thickness of the films on the concentration of calcium or barium ions in the rinsing solution – Fig. 1. For example, there was a fivefold increase of the film’s mass when the 0.05 M CaCl₂ rinsing solution was used instead of 0.15 M NaCl. In most cases 6 bilayers were enough to reduce cathodic currents from 30% to 70% in comparison to bare electrode depending on the electroactive probe type. We demonstrated that multilayers contacted with CaCl₂ solution were less permeable than those contacted with NaCl solution. However, we observed that the decrease of permeability was low compared to the increase of film thickness due to its crosslinking.

This work was supported from the project Interdisciplinary PhD Studies "Molecular sciences for medicine" (co-financed by the European Social Fund within the Human Capital Operational Programme) and the Marian Smoluchowski Krakow Research Consortium - a Leading National Research Centre KNOW supported by the Ministry of Science and Higher Education and COST Action CM1101.

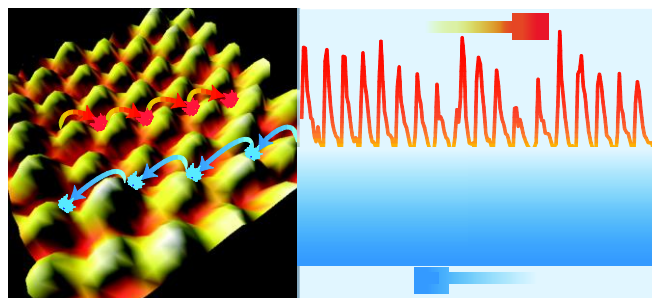
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ST10**Presenting Author: Wuge H. Briscoe****E-mail: wuge.briscoe@bristol.ac.uk**

**Sustained frictional instabilities on nanostructured surfaces:
Stick-slip amplitude coefficient (SSAC)**

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Understanding frictional properties of nanostructured surfaces is important due to their increasing application in modern miniaturised devices.[1] We have performed lateral force microscopy measurements to study the frictional properties between an AFM nanotip and surfaces bearing well-defined nanodomains comprising densely packed prolate spheroids, of diameters ranging from tens to hundreds of nanometres. Our results show that the average lateral force varied linearly with applied load, as described by Amontons' first law of friction, although no direct correlation between the sample topographic properties and their measured friction coefficients was identified.

Furthermore, all the nanodomed textures exhibited pronounced oscillations in the shear traces, similar to the classic stick-slip behaviour, under all the shear velocities and load regimes studied. That is, the nanotextured topography led to sustained frictional instabilities, effectively with no contact frictional sliding. The amplitude of the stick-slip oscillations, σ_f , was found to correlate with the topographic properties of the surfaces, and scale linearly with the applied load. In line with the friction coefficient, we define the slope of this linear plot as the *stick-slip amplitude coefficient (SSAC)*. [2]

We further show that the notion of SSAC is also applicable to describing the frictional properties of surfaces bearing arrays of ZnO nanorods of 20 nm in diameter and 200 – 1,000 nm in length aligned perpendicular to the surface. [3]

We suggest that such stick-slip behaviours are characteristics of surfaces with nanotextures, and that such local frictional instabilities have important implications to surface damage and wear. We thus propose that the shear characteristics of the nanodomed surfaces cannot be fully described by the framework of Amontons' laws of friction, and that additional parameters (*e.g.* σ_f and SSAC) are required, when their friction, lubrication and wear properties are important considerations in related nanodevices.

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ST11

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Development of photocatalyst/ polymer hybrid films for the inactivation of bacteria by visible light

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The hydroxyl radicals produced during in the process of photocatalysis have the ability to inactivate bacteria [1]. Due to its highly advantageous properties, titanium dioxide has been one of the most intensively studied photocatalysts in the past decades. It is well known from the literature that titanium dioxide is only excited by UV light ($\lambda < 380$ nm), which amounts to about 5% of natural sunlight. It is highly desirable, however, that the photocatalytic activity of a photocatalyst in visible light be also as high as possible, allowing significantly higher efficiencies in the degradation or conversion of organic impurities. The latter requirement has urged scientists to modify the absorption band of TiO₂, i.e. to move its light absorption into the visible wavelength range. One method to achieve this is to functionalize TiO₂ particles with metallic substances (e.g. Cu, Ag, Au, Fe etc.) [2]. There are numerous reports in the literature pointing out the advantageous effects of metal and non-metal doping on the photocatalytic activity of TiO₂ and ZnO [3,4].

