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Center for Advanced Studies

**Forum of understanding on Nanomaterials
and their interdisciplinary applications**

Forum of understanding on Nanomaterials and their interdisciplinary applications

3-5 June 2016

Hotel Windsor, Serock (Jachranka), Poland

Scientific and Organizing Committee:

Prof. Michael Giersig, Department of Physics at Freie Universität Berlin

Prof. Stanisław Janeczko, Director of the Center for Advanced Studies at Warsaw University of Technology

Prof. Małgorzata Lewandowska, Department of Materials Engineering at Warsaw University of Technology

Plenary speakers:

Tymoteusz Ciuk, PhD St

Dr. Lech Giersig

Prof. Bartosz Grzybowski

Prof. Leon Gradoń

Prof. Kris Kempa

Prof. Andrzej M. Kłonkowski

Prof. Witold Łojkowski

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Forum programme

3 June 2016 (Friday)

14:30	□	arrival/registration
15:00-17:00		lunch
18.00-19:00		Podium discussion / Conducting Prof. Michael Giersig , Department of Physics at Freie Universität Berlin
20:00-21:30		dinner/grill
21:30- 24:30		bowling

4 June 2016 (Saturday)

7.45-9.00	□	breakfast
9:05-9:45		Prof. Bartosz Grzybowski , <i>The future of chemistry and nanotechnology</i> , Department of Chemistry, Ulsan National Institute of Science and Technology, South Korea
9:50-10:30		Prof. Józef Spałek , <i>Nanosystems as physical systems: selected quantum properties</i> , Marian Smoluchowski Institute of Physics, Jagiellonian University; Academic Centre for Materials and Nanotechnology (ACMIN) AGH University of Science and Technology, Krakow
10:30-10:45		coffee break

11:35-12:15	Prof. Andrzej Kłonkowski , <i>White emitting nano-glass ceramics and nanocomposite</i> , Faculty of Chemistry of the University of Gdansk
12:15-14:00	lunch
14.00-15.30	poster session
15:50-16.30	Prof. Witold Łojkowski , <i>Size effects in nanocrystalline particles</i> , Institute of High Pressure Physics of the Polish Academy of Sciences
16:35-16:40	coffee break
16:40-17:20	Tymoteusz Ciuk, PhD St , <i>Applications of Epitaxial Graphene</i> , Institute of Electronic Materials Technology, Warsaw, Institute of Microelectronics and Optoelectronics, Warsaw University of Technology
17:20-18:00	Prof. Jacek Szczytko , <i>The spin in nanostructures – from bio-med applications to Bose-Einstein condensates</i> , Faculty of Physics at University of Warsaw
20:00 -21:30	dinner
21:30- 24:30	bowling

5 June 2016 (Sunday)

	<input type="checkbox"/>	
7:45-9:00		breakfast
9:05-9:45		Prof. Kris Kempa , <i>Plasmonics of nano materials for applications: from high efficiency solar cells, to metaterial superconductors, to terahertz cancer treatment</i> , Department of Physics at Boston College, USA
9:50-10:30		Prof. Maciej Wiznerowicz , <i>Cancer Nanotechnology</i> , Poznan University of Medical Sciences, Greater Poland Cancer Centre, International Institute for Molecular Oncology, Poznan
10:30-10:45		coffee break

10:50-11:30	Dr. Lech Giersig , <i>Systems for measurement of thermal properties of thin films</i> , Presentation of the NETZSCH-Gerätebau GmbH BU „Analyzing & Testing” company
11.35- 12.15	Dr. Leszek Stobiński , <i>New Graphene Laboratory at Warsaw University of Technology, Faculty of Chemical and Process Engineering - issues, prospects and tasks</i> , Faculty of Chemical and Process Engineering WUT
12:30- 14:00	lunch
14:00-14:40	Prof. Leon Gradoń , <i>Formation of nanostructured functional particles</i> , Faculty of Chemical and Process Engineering WUT
14:40-15:00	Conclusion remarks
15:00	departure

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Lectures

Nanosystems as physical systems: selected quantum properties

Józef Spałek

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and
Academic Centre for Materials and Nanotechnology (ACMIN)
AGH University of Science and Technology, Al. Mickiewicza 30, 30-059 Kraków

In this talk I shall define elementary introduction to electron properties of nanosystems. Particular emphasis is put on the specific quantum properties and the role of interactions between electrons. Few historical experimental results which have led to the creation of nanophysics as a well define discipline, are briefly overviewed.

Work supported by the National Centre of Science (NCN) through the Grant MAESTRO No. DEC-2012/04/A/ST3/00342

White emitting nano-glass ceramic and nanocomposite materials

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Karol Szczodrowski², Dorota Wileńska¹ and Jacek Ryl³

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Presented are two types of luminescent nanomaterials doped with Eu^{3+} , Tb^{3+} and Tm^{3+} ions. The first one is based on nano-glass ceramics triply co-doped with above mentioned ions and prepared by nucleation-crystal growth procedure of the glasses obtained *via* melt-cooling process [1]. In the second one is used a triply co-doped nanocomposite prepared *via* sol-gel- method [2]. To study whether in the first case the nano-glass ceramics as a matrix could improve luminescence properties of phosphors were compared the triply co-doped nano-glass ceramics and its vitreous counterpart of the same composition.

For the studied materials optical absorption, luminescence and excitation spectra were recorded as well as time resolved luminescence techniques was used. Measured luminescence lifetimes show that the triply co-doped glass possesses the lifetime distinctly longer than in the case of its nano-glass ceramic counterpart. Two luminescence effects were analyzed, *viz.* cross-relaxation $\text{Tb}^{3+} \rightarrow \text{Tb}^{3+}$ energy transfer and energy transfer $\text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$ and *vice versa*. Structure of the nano-glass ceramic and nanocomposite matrices were determined by XRD and SEM techniques. The CIE diagram suggests in each case that the vitreous and glass-ceramic materials co-doped with the selected lanthanide ions can be recognized as white phosphors (see Fig. 1).

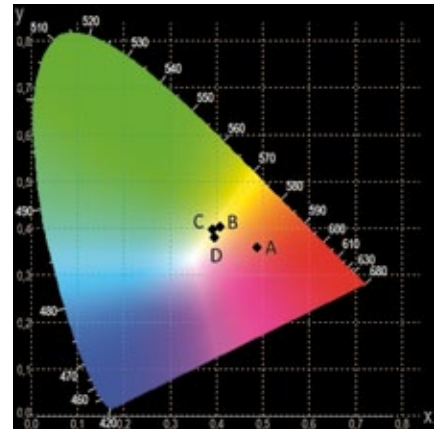


Fig. 1. The CIE chromaticity diagram of the GPBOSF:3Eu12Tb5Tm nano-glass ceramics, where excitation wavelength λ_{exc} was as follows: (A) 393 nm; (B) 378 nm; (C) 368 nm and (D) 358 nm [1]

References:

- [1] A.M. Kłonkowski, W. Wiczek, K. Szczodrowski, D. Wileńska, *J. Phys. D: Appl. Phys.* in the press.
- [2] A.M. Kłonkowski, W. Wiczek, D. Wileńska, K. Szczodrowski, *J. Ryl*, *sended to Adv. Opt. Mater.*

Size effects in nanocrystalline particles

Witold Łojkowski^{1,2}, Jacek Wojnarowicz¹, Anna Świdarska-
-Środa¹, Krzysztof Żur³, Agnieszka Omiotek¹, Agnieszka
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Nanotechnology main aim is to exploit size dependent properties of materials, which mainly appear when their dimension becomes less than 100 nm. In the present talk we will present examples of size dependent properties of nanoparticles (NPs), as well as some methods to control their size.

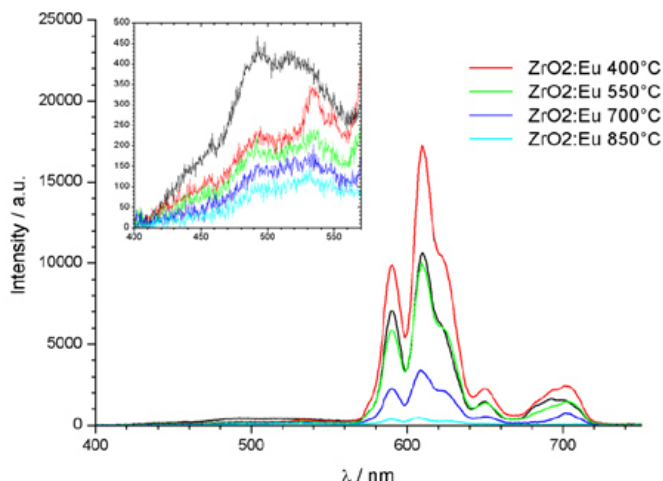


Fig. 1. Photoluminescence of ZrO₂:10 wt% of Eu³⁺ nanoparticles as a function of particles size. The size change was caused by annealing for 60 min at the indicated temperatures.

The most straightforward example of size dependent NPs property is density. On the example of ZnO and ZrO₂ NPs we will show how the measured by means of helium pycnometry density decreases as a function of their size. The effect results from contribution of surfaces to density. Thus the possibility to create materials with tuned density emerges. Besides property control, the NPs size is also influencing their thermodynamic stability, and this will also be illustrated.

On the example of hydroxyapatite NPs we will show how we can tune the biological activity of this material, which is used in bone regrowth technology in regenerative medicine. The smaller the NPs size, the higher is the concentration of calcium ions in a suspension of such NPs, which is important for bone growth stimulation.

Finally, on the example of Eu^{3+} doped zirconia NPs we will show how the optical properties are size depended. This material displays photo-luminescence that is dependent on the oxygen content in the ambient atmosphere. Both the luminescence intensity and the sensitivity of the material as oxygen sensor decay strongly as the particles size increases (Fig.1).

The size control methods that we used were: chemical composition of the substrates used during synthesis (ZnO NPs size control); time of synthesis (HAP NPS size control) and post synthesis annealing (ZrO_2 NPs).

The work presented was funded by the following projects:
SHYMAN FP7 Project and GOIMPLANT Eranet Project, as well as IHPP statutory funding

Applications of Epitaxial Graphene

Tymoteusz Ciuk^{1,2}, Wlodek Strupinski¹, Iwona Pasternak¹, Aleksandra Krajewska^{1,3}, Jan Sobieski^{1,4}, Aleksandra Przewloka⁵, Oleg Petruk⁶, Andrzej Kowalik¹, Iwona Jozwik¹, Andrzej Rychter⁷, And Jacek Baranowski¹

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Epitaxial growth of graphene on SiC, Cu and Ge substrates are described and analyzed from the point of view of various applications.