For the purposes of practical application it is essential to attach the photocatalyst particles to different surfaces [5,6]. A group of binding compounds suitable for this purpose are polymers [5]. This method enables the preparation of reactive surfaces applicable to sewage purification and to the degradation or elimination of various harmful molecules and bacteria from the air.

Nosocomial infections caused by multidrug-resistant microorganisms, such as methicillin-resistant *Staphylococcus aureus* (MRSA), *Acinetobacter baumannii* and *Pseudomonas aeruginosa* can be observed frequently in hospital settings. These bacteria can be acquired through contact with infected surfaces, air or water. Beside the antibiotic and conventional treatments it is very important to prevent the spread of nosocomial infections.

Noble metal-modified TiO₂ photocatalysts were synthesised in order to move the light absorption of initial TiO₂ into the visible wavelength range. The optical spectra of the silver, gold and copper modified photocatalysts shows an intensive light absorbance in the 390-530 nm range so the irradiation with LED light source ($\lambda = 405$ nm) produced enhanced photo absorption supported the photocatalytic activity of the reactive surface samples. Photooxidation of ethanol vapour on catalyst films was examined by a gas chromatograph using different light sources. The noble metal functionalized TiO₂ were 63- 97% efficient photocatalysts than the initial TiO₂. Next we prepared mechanically stable, acrylic polymer-based photocatalyst composite layers by spray coating method. According to the results the photocatalyst particles embedded in the polymer matrix were preserved their photocatalytic activity with satisfactory mechanical stability.

The antibacterial effect of the photocatalyst/ polymer nanohybrid films was tested with different test methods. The nanohybrid films could inactivate 99.9 % of MRSA bacteria after 2 h of illumination with visible light source (Fig. 1).

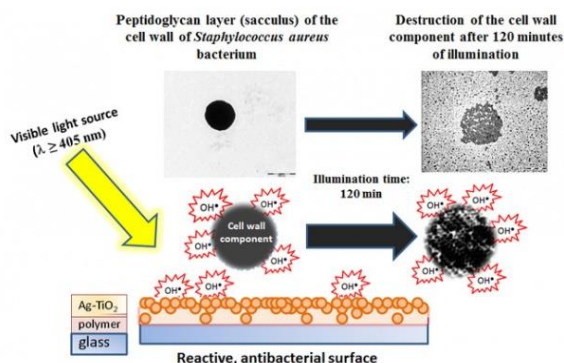


Fig. 1 Photocatalytic degradation of the *Staphylococcus aureus* bacterial cell wall on the surface of photocatalyst/ polymer hybrid coating under LED light illumination ($\lambda = 405$ nm).

For air cleaning the antibacterial activity of a reactive light source – using Ag-TiO₂ photocatalyst on inner coating surface of the lamp – was investigated against airborne microorganisms. The reactive light could kill 96 % of

naturally occurring airborne microorganisms after 48 hours of visible light illumination in indoor air sample. With the photoreactive coatings, an extensive disinfectant film was developed and successfully prepared.

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Acknowledgements

This research was financed by the TÁMOP 4.2.2.A-11/1/KONV-2012-0047, as well as by the MTA-SZTE Supramolecular and Nanostructured Materials Research Group and by the Hungarian National Office of Research and Technology (NKTH) under contract no. TECH-09-A2-2009-0129 (NANOSTER).

ST12

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Kinetic aspects of Ag⁺-ions releasing mechanism from nano-Ag/hydrogels synthesized by γ -irradiationJ. Krstić,^a J. Spasojević,^a A. Radosavljević,^a
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Nano-Ag/ hydrogel nanocomposites were synthesized with γ -irradiation as a highly suitable tool for enhanced nano-Ag technologies and biocompatible controlled release formulations. In this study, we elucidated the kinetic aspects of Ag⁺ ions releasing mechanism on the simple nano-Ag/PVA hydrogel nanocomposites, as a model system. Recent studies have suggested that Ag nanoparticles exert toxicity on bacteria and other organisms not by direct particle specific effect but by released Ag⁺ ions [1, 2].

The release of any kind of drugs occurs only after the fluid penetrates into the polymeric network and dissolves the drug, therefore complete swelling study of the nano-Ag/PVA hydrogels, containing different concentration of Ag nanoparticles (6, 10, 12, 110, 276, 419 mol cm⁻³ which were labeled with S1, S2, S3, S4, S5, S6, respectively) was performed. Different model approximations were applied for early time of swelling, late time and Eters valid for whole range of swelling. [2]

Oxidation-reduction process of Ag⁺ releasing mechanism from the surface of the NPs was in agreement with the greater solubility of smaller nanoparticles revealed by the Ostwald-Freundlich relation as well as larger surface to volume ratio which increases the rate of Ag⁺ ions release. On the other hand, heterogeneous oxidation reaction and obtained Ag⁺ ions release concentrations in buffered medium at 37 °C, also allows to obtain the overall cell voltage and the Gibbs free energy, according to the Nernst expression with an emphasis on the bactericidal effectiveness and system thermodynamics that provided the killing power of the nano-Ag/PVA devices. Cell potential of the synthesized nanosystems was obtained with applying Plieith prediction of negative shift in the Ag standard electrode potential for small metal NPs (<25 nm) (Fig. 1). [3]

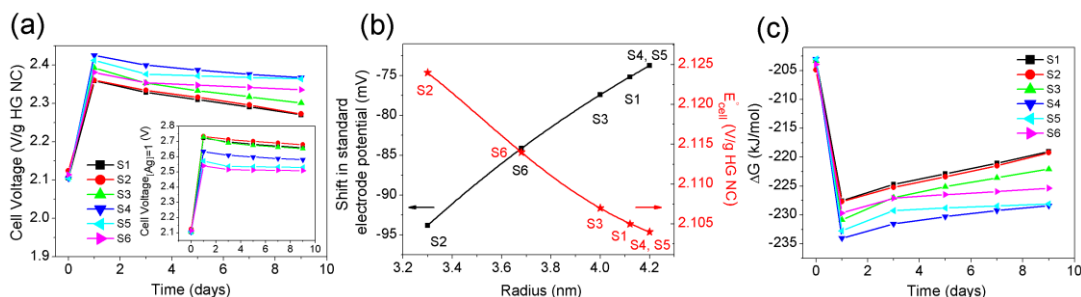


Fig. 1 (a) Cell potential, (b) plot of the shift in the standard electrode potential of the Ag nanoparticles and corresponding standard cell electrode potentials (E°_{cell}) as a function of radius (r), and (c) Gibbs free energy (ΔG).

The elements of pharmacokinetic drug delivery paradigm to the nano-Ag/PVA hydrogel, as a model system, were used for the evaluation of Ag⁺-ions release kinetics and release mechanism. The amount of the Ag⁺-ions released *in vitro* by the nano-Ag/PVA hydrogel device was in the antimicrobial parts per million concentration range. The modeling of the Ag⁺ ions release kinetics with the elements of the drug-delivery paradigm revealed the best fit solution ($R^2 > 0.99$) for the Kopcha and Makoid-Banakar's pharmacokinetic dissolution models. The term A/B, derived from the Kopcha model, indicated that the nano-Ag/PVA hydrogel was mainly an Ag⁺-ions diffusion-controlled device. Makoid-Banakar's parameter and the short time approximated Ag⁺-ions diffusion constant reflected the importance of the size of the Ag nanoparticles. However, it appeared that the cell oxidation potential of the Ag nanoparticles depended on the diffusion characteristics of the fluid penetrating into the Ag/PVA nanosystem. [2]