Technology of epitaxial CVD growth of graphene on SiC [1] is presented and confronted with the requirements of large-scale fabrication of graphene-based devices. The applicability of quasi-free-standing bilayer [2] and monolayer [3] is verified with respect to their electrical stability throughout the device processing cycle. Special attention is paid to magnetic field detection. A Hall effect sensor [4] is presented that is optimized with respect to carrier concentration and mobility, geometry of the active layer, $1/f$ noise level, magnetic resolution and an encapsulation method that assures stability of the sensor's electrical parameters over time and temperature.

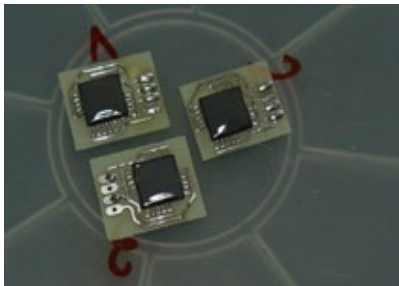


Fig. 1. Graphene Hall effect sensors

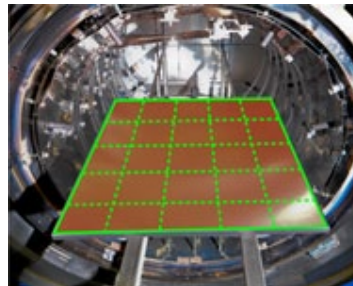


Fig. 2. 50 [cm] × 50 [cm] polycrystalline copper foil covered with monolayer CVD graphene

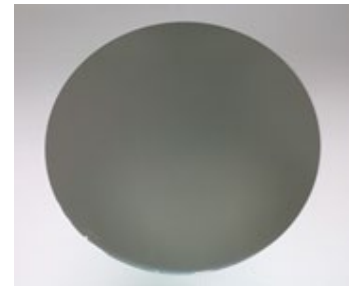


Fig. 3. 8-inch Ge(001)/Si(001) substrate covered with monolayer CVD graphene

The up-scaling of graphene growth on polycrystalline copper foil for industrial applications is verified and exemplified with a Seco/Warwick prototype system dedicated for 2500 [cm²] substrates. The issue of graphene transfer from copper onto dielectric substrates by means of electrochemical delamination [5] is raised and the applicability of this technology is verified through a demonstration of a A4-format graphene heating glass.

Large-area high-quality graphene films synthesized by the CVD method on Ge(001)/Si(001) are presented. Their monolayer character, uniformity over the nanofacet structures of the Ge(001) surface, domain orientation and interaction with germanium substrate are confirmed by SEM, STM, STS/CITS, LEED and XPS techniques [6,7]. The applicability of graphene grown on germanium in electronics, in particular in CMOS technology is analyzed.

References:

- [1] Strupinski, W., Grodecki, K., Wyszomolek, A., et al., "Graphene Epitaxy by Chemical Vapor Deposition on SiC", Nano Letters, 11(4) (2011), 1786-91.
- [2] T. Ciuk, W. Strupinski, "Statistics of epitaxial graphene for Hall effect sensors", Carbon 93, 1042-1049 (2015).
- [3] T. Ciuk, P. Caban, W. Strupinski, "Charge carrier concentration and offset voltage in quasi-free-standing monolayer chemical vapor deposition graphene on SiC", Carbon 101 (2016) 431-438.
- [4] T. Ciuk, O. Petruk, A. Kowalik, I. Jozwik, A. Rychter, J. Szmids, and W. Strupinski, "Low-noise epitaxial graphene on SiC Hall effect element for commercial applications", (Applied Physics Letters #:16-02016R).
- [5] Ciuk, T., Pasternak, I., Krajewska, A., Sobieski, J., Caban, P., Szmids, J., Strupinski, W., "Properties of chemical vapor deposition graphene transferred by high-speed electrochemical delamination", (2013) Journal of Physical Chemistry C, 117 (40), pp. 20833-20837.
- [6] I. Pasternak, P. Dabrowski, P. Ciepielewski, V. Kolkovskiy, Z. Klusek, J. M. Baranowski, W. Strupinski, "Large-area high-quality graphene on Ge(001)/Si(001) substrates", Nanoscale (2016) DOI: 10.1039/C6NR01329E
- [7] I. Pasternak, M. Wesolowski, I. Jozwik, M. Lukosius, G. Lupina, P. Dabrowski, J.M. Baranowski, W. Strupinski, "Graphene growth on Ge(100)/Si(100) substrates by CVD method", Scientific Reports 2016, DOI:10.1038/srep21773

The spin in nanostructures – from bio-med applications to Bose-Einstein condensates

Jacek Szczytko

Nanostructure Engineering, Institute of Experimental Physics, Faculty of Physics,
University of Warsaw, ul. Pasteura 5, 02-093 Warsaw, Poland

I will present various aspects of nanomagnetism investigated at the Faculty of Physics of the University of Warsaw. The magnetic and optical properties of magnetic nanoparticles for bio-med applications will be discussed: adsorption of doxorubicin onto the surface of nanoferrites can provide a facile preparation process for potential drug carriers (fig A), polypyrrole microvessel structures modified with superparamagnetic nanoparticles can be used as potential carriers of nucleotides (fig B). SQUID measurements indicated that the incorporated nanoparticles retained their superparamagnetic properties (fig A, B). The measurement of the optical properties of a composite material made of ferromagnetic metal nanoparticles embedded in a dielectric enabled quantitative determination of the magnetic moment and the plasma frequency of a single nanoparticle, and from this the size of the nonmagnetic shell of magnetic nanoparticles (fig C). Monte Carlo simulations of interacting nanomagnets allowed for modelling of the physical properties of clusters of nanoparticles. In the presence of dipole-dipole interactions, the effect of both particle volume and interparticle separation was investigated with respect to the characteristic parameters of hysteresis loops and zero field cooled and field cooled magnetization curves (fig D). The nanostructures built of the layers of semimagnetic semiconductor reveal the strong light-matter coupling and lead to the Bose-Einstein condensation of spin-polarized polaritons (i.e. hybrid exciton-photon quasiparticles) in the microcavity (fig. E).

See figures on the next page.

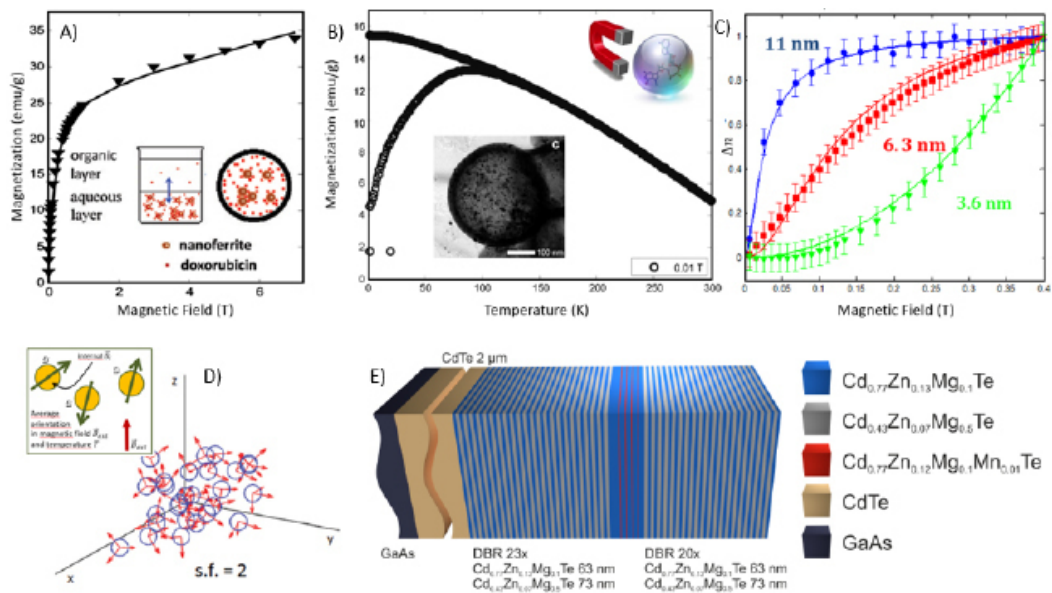


Fig. A. Journal of Physical Chemistry C 116 (9) 5598-5609 (2012)

Fig. B. Biomacromolecules 14 (6) 1867-1876 (2013)

Fig. C. Physical Review E 87 (3) 033201 (2013), Physical Review E 87 (6) 062322 (2013)

Fig. D. Physical Review B 88, 144421 (2013)

Fig. E. Applied Physics Letters 107, 201109 (2015)

Plasmonics of nano materials for applications: from high efficiency solar cells, to metamaterial superconductors, to terahertz cancer treatment

Kris Kempa

Boston College, Boston, USA

Plasmonics and metamaterials are rapidly developing fields of physics and material science, with many already realized and exciting new potential applications. While plasmonics is an old field, having roots in the gaseous plasma physics [1], physics of metamaterials is relatively young, beginning with the seminal, pioneering work of Sir John Pendry [2]. This talk will focus on chronological developments in each field, and their applications. It will be shown, how plasmonic/metamaterial effects can improve solar cells, so they could achieve efficiencies beyond the limitations of the Shockley-Queisar limit. In this context, the concepts of superabsorption and hot-electron plasmonic protection (HELPP) will be discussed [3]. The last effect relies on ultra-fast electron-plasmon scattering, which exceeds that for electron-phonon scattering, usually the fastest. Thus, plasmons can interfere with the electron-phonon scattering, and this interference can, in general be constructive or destructive. The flexibility of the metamaterial design allows for the plasmonic resonances to occur at any desired frequency, and thus controls this interference. This control can be exploited in many other systems, such as thermoelectrics or superconductors. I will discuss some of these cases, including very recent experiments confirming the interference. Finally, I will discuss the exciting topic of molecular dissociation based on excitation of vibrational motions of a molecule. This idea could lead to a new paradigm in treatment of genetic abnormalities (e.g. DNA mutations), such cancer.

References:

- [1] Y. Wang, E. W. Plummer, and K. Kempa, "Foundations of Plasmonics", in *Advances in Physics*, Vol. 60, No. 5, September-October 2011, 799-898.
- [2] J.B. Pendry, *Phys. Rev. Lett.* 85 (2000), p. 3966.
- [3] J. Kong, A.H. Rose, C. Yang, J. M. Merlo, M.J. Burns, M. Naughton, and K. Kempa, *Opt. Express* 23, A1087-A1095 (2015).