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ST13**Presenting Author: Krzysztof Szczepanowicz****E-mail: ncszczep@cyf-kr.edu.pl****Targeted drug delivery system based on polyelectrolyte nanocapsules****K. Szczepanowicz,^a A. Karabas,^b M. Bzowska,^b S. Łukasiewicz,^b P. Warszyński^a**^a*Jerzy Haber Institute of Catalysis and Surface Chemistry PAS, niezapomianejk 8, 30-239 Krakow Poland*^b*Faculty of Biochemistry, Biophysics and Biotechnology, Jagiellonian University, Krakow Poland*

One of the first concept of drug targeting was suggested by Paul Erlich almost a century ago. The hypothetical ‘magic bullet’ consisting of two principal components was proposed. The first component should recognize the target and bind to it, the second should perform therapeutic action. After four decades of research, there have not yet been produced an effective, generally applicable, site-specific drug-delivery system. Drug containing nanocapsules with specially functionalized surface are promising candidates as magic bullets. Nanoencapsulation has high application potential in medicine since it can be used to improve the compatibility of lipophilic, poorly water-soluble or even water-insoluble active compounds with physiological fluids and can protect therapeutic molecules from the destructive influence of an external environment. The ability to penetrate cells by nanocapsules makes them promising candidate for drug delivery system. Moreover, they can be functionalized to achieve “intelligent targeting”, i.e. the delivery to the specific cells or organs. That should not only significantly decrease deleterious side effects, but also may drastically enhance therapy efficiency. Various approaches were proposed to accomplish this goal. The layer-by-layer adsorption of charged species like polyelectrolytes, nanoparticles, proteins, organic molecules, etc. is considered as a convenient method to obtain multilayer nano and microcapsules’ shells on colloidal cores. Therefore, the aim of our work was to develop the method of encapsulation of emulsion droplets containing active substance in polyelectrolyte multilayer shell, their surface modification by pegylation in order to eliminate non-specific bindings (elimination of opsonization and fast clearness) and by immobilization of targeting ligands. Nanocapsules were prepared using a method proposed by Szczepanowicz et al. [1]. The oil droplets/cores stabilized by an AOT/Polycation surface complex were encapsulated with shells formed by layer-by-layer adsorption of polyelectrolytes. The average size of the obtained capsules ranged from 60–120 nm. Analysis of internalization of synthesized nanocapsules in HEK 293 cells indicated that they can easily penetrate cells. We tested also cytotoxicity of the nanocapsules in the co-culture with a human cell line HEK 293 using MTT, LDH and ATP assay. The results of that bioassays have shown that the our nanocapsules can be used in high concentrations without harming the cells. Moreover the influence of physicochemical properties of obtained nanocapsules (charge, size, surface modification) on viability, phagocytosis potential and endocytosis was elucidated with mouse murine macrophages cell line - RAW 264.7 and human leukemic monocyte cell line - THP-1.

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Acknowledgements

The work was financed by NCN project DEC-2011/03/D/ST5/05635 and the Marian Smoluchowski Krakow Research Consortium - a Leading National Research Centre KNOW supported by the Ministry of Science and Higher Education and COST Action CM1101

ST14

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Liquid-Filled Capsules as Fast Responsive Photochromic Materials

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Here we report a simple and universal methodology for the preparation of fast responsive photochromic materials based on encapsulation of the photoactive molecules within liquid-core capsules. In this way, solids with solution-like color fading kinetics are obtained, which are about one order of magnitude faster than those measured upon direct dispersion of the photosensitive molecules into rigid polymer thin films and solid particles. This rapid decoloration response matches the best results reported so far using other approaches to prevent matrix effects on photochrome performance. In our case, however, the fast responsive behavior is attained independently of the nature of the photochromic compound and encapsulating matrix used, while it does not require any further chemical modification of these substances. In addition, by properly selecting the nature of the liquid core, the capsules prepared display high stability both in time and upon redispersion in a variety of solvents without compromising their photochromic performance. This facilitates their subsequent use for the fabrication of functional materials where fast relaxation of photoinduced color changes is required, as we have demonstrated by preparing capsule-containing polymer films and test lens matrices with relatively high photochrome loadings (up to 0.1% w/w). Although future work is needed to attain the high transparency levels required for some applications, in their present form these materials could already be of use as fast responsive agricultural films, awnings and elements for optical data processing devices.

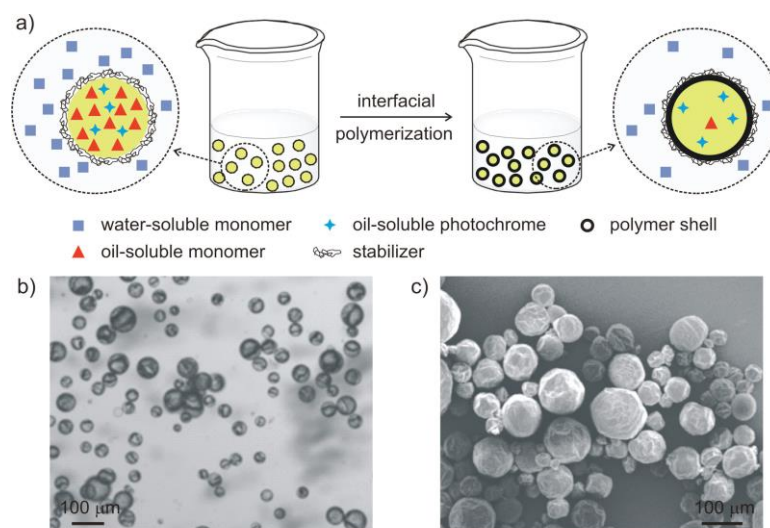


Fig. 1 a) Schematic representation of the synthesis of the hollow PA capsules containing photochromic solutions. b) Optical microscopy image of PA_{tol} capsules. c) SEM image of PA_{tol} capsules..

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ST15**Presenting Author: Paulino Alonso-Cristobal****E-mail: pacristobal@ucm.es****Development of a DNA sensor based on upconversion nanoparticles and graphene oxide****P. Alonso-Cristobal,^a J. Rubio-Retama,^a E. Lopez-Cabarcos,^a O. Muskens^b, A. Kanaras^b**^a*Department of Physical Chemistry II, Faculty of Pharmacy, Complutense University of Madrid, Spain.*^b*Faculty of Physical Sciences and Engineering, University of Southampton, United Kingdom.*

Upconversion Nanoparticles offer a unique type of Anti-Stokes fluorescence emission under excitation with a 980 nm laser diode. This emission has very interesting properties due to the low background fluorescence, enormous resistance to photobleaching and no blinking effects. The rare-earth (RE) doped NaYF₄ nanoparticles present this upconversion fluorescence and present very high chemical stability. All of these characteristics make the RE-doped NaYF₄ nanoparticles (UCNPs) as interesting starting material for the development of robust and reliable sensors and biosensors.

Graphene Oxide (GO) is a 2-Dimensional material capable of quenching the upconversion fluorescence when the UCNPs are close to the surface of GO. We modified the surface of the UCNPs and functionalized with a sequence of ssDNA. The different affinity between the ssDNA and the dsDNA to the GO, attributed to the π - π interactions between the ssDNA and the GO, permitted us to obtain a highly specific sensor with a very low detection limit.

In this work we present our results of the synthesis, surface engineering and functionalization of the UCNPs and the evaluation of the UCNPs-GO FRET pair as a sensor for a specific sequence of DNA.