Cancer Nanotechnology

Maciej Wiznerowicz

Poznan University of Medical Sciences, Greater Poland Cancer Centre, International Institute for Molecular Oncology, Poznan, Poland

Cancer therapies are currently limited to surgery, radiation, and chemotherapy. All three methods risk damage to normal tissues or incomplete eradication of the cancer. Nanotechnology offers the means to target chemotherapies directly and selectively to cancerous cells and neoplasms, guide in surgical resection of tumors, and enhance the therapeutic efficacy of radiation-based and other treatment modalities. All of which, can add up to a decreased risk to the patient and an increased probability of survival.

Nanotechnology may also drive advances in other aspects of clinical oncology and cancer research. The examples of the research areas include: (1) Development of next generation nanoparticles; (2) Understanding nanoparticle delivery mechanisms and implications of systemic distribution; (3) Techniques and tools to overcome failure of therapy; (4) Tools and devices aimed specifically at monitoring the tumor microenvironment; (5) Technologies suitable for biomarker discovery and screening; (6) Technologies for cancer molecular targeting, discovery, and validation; (7) Devices and tools capable of penetrating cellular and/or physiological barriers; (8) Integration of modeling and simulation approaches to guide rational nanomaterials design.

Biological processes, including ones necessary for life and those that lead to cancer, occur at the nanoscale. Thus, in fact, we are composed of a multitude of biological nano-machines. Nanotechnology provides researchers with the opportunity to study and manipulate macromolecules in real time and during the earliest stages of cancer progression. Nanotechnology can provide rapid and sensitive detection of cancer-related molecules, enabling scientists to detect molecular changes even when they occur only in a small percentage of cells. Nanotechnology also has the potential to generate entirely novel and highly effective therapeutic agents. Finally, nanotechnology provides new molecular contrast agents and materials to enable earlier and more accurate initial diagnosis as well as in continual monitoring of cancer patient treatment.

Systems for measurement of thermal properties of thin films

Lech A. Giersig

Netzsch Gerätebau GmbH, Selb

NETZSCH

NanoTR and PicoTR, thermal analysis systems have been developed successfully, which are the world's first instruments that can measure thermophysical properties of thin films.

Thin film: Metal, ceramics, organic films, etc.

Thickness of film:

- NanoTR: 300nm...up to...10 μm
- Pico TR: 10 nm...up to...1 μm

Measurement items:

- Thermal diffusivity
- Thermal effusivity
- Thermal conductivity

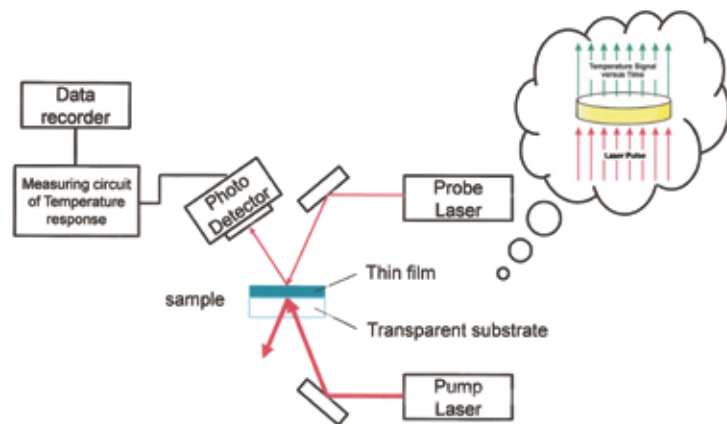
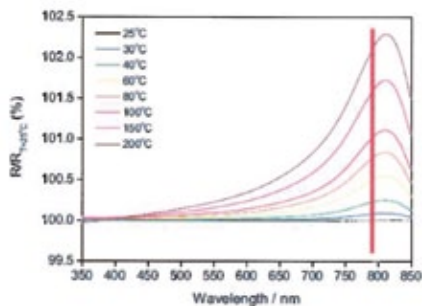


Fig. 1. Measurement principle. According to Dr. Baba, this is „Ultra Fast Laser Flash”. The figure is based on JIS R 1689

What is “Thermoreflectance”?

Thermoreflectance is a phenomena in which reflectivity of material changes as its temperature change. Based on the observed intensity of reflected light against irradiated to objects, the temperature change of the object can be evaluated.

Very fast temperature change can be evaluated!



$$\Delta T = \left[\frac{1}{R} \frac{\partial R}{\partial T} \right]^{-1} \frac{\Delta R}{R}$$

$\lambda = 780 \mu\text{m}$

Fig. 2. Relative reflectivity change spectra of Aluminum thin film ($t=100 \text{ nm}$)
J. Ishii, J. Shimizu, Proc. 27th Jpn Symp. Thermophys. Prop. (2006) 322

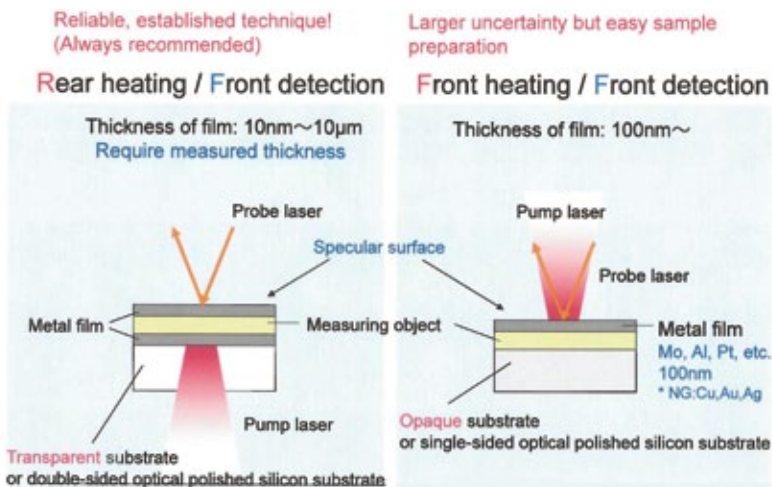


Fig. 3. Two modes of the measurement

NanoTR



Pulse width = 1 ns

PicoTR



Pulse width = 0.5 ps

Fig. 4. NanoTR - Nanosecond Thermoreflectance; PicoTR - Picosecond Thermoreflectance.
Manufactured by AIST start-up „PicoTherm Corporation“ / NETZSCH can sell exclusively!

New Graphene Laboratory at WUT, Faculty of Chemical and Process Engineering – issues, prospects and tasks

L. Stobinski^{1*)}, M. Mazurkiewicz-Pawlicka¹, A. Malolepszy¹,
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¹ Faculty of Chemical and Process Engineering, Warsaw University of Technology, Warynskiego 1,
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*) Head of Graphene Laboratory, L.Stobinski@ichip.pw.edu.pl

New Graphene Laboratory at Warsaw University of Technology, Faculty of Chemical and Process Engineering was opened on the 24th September 2015. Preparation of the standardized forms of graphene oxide (GO) and reduced graphene oxide (rGO) flakes for the research purposes and industrial applications will be our main target. Looking for a new applications of chemically and physically well-characterized GO (Fig. 1) and rGO (Fig. 2) flakes creates a good occasion and common platform for our future cooperation with other scientific units from different fields, e.g. biomedical, material sciences, analytical sciences, etc. During this presentation we will demonstrate: i) our advanced synthesis, ii) physicochemical analysis of GO and rGO and a new graphene composites, iii) Graphene Laboratory modern equipment.

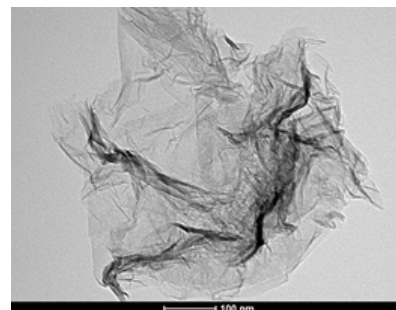


Fig. 1. GO flake

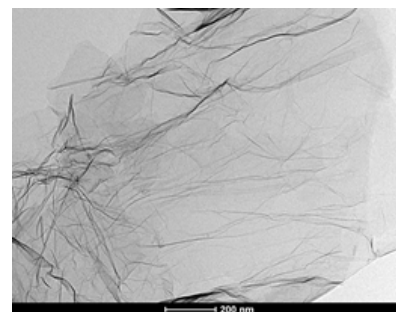


Fig. 2. rGO flake

Formation of nanostructured functional particles

Leon Gradoń

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The structure of matter, on both an atomic and macroscopic scale, is a result of the interplay between the requirements of the physical forces operating between the individual parts and the mathematical requirements of space filling.

Materials of interest in solid-state chemistry typically possess a crystalline structure; thus, their functional properties are controlled by the packing of atoms or ions in three-dimensional space. Similarly, nanoparticles are useful building blocks for nanomaterials, the function of which is determined in spatial structure of the component nanoparticles. With regards to desirable morphologies for nanomaterials, high surface area porous or hollow structures are frequently preferred for a wide range of applications. Catalysis, chromatography, the controlled release of drugs, low dielectric constant fillers, sensors, pigments, microelectronics and electro-optics, all represent examples of applications of nanostructured objects, particles particularly.

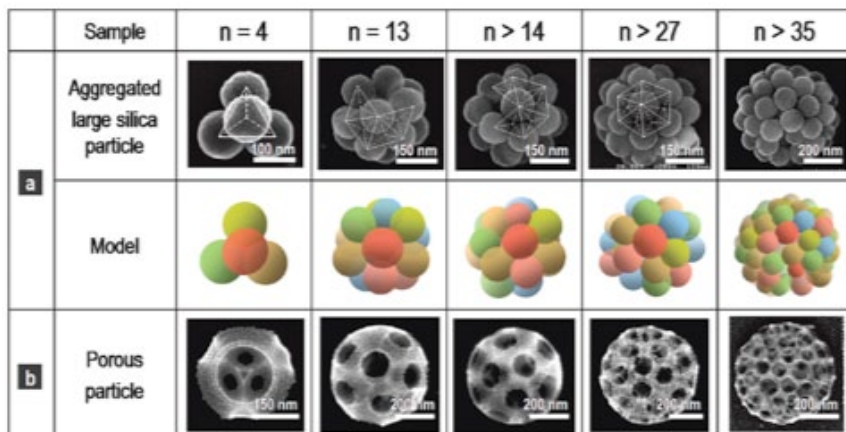


Fig. 1. Nanostructured particles - examples

Final topology of the nanostructure defines its functionality. Hollow and porous materials are frequently prepared from a colloidal crystal template.

In the case of the subject of this paper, the nanostructured particles are produced with the spray-drying technique. The precursor is atomized to form spherical droplets, which contain hosting and templating particles with defined diameters and concentrations. Droplets are carried into a tubular reactor by carrier gas for drying when solvent is removed. The composite structure consisting hosting and templating particles depends on the organization of both types of particles during drying. The theoretical approach of the possible equilibrium of particles packing and the kinetics of the self-organization of the structures is proposed for definition of the parameters of the spray drying. In the next step the composite particles are moved into the furnace where the template material is removed and final structure of desired particle after its possible sintering is formed.

Particles of different morphology are produced, at assumed conditions of production including diameter and concentration of hosting and templating particles, their zeta potentials, flow rate of droplets through a dryer and droplet evaporation rate. The topology of produced particles and their potential functionality is presented.

Posters

Differentiating Charged from Non-Charged Ferroelectric Domain Walls in Single Crystalline LiNbO_3 by μ -CARS and μ -Raman Spectroscopy

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We report here on μ -CARS and μ -Raman spectroscopical investigations of charged domain walls (CDWs) in ferroelectric LiNbO_3 (LNO) single crystals. While μ -Raman spectroscopy showed no differences between CDWs and non-charged domain walls, μ -CARS spectroscopy revealed a variety of subtle features that may be directly correlated to the structural properties of these CDWs (see Fig. 1). Notably, both μ -Raman and μ -CARS measurements were deduced from exactly the same surface spot using a combined μ -Raman/ μ -CARS setup from Soliton GmbH. While μ -Raman was performed at wavelengths of 532 nm, 633 nm and 785 nm, we used a 900 ps Nd:YAG pulsed laser excitation @ 1064 nm as the pump beam in our μ -CARS investigations and a Stokes beam supercontinuum ranging from 1080-1700 nm, as generated through the same Nd:YAG pump laser guided through a photonic crystal fiber (PCF). To our surprise, structural changes of CDWs were easily discernable by μ -CARS as clearly revealed in Fig. 1. This interesting behavior will be detailed on the poster.

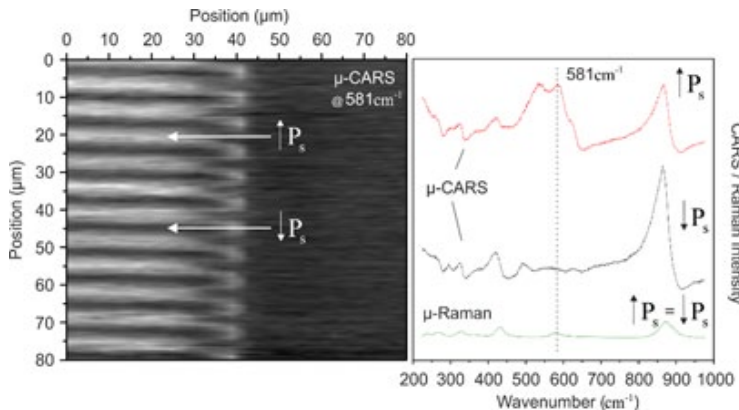


Figure 1: The μ -CARS map (left) recorded at 581 cm^{-1} , depicts the clear distinction of charged domain walls in periodically poled LiNbO_3 (LNO) single crystals. These walls are not “seen” by μ -Raman spectroscopy (see right picture, bottom spectrum), in contrast to μ -CARS (right picture, top and middle spectra) that reveals a series of pronounced bands below 600 cm^{-1} , when recorded at specific surface spots. P_s indicates the direction \uparrow and \downarrow of spontaneous polarization in neighboring domains, separated by charged/non-charged domain walls.

Domain walls (DWs) in ferroelectric single crystals constitute ideal candidates for optical, electronic and topological investigations down to the 1-nm length scale. In fact, 180° DWs separating so-called c-domains may be viewed as delta-distribution-like discontinuities in both the optical refractive index and charge distribution penetrating the whole single crystal of millimeter thickness [1,2]. Nevertheless, these DWs may show widths as thin as one single unit cell only, i.e. < 0,5 nm in size. Hence, only very few optical investigations of these peculiarities have been reported to date, for instance by using optical near-field microscopy [3] and/or non-linear optical methods such as near-field electrooptics [4] or Cerenkov second-harmonic generation [5]. μ -Raman spectroscopy was also widely applied to ferroelectrics [6], however, with the clear focus of deducing a domain contrast rather than focusing on the tiny domain walls themselves. These works allowed investigating (de-) polarization and cross-talk effects occurring for μ -Raman inspection on solid samples, as is elegantly addressed by the Porto notation [7]. Also it was possible to deduce absolute domain orientations in such perovskite ferroelectrics through combined μ -Raman / scanning force inspections [8,9].

Recently, we were able to engineer charged domain walls (CDWs) into these LNO single crystals [10]. In contrast to 180° DWs, CDWs are inclined with respect to the sample surface. As a consequence, both the electric field distribution and charge screening left and right to that (charged) domain wall become asymmetric thus having a clear structural impact. It is these CDWs that are in the focus of our combined μ -Raman and μ -CARS investigations as presented here.

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Up-Conversion in Magnetic Field and Magnetic Properties of Up-Converting Nanoparticles Doped with Rare Earth Elements, for Bio-Medical Imaging and Treatment

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Fluorescence imaging plays an important role in biomedicine. Typical techniques are based on fluorophores that are excited with ultraviolet (UV) light, which has several disadvantages, such as a small penetration depth into the tissue, autofluorescence from other fluorophores in the sample, and the possibility of damaging the sample during the test. The sensitivity and resolution of fluorescence imaging can be improved when a two-photon process and near-infrared light (NIR) is used for excitation within the “optical transmission window” of biological tissues (700–1000 nm). This approach offers several advantages: an increase of optical contrast, a greater depth of light penetration, minimized autofluorescence and reduced light scattering. Furthermore, NIR does not cause radiation damage to cellular functions and structures. Nanoparticles doped with rare earth metal ions exhibit paramagnetic properties that allow to use them for imaging cancer cells by using magnetic resonance imaging (MRI). Another field of application of the nanoparticles is the selective cancer cells killing in living organisms by hyperthermia. Optical properties of these nanoparticles allow one to use them in biology and medicine as fluorescent markers (VIS) and in photodynamic cancer therapy. In this therapy cancer cells are killed by reactive oxygen species (ROS) produced due to ultraviolet radiation (UV) from up-conversion process.

In this study we present results of magnetic measurements of up-converting nanoparticles and up-conversion performed in magnetic field. Magnetic properties of $Y_3Al_5O_{12}$ and $NaYF_4$ nanoparticles doped with Er^{3+} , Yb^{3+} and Gd^{3+} were measured using SQUID magnetometry. Measurements were performed in temperatures from 2.0 K to 350.0 K and magnetic fields up to 7.0 T. Magnetization of the measured particles shows linear increase with dopant concentration and can be reasonably described by a combination of the Brillouin functions appropriate for the proper spins (e.g. $J=15/2$ for Erbium and $J=7/2$ for Ytterbium), especially for the lowest REE concentrations. Up-conversion mea-

measurements with confocal microscopy system were performed in temperatures from 4.0 K up to room temperature and magnetic fields up to 9.0 T. UC excitation was performed using 980 nm laser. Results show that up-conversion process may be influenced with magnetic field.

The observed paramagnetism of up-converting nanoparticles opens a possibility to use magnetic field as an additional control of multifunctional nanoparticles with optical and magnetic properties. Although at the temperature of human body, the measured nanoparticles reveal rather weak paramagnetism and properties of samples are dominated by their diamagnetism, the possibility of UC luminescence intensity peak shifting using magnetic field modulation broadens the horizons for more precise bio-medical applications.

Influence of inhalable dextran-based drug nanocarriers on the dilational viscoelasticity of air-water interface

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Determination of the surface activity of newly developed drug formulations that are intended to deposit in the alveoli is very important for the safety assessment of aerosol therapy. Polyaldehyde dextran nanoparticles (NPs) which are potential drug carriers can be formulated into fine powder by means of spray drying and administered to the respiratory system as aerosol released from a dry powder inhaler (Jabłczyńska et al., 2015). The dynamic surface tension of alveolar fluid during breathing cycle may be influenced by nanoparticles, which are adsorbed on the air-water interface. The presented work concerns the visco-elastic properties of the air-water interface on which dextran-based NPs adsorb.

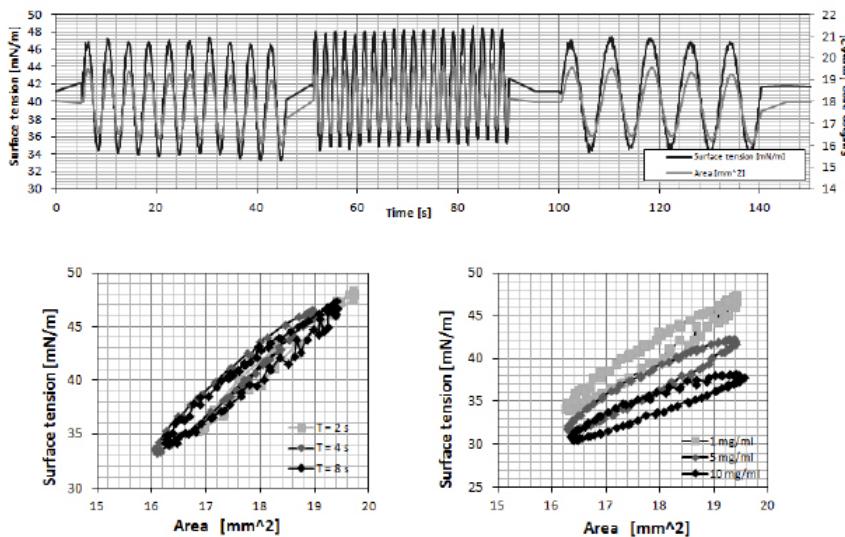


Fig. 1. Polyaldehyde dextran nanosuspension surface tension response to surface area change in harmonic oscillation experiment.

The dynamic surface tension of the aqueous samples of NPs (1-10 mg/ml) was determined by the axisymmetric drop shape analysis using PAT-1M system (Sinterface, Germany). Changes in surface dilational elasticity and viscosity manifest in different surface tension hysteresis shape and tilt. The results showed that with increasing frequencies of oscillation the dilational elasticity increases while dilational viscosity decreases. It was also found that surface elasticity of the oscillating drop is noticeably lower for increased NPs concentration, what suggests that presence of NPs reduces the amplitude of surface tension variations during harmonic perturbations of air-liquid interface.