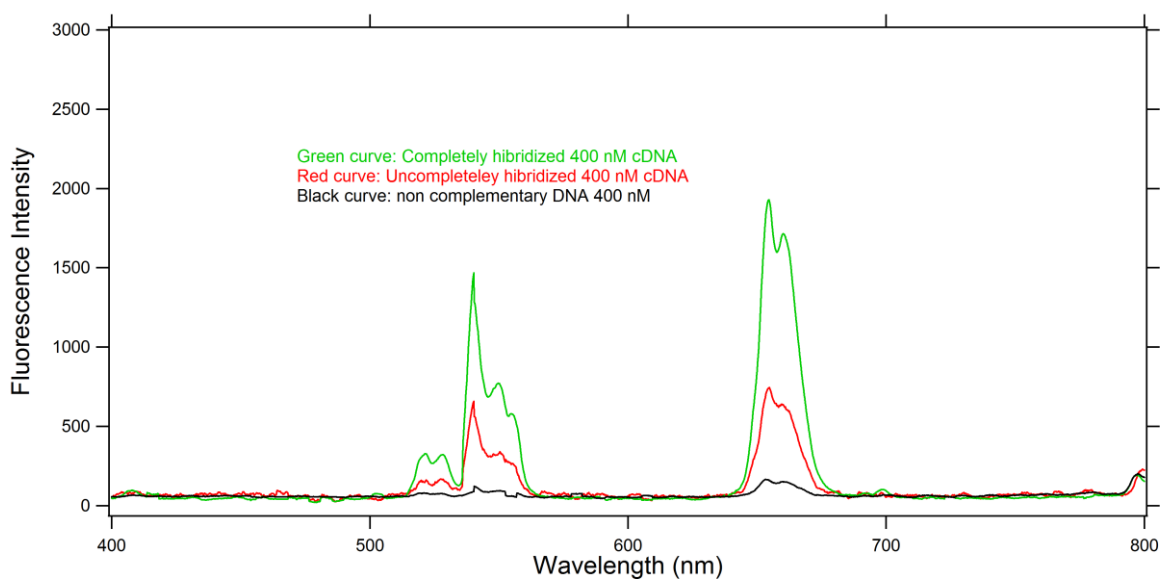


Fig. 1 Upconversion fluorescence spectra from the UCNPs-GO with hybridized complementary DNA (green), uncompletely hybridized cDNA (red) and non complementary DNA (black).

Our study revealed a high sensitivity from the sensor to the hybridization conditions, as well as a concentration-dependant fluorescence recovery which could be used for the quantification of the cDNA with a low detection limit.

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ST16**Presenting Author: Georgia Pilkington****E-mail: georgia.pilkington@bristol.ac.uk****Dendritic nanofluids mediating surface forces****G. A. Pilkington,^a W. H. Briscoe^a**^a*School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, United Kingdom*

Fluids containing nano-sized structures are increasingly employed in modern technologies, ranging from lubrication fluids to drug delivery. Despite their numerous applications, our fundamental understanding of the surface forces mediated by nanofluids is still relatively limited [1]. In particular, due to their nanosize and related characteristics, the applicability of established surface force theories, such as the DLVO theory, [2,3] remain unclear.

With several tunable parameters such as the size, surface and interior chemistry, dendritic macromolecules (or dendrimers) [4] offer a unique model nanofluid for investigating the effect of nanostructures on classic colloidal phenomena. Recently we have performed complementary small angle X-ray scattering (SAXS) and X-ray reflectivity (XRR) [5] measurements to study the interactions between negatively charged polyamidoamine (PAMAM) dendrimers in the bulk and at the mica-water interface. Using a version of the surface force apparatus (SFA), we have then directly measured the surface forces mediated by these dendritic nanofluids under nano-confinement. Furthermore, we have studied how the interactions can be influenced by the presence of a number of ionic surfactants, including cationic surfactant dodecyltrimethylammonium bromide (DTAB) and anionic surfactant sodium dodecyl sulfate (SDS).

We find that, in the bulk solution, the adsorption of DTAB at a concentration just above its CMC to the dendrimer surfaces leads to the formation of a dendrimer-surfactant complex. Under nano-confinement in the SFA, we observe short range interactions between confining surfaces due to the structuring of these dendrimer-surfactant complexes. For anionic surfactant SDS which is similarly charged to the dendrimers, the dendrimers and the surfactant remain non-interacting which leads to a binary depletion interaction when confined in the SFA.

From these measurements, we have gained insight into the complex effects of dendritic nanofluids on surface interactions and how these may be tailored with ionic surfactants. Such interactions bear fundamental relevance to how nanostructures interact with lipid mesophases encountered in complex biological systems such as cell membranes, as well as to the design of drug delivery systems employing dendrimers where such interactions are an important consideration.

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