Work supported by NCN project no. 2014/13/N/ST8/01667

Reference:

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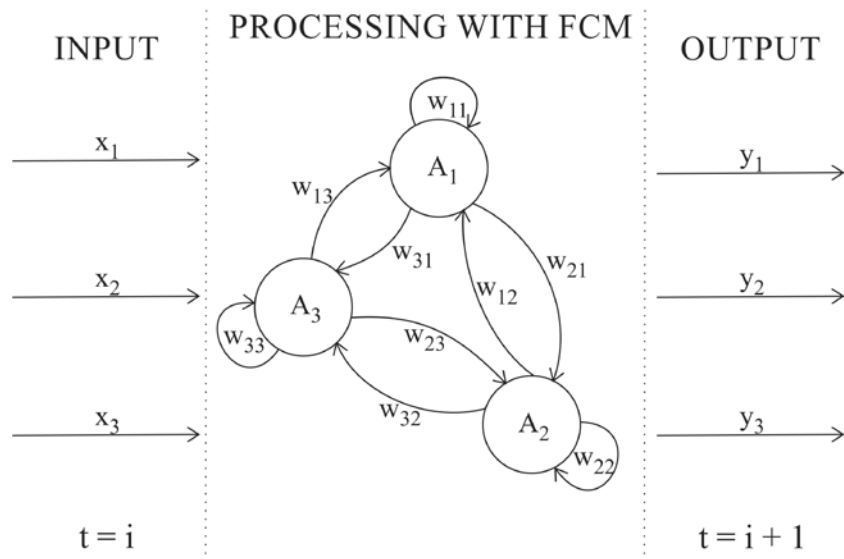
Modelling with Fuzzy Cognitive Maps

The Case of Time Series

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In many areas of science there is a need for modelling approaches that represent knowledge in an abstract, generalized way. This need manifests itself mainly when models are designed to be interpreted and used by human beings, but not exclusively. Abstraction comes in hand as well when we deal with very large data sets. When standard numerical methods are inadequate to describe the data, it might be beneficial to turn towards granular models, based on concepts, where knowledge is aggregated and represented in an abstract fashion. Concepts-based methods facilitate smooth human-computer interactions as they allow to represent knowledge in form of relationships between phenomena – just like humans do.



An example of a concepts-based approach are Fuzzy Cognitive Maps (FCMs) introduced in 1986 by B. Kosko, [1]. FCMs are described with weighted directed graphs. Nodes represent concepts (in other words: variables, phenomena, knowledge aggregates). Edges represent relationships between the nodes. Each edge has a weight quantifying strength of the relationship. Weights are real numbers from the $[-1; 1]$ interval. Construction of an FCMs consists of two phases: extraction of concepts and weight matrix learning.

In our research we focused on application of FCMs to time series modelling. We are developing a procedure first introduced in 2008 by W. Pedrycz et al., [2]. Empirical studies show great suitability of this method. However, it is worth to highlight that FCMs are successfully applied to a variety of different problems, including classification, regression, and systems modelling.

In future we plan to employ Fuzzy Cognitive Maps to the so called strong Natural Language Processing – strong NLP, which aims at “real” information understanding. Mining concepts from text data, joining them with numerical (calculable) concepts, and detecting relationships between them is a vital research area in the era of large scale and heterogeneous systems.

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Rigorous analysis of many-electron effects in nanosystems: Quantum dot-ring nanostructure

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We discuss, on example of quantum dot-ring nanostructure (DRN) [1,2], general effects coming from the interelectronic Coulomb interactions for $N_e=2$ and 3 electrons. Explicitly, we determine many-particle states and calculate accurately also the 3- and 4-state interaction terms, usually omitted in the analysis. For that purpose, the single-particle wave functions are determined first and represent an input to the subsequent calculation of the microscopic parameters, which in turn serve as an input in defining Hamiltonian. The Hamiltonian is diagonalized rigorously with the help of the Lanczos method [3]. It turns out that both the 3- and 4-state interactions are essential in obtaining the correct energies for nanosystems, and sometimes, are of comparable magnitude with the two-state exchange interaction and the so-called correlated hopping terms [4]. With the increasing size of DRN, the role of two-state interactions becomes dominant. Our analysis puts on a microscopic basis the Coulomb-blockade effects, as well as introduces a model system for which we can discuss precisely the role of all terms representing many-particle interactions in the Hamiltonian.

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Virus-like particles loaded with functionalized magnetite nanoparticles as a potential biomedical application

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Magnetite nanoparticles with their superparamagnetic properties can be very useful in biomedical applications, especially as therapeutic agents for cancer treatment by hyperthermia or contrast agents in Magnetic Resonance Imaging (MRI). Combination of magnetite with certain viruses can lead to achieving localized antitumor agents. Coating with Brome Mosaic Virus (BMV) – plant virus and Hepatitis B Core Antigen (HBcAg) coming from mammalian Hepatitis B Virus (HBV) – were used as nanocarriers for magnetite cargo.

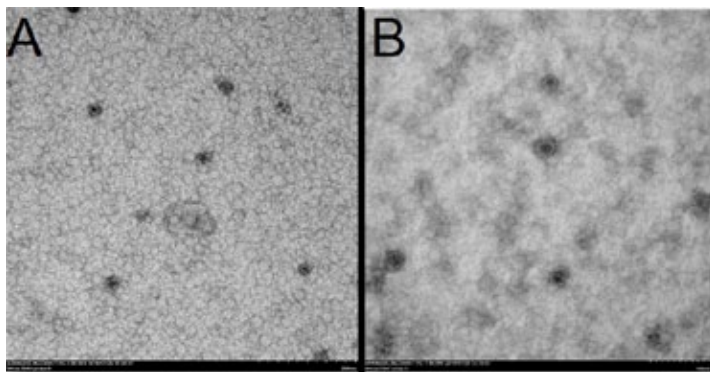


Fig. 1. Virus Like Particles (VLP) with superparamagnetic iron oxide nanoparticles cores and:
A: Brome Mosaic Virus (BMV)
B: Hepatitis B Core Antigen (HBcAg) coming from mammalian Hepatitis B Virus (HBV)

Iron oxides nanoparticles with core diameter of 15 nm were synthesized by thermal decomposition and functionalized with HOOC-PEG-PL in order to achieving water solubility and special charge for assembly process of viruses. Nanoparticles were characterized by Transmission Electron Microscopy (TEM), Dynamic Light Scattering (DLS), Zeta Potential and Fourier Transformed Infrared Spectroscopy (FTIR).

Structures formed by both of the coating proteins are relatively small (around 28 – 40 nm) in their native state and icosahedral which is meaningful for encapsulating spherical nanoparticles. Assembling process is mainly connected

with electrostatic interaction between cargo and coating protein. To achieve VLP from various viruses two disparate protocols were applied for each object.

Creation and size of the VLPs with magnetite cores were confirmed by TEM microscopy. Hydrodynamic radiuses and polydispersity were established by DLS. Spectroscopic characterization of VLPs was also made with FTIR.

This work was supported by UMO-2012/06/A/ST4/00373 grant from National Science Centre (Poland)

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Dielectric cavities for WSe₂ monolayers

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Transition metal dichalcogenides (TMDs) like MoS₂, MoSe₂, WS₂ or WSe₂ have attracted recently considerable attention. Of particular importance are single layers of TMDs, which contrary to bulk material, exhibit direct band-gap. This property resulting in efficient emission rises many possibilities for applications in opto-electronic devices. Moreover, emission can be enhanced by incorporation of the monolayer into the optical cavity as it was shown for MoS₂ [1,2]. In our work we demonstrate possible realization and optical properties of optical cavities incorporating WSe₂ monolayers.

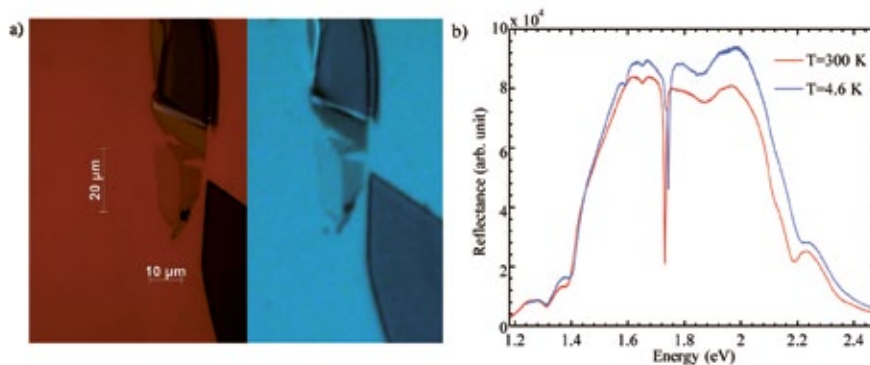


Fig. 1. a) Image of a WSe₂ monolayer before (left) and after (right) the second growth process; b) reflectance spectra in two temperatures from the cavity structure in the vicinity of the WSe₂ single layer.

The procedure of sample fabrication consists of two growth processes of dielectric layers divided by the deposition of WSe₂ monolayers. In each process subsequent TiO₂ and SiO₂ layers are produced, resulting in total in formation of two distributed Bragg reflectors separated by $\lambda/2$ SiO₂ cavity. Between two growth processes exfoliated monolay-

ers of WSe_2 are deposited on the samples top surface by means of an all-dry polydimethylsiloxane- based transfer technique. Before fabrication numerical simulations based on transfer matrix method were preformed in order to obtain thicknesses of dielectric layers required to achieve desired optical properties of the whole structure at liquid helium temperature. Energy of the cavity mode should be possibly close to 1.75 eV, which is the energy of the exciton resonance in WSe_2 monolayers, with the maximum of the electric field amplitude at the position of the single layer. Microscopic images of a selected sample before and after the second growth process in Fig. b shows no visible influence on WSe_2 monolayer. The cavity mode energy obtained from the reflectance spectra shown in Fig. b) equal to 1.74 eV is very close to desired value of 1.75 eV.

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Polysaccharide-based nanoparticles entrapped in alginate microspheres as novel anticancer drug delivery system

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Malignant tumors are the second cause of death in the world after cardiovascular disease. Developing the effective and safe cancer therapy could significantly decrease the amount of deaths and increase the live quality of cured patients. Nowadays medicine has developed a wide range of anticancer chemotherapeutics but at the same time there is a lack of an effective drug delivery methods. In conventional therapy the anticancer chemotherapeutics are delivered via vascular or oral route, which results that the drug particles are nonspecifically absorbed by the all cells in the organism what cause many harmful side effects and at the same time less effective therapy because of reduction of the drug concentration in the cancer cells. Therefore, development of the targeted drug delivery system which will selectively release drug into the cancer cells is a key challenge of modern medicine.

The aim of this work was to investigate the interaction between cancer cells and dextran-based nanoparticles containing the anticancer drug (doxorubicin), released from the alginate microspheres covered with chitosan multilayer. The microspheres would be delivered to the tumor supplying blood vessel. In proposed drug delivery system, the anticancer drug would be delivered precisely to the cancer cells by a novel approach connecting: transcatheterial embolization of the tumor supplying blood vessel by the alginate microspheres with nanoparticles, and the structure of dextran-based nanoparticles imitating the free glucose, which cause increased absorption of the nanoparticles in the cancer cells due to their increased glucose requisition.

During the research the physicochemical properties of the alginate microspheres and its stability in the physiological environment were investigated. Moreover, the kinetics of the nanoparticles with doxorubicin release from the alginate microspheres covered with chitosan layers was characterized, depending on the thickness of the chitosan multilayer. Further the cytotoxicity study of the alginate microspheres with chitosan multilayer containing nanoparticles was performed to determine the therapeutic and targeting effect of the released nanoparticles containing doxorubicin on the HeLa cells during the *in vitro* cell culture.

Polariton lasing of semimagnetic exciton-polaritons

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The field of nanostructure engineering is growing fast and enables to construct new appliances. Due to the rescaling devices we have an access to the phenomena previously unobservable. Nanoengineering allows us to fabricate different structures with high precision. The past decade has encounter extremely fast development in the studies on quantum phenomena in a semiconductor microcavity field. The works devoted to the interaction between light and matter show that as a result of strong coupling between a photonic and an excitonic ground state, two new states arise: upper and lower exciton-polaritons. Studies include the area of nonlinear interactions as Bose-Einstein condensation [1], polariton lasing [2].

In our work we investigate polariton lasing in a semimagnetic semiconductor microcavity. Our microcavity sample consist of two Bragg mirrors consisting of alternating (Cd,Zn,Mg)Te layers with various magnesium, zinc and cadium concentration embedding a cavity with four quantum wells containing 0.5% of manganese [3,4]. We modified a confocal optical microscopy setup to detect angularly resolved photoluminescence spectra. Sample was pumped nonresonantly with a fs laser pulses. The II-VI semiconductor structures suffer from photonic disorder, more pronounced than in III-V semiconductors. However in the confocal microscopy setup we have the ability to a precise positioning of the excitation spot on the sample surface and we could determine the places with homogenous (over tens of μm) potential distribution.

We observe different effects depending on excitation power. Starting from low power we could observe accumulation of polaritons at the bottleneck at lower polariton branch. For higher excitation power the population at the *bottleneck* decreases and the polaritons accumulate at the bottom of lower polariton branch, where the intensity starts to dominate over the intensity at the bottleneck. Above threshold we observe polariton lasing, what turn on to the nonlinear interaction regime. The energy shift due to polariton - polariton interactions is clearly visible. In our work we demonstrate a detailed study of the threshold of polariton lasing in semimagnetic semiconductor microcavity in a localised minima, where the non-linear effects are much stronger.

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Structural evolution of Al-Si/AlN nanomultilayer upon low temperature annealing

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Thin films and multilayers constitute an important class of nanostructured materials and they are of considerable interest in a number of applications. One of the newest concept is to build up a new class of brazing fillers by employing the size-dependent melting behaviour of metal confined in a nanostructured multilayer geometry. The use of such a nanoarchitected configuration can reduce the processing temperature, thus allowing benign joining of heat sensitive materials. Although, the advantageous behaviour of nanomultilayers can be expected, the fundamental understanding of the phenomena and accompanying mechanisms taking place is still missing. Therefore, the aim of the study was to evaluate the structural evolution in Al-Si/AlN nanomultilayer upon annealing.

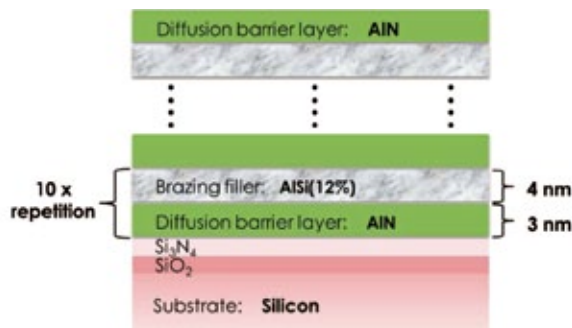


Fig. 1. Configuration of Al-Si/AlN system

The nanomultilayer (NML), as produced by magnetron sputtering, consisted of 3 nm thick AlN barrier layers alternated by 4 nm thick Al-Si(12%) braze filler metal layers (bulk $T_m=577^\circ\text{C}$) The bilayer of AlN/Al-Si was repeated 10 times on the Si substrate and covered with the final AlN surface layer (Fig. 1). Such produced system was heat treated at different temperatures for 10 minutes and examined by Scanning Electron Microscope (SEM) and Scanning Transmission Electron Microscope (STEM).

Prior to the annealing, the polycrystalline Al-Si nanolayers were homogenous in terms of chemical composition suggesting that magnetron sputtering resulted in supersaturated solid solution. The first observed microstructural changes occurred at $300^\circ\text{C} < T < 400^\circ\text{C}$ revealing visible phase separation within the Al-Si layers into Al-rich and Si-rich regions. As an outcome, branch-shape structures consisting of Al and Si emerged on the NML surface (Fig. 2).

In-depth analysis of the branch-shape structure revealed 25% of Si on its cross section, which is far away from the eutectic composition designed in this system. This may be a strong argument in favour of an intensive Si diffusion out of the NML, preferably through the grain boundaries and interfaces. On the other hand, looking along the section one can notice that the AlN nanolayers in the central part under the branch-like structure were locally damaged and fractured and their fragments were embedded in the branch-shape metal protrusion (Fig. 3).

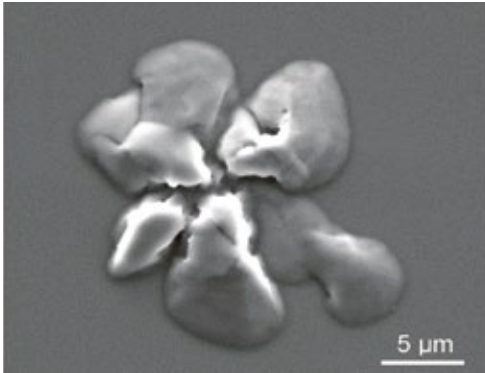


Fig. 2. Branch-shape structure on the nanomultilayer surface after annealing at 400°C for 10 minutes

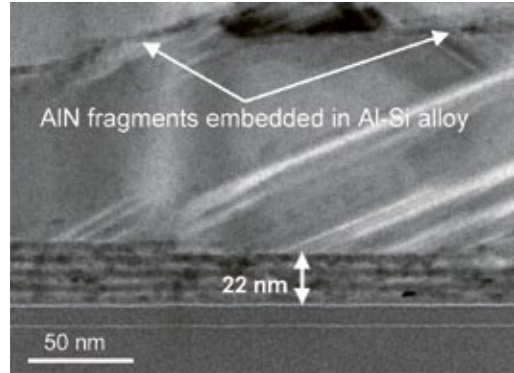


Fig. 3. Central part of the NML under the branch-shape structure

The results show that the structural evolution of the NML occur at the temperature well below the melting point of the bulk eutectic Al-Si alloy ($T_m=577^\circ\text{C}$) and consists of two subsequent stages. In the first stage, intensive phase separation within the metallic layers takes place. In subsequent stage, two processes occur simultaneously, i.e. fast diffusion and melting at reduced temperature, leading to the migration of Al and Si out of the NML.

Influence of process parameters on morphology and wettability of TiO₂ nanotubular layer fabricated by electrochemical anodization

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Titanium and its alloys are widely used in medical application, especially for bone implants, due to their good mechanical properties, high biocompatibility and corrosion resistance. Despite that, there are still some limitations related to long time needed to reach full integration of titanium implant with bone tissue. Therefore, it is of a great importance to develop surface modifications which could stimulate osseointegration process and enhance connection between implant and tissue. Nowadays, nanotubular TiO₂ layers has been widely investigated as a potential surface modification of titanium and its alloys as the morphology of the nanotubes can be easily controlled by process parameters such as anodization time and voltage applied and they can change the surface properties for directed cell-surface interaction. It has been shown that cell attachment and proliferation is strongly related with physico-chemical properties of the surface, especially the wettability. Hence, this work concerns about the anodiza-

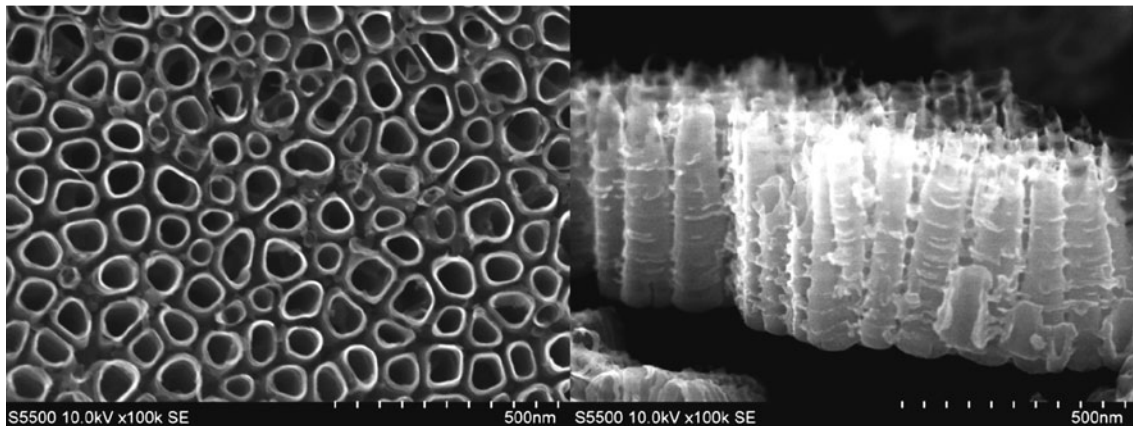


Fig. 1. TiO₂ nanotubes fabricated by electrochemical anodization at 20 V for 3 min

tion process parameters and how it affects the morphology of obtained titania nanotubes as well as the wettability of the layer. TiO_2 nanotubes (NTs) were fabricated on a titanium substrate by electrochemical oxidation in a mixture of glycerol, deionized (DI) water and ammonium fluoride at different constant voltage (10, 20 and 30 V) for various periods of time (1, 3, 5, 10 and 40 min). The morphology of as-obtained samples were investigated by scanning electron microscopy. The diameter, wall-thickness and height of nanotubes were established using ImageJ software. The wettability of nanotubular oxide layer was determined by water contact angle measurement - WCA (sitting drop method) with DI water used as a standard liquid. The results revealed that anodization time influence in particular wall-thickness and height of the nanotubes – the wall-thickness decrease with increasing time of the process, the height for short periods of time (1, 3, 5 and 10 min) increase systematically and drop for nanotubes fabricated for 40 min. The most uniform and well-ordered nanotubes were obtained for 20 V. Layers anodized at 30 V did not possess fully formed nanotubular structure. For the layers produced at voltage of 10 V, the bigger diameter of the NTs is, the wettability of the layer increases. For nanotubes fabricated at voltage of 20 V the wettability decrease for nanotubes with diameter up to 100 nm, while for larger values of diameters (above 100 nm) the WCA begins to grow. Increase in height of TiO_2 NTs results in decrease of values of WCA.

Functionalization of superparamagnetic iron oxide nanoparticles (SPIONs) with dihexadecyl phosphate (DHP). New solution to an old issues

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Introduction

Superparamagnetic iron oxide nanoparticles (SPIONs) have been widely studied and many of their properties are thoroughly investigated and described. So far, SPIONs are proven to be highly useful in such applications as for example: magnetic hyperthermia, targeted drug delivery, magnetic resonance imaging (MRI) contrast agent, cell imaging. Nonetheless, SPIONs related treatments and technologies still require further development in order to become fully controllable, reliable and safe. SPIONs properties can be designed and finely tuned by applying surface functionalization. This approach allows to control crucial parameters such as solubility, cellular uptake, toxicity, affinity and many more. Therefore obtaining novel ways of SPIONs functionalization is a necessity for further development.

Objectives

The aim of this study was to investigate a novel way of SPIONs surface functionalization with inexpensive and nontoxic dihexadecyl phosphate (DHP) followed by characterization and analysis of the obtained nanoparticles.

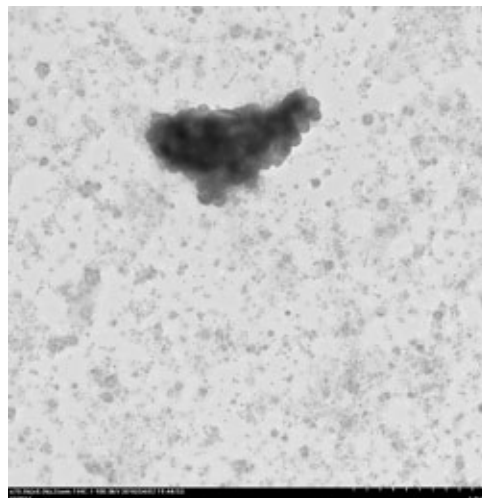


Fig. 1. TEM image of 15 nm superparamagnetic iron oxide nanoparticles (SPIONs) coated with dihexadecyl phosphate (DHP)

Methods

SPIONs were obtained via thermal decomposition of iron (III) acetylacetonate Fe(acac)₃. Functionalization was performed as follows: DHP was dissolved in hexane and mixed with SPIONs suspended in chloroform. Subsequently, water was added. As obtained solution was sonicated for 3h. After sonication, solution was left undisturbed overnight. Then, transparent phase was collected and filtered through 0.22µm pores. Filtrate was centrifuged, resuspended in water and used for analyses. DHP-SPIONs were analyzed with transmission electron microscopy (TEM), dynamic light scattering (DLS), zeta size measurement and Fourier transform infrared spectroscopy (FTIR).

Results

Obtained DHP-SPIONs are water soluble, which confirms that functionalization was successful. Zeta size measurement indicates good colloidal stability. DLS measurement shows some size discrepancies, which could be probably overcome by tuning functionalization conditions. More detailed results will be presented in the future.

This work was supported by UMO-2012/06/A/ST4/00373 grant from National Science Centre (Poland)

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Condensation of semimagnetic exciton-polaritons induced by magnetic field

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Nowadays we observe increasing interest in nanotechnology field. It gives us an opportunity not only for fabrication of devices in nanoscale, but also enables us to go deeper in exploring quantum physics phenomena. Over the last years exciton-polaritons are attracting significant attention. Many effects like Bose-Einstein condensation [1] and polariton lasing [2] were observed. However, the investigation on the effect of magnetic field on exciton-polariton coherent phenomena is still at early stage, even though many interesting phenomena such as the Meisner [3] or magnetopolaron [4] effects are predicted. In our work we focused on magnetic field dependence of exciton-polariton condensate in semimagnetic semiconductor microcavity. Our structure contains four quantum wells (QWs) with 0.5 % of manganese, placed between two Distributed Bragg Reflectors [5, 6]. Excitons confined inside QWs couple to the photonic mode giving rise to two eigenstates called upper and lower exciton-polaritons. Incorporation of manganese in QWs leads to the increased magnetic effects due to the s,p-d exchange interaction between localised

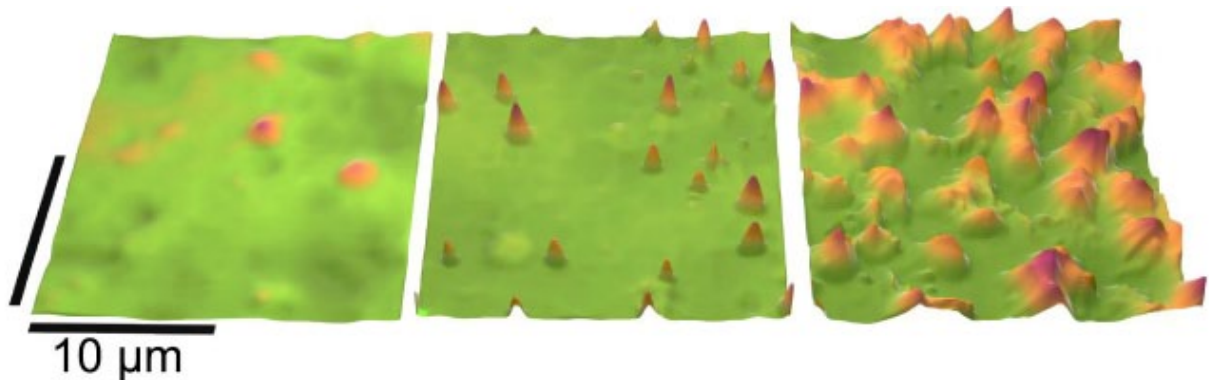


Fig. 1. The emission maps below and above the condensation threshold in magnetic field

electrons of d5 shell of Mn²⁺ and band electrons. By using a confocal microscope with built in magnet up to 9 T we scanned a large area of a sample surface and detected angularly resolved photoluminescence and reflectivity spectra for different positions on the sample. The measurements are performed at the liquid helium temperature. The emission maps below and above the condensation threshold in magnetic field are illustrated in the Figure. For small pumping power and low magnetic field we observe incoherent emission distributed over a large area. This map allows to track the potential distribution for polaritons due to the photonic disorder. By increasing the excitation power and/or magnetic field we observe a condensation of exciton-polaritons into potential minima. Above the threshold the condensate gets further localised and we observe the emission from localised spots, multicomponent in energy. In our work we demonstrate the spectral and spatial distributions of exciton-polaritons and we examine the polarisation of emitted light, very sensitive to magnetic field due to semimagnetic semiconductor structure.

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Properties of methyltrimethoxysilane (MTMS)-aerogel spheres

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The very first aerogels were obtained in the thirties of the twentieth century. However, their practical application was not found. Currently they are encountered mainly as insulation in construction, aerospace, and as a primer for the catalysts of certain chemical reactions. Our goal is to adopt aerogel structures and its unique properties in separation processes, such as: oil - water and oil - gas separation or gas-liquid contactor (CO₂ separation from gas stream), in order to increase separation effectiveness. But before that, investigation of aerogel spheres properties is

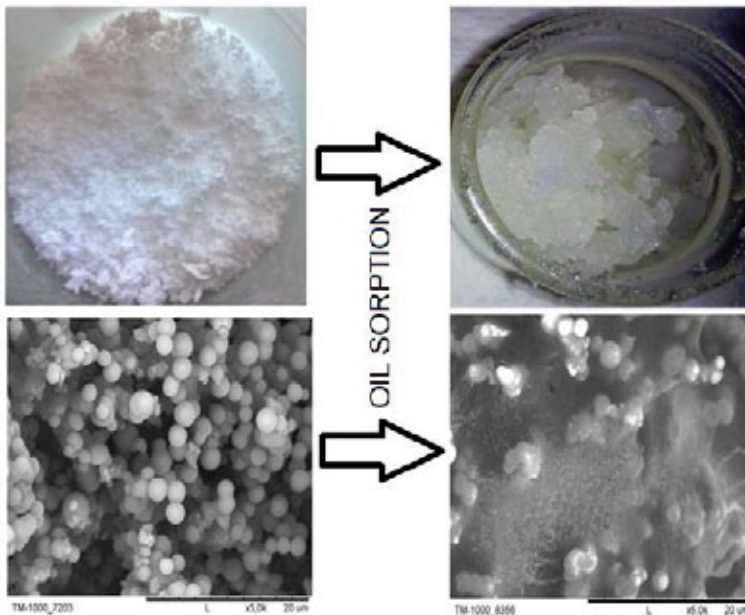


Fig. 1. Photo and SEM picture of aerogel before and after oil (EDHS) sorption.

needed. Aerogels are highly porous solid materials with very low density (and hence low weight) and good thermal insulation. Due to its hierarchical porosity (in micro- and nanoscale), aerogels are highly effective as sorbents, used to absorb oils and other mineral and organic liquids. Aerogels with methyltrimethoxysilane (MTMS) used as a precursor have hydrophobic, oleophilic and oil-sorptive properties (Yun S. et al. RSC Adv. 2014, 4, 4535).

Aerogel spheres are organosilicon structures, synthesized in two step sol-gel process. The precursor is mixed with methanol and the oxalic acid solution, so the water of the acid solution promotes the hydrolysis reaction – acid step. After set amount of time, the ammonium hydroxide solution is slowly added, where the alkaline medium favors the condensation of silanols, increasing the reaction rate and forming a sol – basic step. Synthesis of aerogel spheres was carried in different MTMS concentrations and in variety of drying temperatures. Aerogels were imaged by SEM and investigated by FT-IR spectroscopy. Aerogel porosity and volume shrinkage during drying sequence was measured. Average porosity was above 80% and reached even 95%. Sorption was carried on two different oils (diesel and vegetable oil) and adsorption isotherm was obtained. Results shows that aerogel spheres can adsorb 3 to 9 grams of oil per gram of its own weight. Which is similar to those in literature (Yun S. et al. J. Mater. Chem. A. 2014, 2, 14542-14549).

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Nano hydroxyapatite for tough, strong and resorbable orthopaedic implants

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Hydroxyapatite (HAp) is a major inorganic component of human hard tissues, such as bones and teeth. Its content determines their microstructures and physical properties of hard tissues. It is one of few materials that are classed as bioactive, meaning that it will support bone ingrowth and osseointegration when used in orthopaedic, dental and maxillofacial applications. Its application is limited because of brittleness of HAp ceramic.

The Institute of High Pressure Physics of the Polish Academy of Sciences (IHPP) has developed technologies of the calcium deficient nano- synthesis (called GoHAP), obtained by microwave reactor and the high pressure consolidation technology for ceramic material. Those techniques aim to obtain materials close to the natural structure

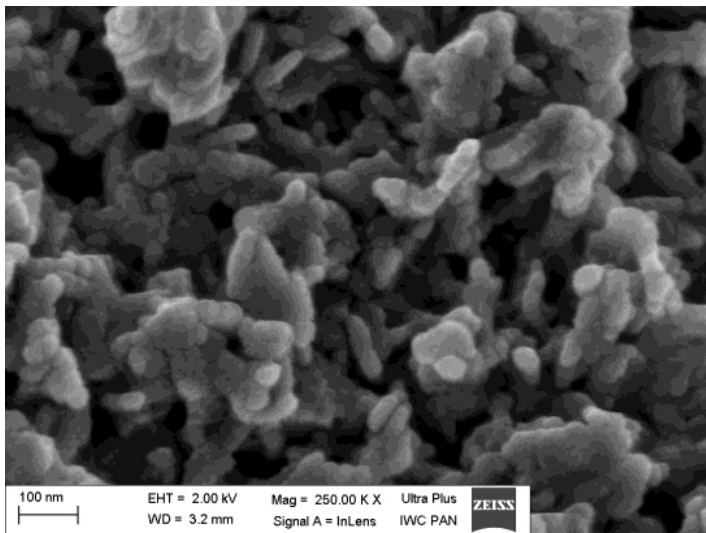


Fig. 1. SEM micrographs of GoHAP powders

and mechanical properties of the bone tissues. Obtained GoHAP ideally mimics the natural hydroxyapatite found in human body. The prepared powder has plate and crystalline structure and is characterized by grain size in the range 5-25 nm; specific surface area is 237m²/g. The morphology of the powder can be controlled, thanks to microwave reactor (1). Figure 1 shows the structure of GoHAP.

The aim of the work is to develop resorbable, tough, strong and biocompatible hybrid composite implants according to patient's needs. Nano HAp and polymer composites are investigated to solve problem of HAp brittleness. We developed isostatic pressure techniques for forming dense ceramic- polymer composites. Our technique permits obtaining bulk material while the bio-compatible nanostructure is preserved.

Research is realized within the "GoIMPANT " Project and it is founded by M-Era.Net program of The National Centre for Research and Development, co-financed from European Union, Regional Development Fund

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Mixed-fiber depth filters to removal of submicron particles from water during filter loading

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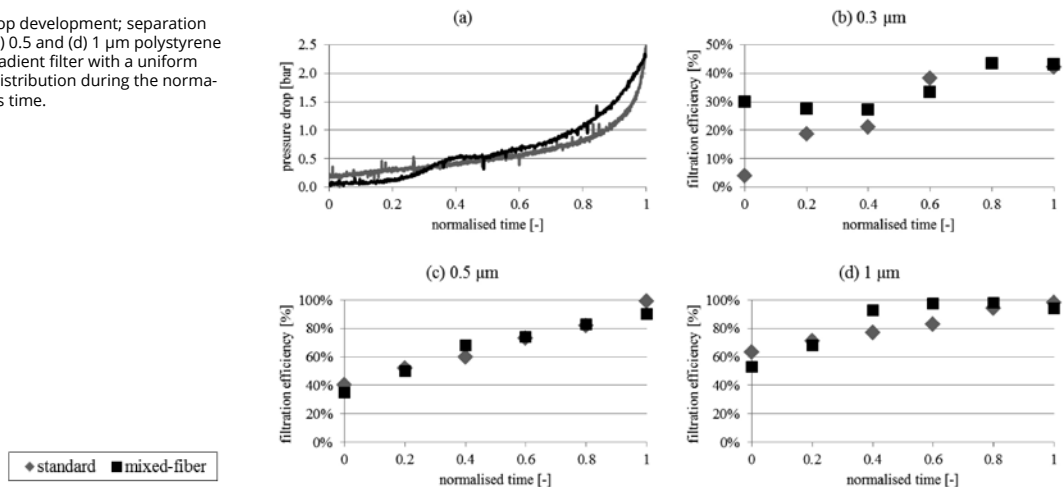
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Melt-blown technique was used for formation of polypropylene fibrous filters characterized by bimodal distribution of fibers. Such filters were tested under constant flow conditions in the industrial scale experiment. A pressure drop on the filter, filtration efficiency, retention capacity and porosity of the filter structure filled with the deposit were measured during the working time of the filter.

The results shown in Fig. 1 indicate that all of the filtration parameters are significantly affected by changes of the filter morphology. The addition of nanofibers highly increases the filtration efficiency of the entire fibrous fabric especially for the particles of most-penetrating size. It also increases the retention capacity of the fibrous structure. By a proper filter design of the mixed-fiber filter structures an efficient nanoparticles separation from water was proved to be possible.

Fig. 1. (a) Pressure drop development; separation efficiency of (b) 0.3, (c) 0.5 and (d) 1 μm polystyrene latex particles by a gradient filter with a uniform and a bimodal fiber distribution during the normalized filtration process time.



Superparamagnetic iron oxide nanoparticles for bioimaging of myoblasts and mesenchymal stem cells for potential use in post-infarction heart stem cells therapy

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Stem cell therapy in the recovery of the cardiac muscle function after myocardial infarction is a very promising and thoroughly researched concept. The basis of this therapy is the transplantation of stem cells directly between the scar composed of connective tissue and healthy cardiac muscle tissue. However, to date, this procedure struggles with low cell retention in the place of injection, low percentage of stem cells survival. Lastly, the methods of imaging of these cells *in vivo* need to be improved. Superparamagnetic iron oxide nanoparticles (SPIONs) are widely used as a contrast agent in magnetic resonance imaging (MRI). It was also investigated as an agent for direct labelling of cells in stem cells therapy.

Here, we present a simple and cheap method of synthesis of high quality, biocompatible SPIONs for direct cell labelling. They are tested *in vitro* for their cytotoxicity, influence on differentiation potential and cell retention.

Nanoparticles were synthesized using thermal decomposition of iron (III) acetylacetonate – $\text{Fe}(\text{acac})_3$. As a capping ligand oleic acid was used, providing both the reduction force for reaction and colloidal stability of the synthesized

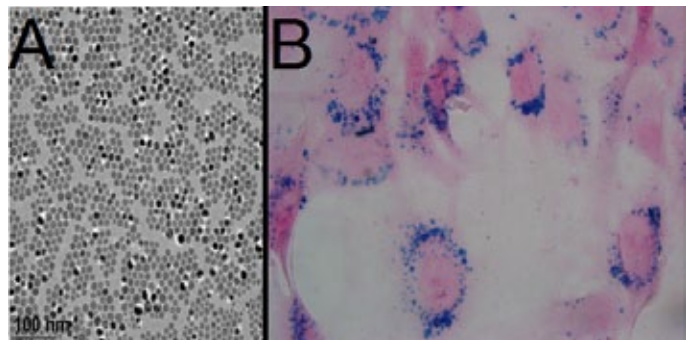


Fig. 1.

A: TEM image of 15 nm superparamagnetic iron oxide nanoparticles (SPIONs) coated with *meso*-2,3-dimercaptosuccinic acid (DMSA).

B: Prussian blue staining for visualization of iron oxide nanoparticles in myoblasts.

nanoparticles. *meso*-2,3-dimercaptosuccinic acid (DMSA) was used for ligand exchange reaction, yielding hydrophilic nanoparticles. Particles were analyzed with TEM, FT-IR, DLS, zeta potential, SQUID.

Human myoblasts and human mesenchymal stem cells (hMSCs) were used for tests and were treated with various concentrations of DMSA-coated nanoparticles. Our results shows that nanoparticles shows no significant toxicity in MTS tests. Cells retain their potential for differentiation as they form multinuclear myocytes. We observed that nanoparticles stay in cells for up to two weeks. Next steps in our research will be tests *in vivo* in mice.

This work was supported by UMO-2012/06/A/ST4/00373 grant from National Science Centre (Poland) and PBS3 nr 247019 grant from National Centre for Research and Development in Poland

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Amylopectin Nanoparticles Preparation by Self-Assemble Method

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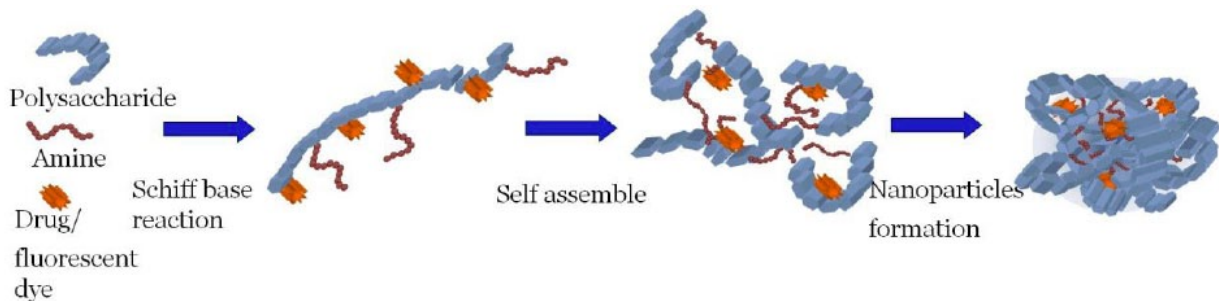
Introduction

Amylopectin is one of the two glucosidic macromolecules that form starch. It is highly branched polysaccharide consists of α -D-(1-4) linked glucose segments connected by α -D-(1-6) branch points glycopyranose. Amylopectin is biocompatible, non-toxic, stable, biodegradable and low cost polymer. It is widely used in the food, paper and chemical industry.

The objective of the present work was to obtain alginate nanoparticles, using self-assemble process. The principal experiment goal was to develop NPs synthesis in mild conditions, without use of organic solvents or surfactants. The main aim of presented study was to evaluate the ability of control the NPs properties (size) through synthesis conditions and use of different amino acids as coiling agents.

Experimental methods

Our original method of nanoparticles synthesis (patent No. 398450) is based on modified amylopectin self-assembly in water environment. First amylopectin molecules are partially oxidized (IO_4^-) to form aldehyde groups along the chain. Nanoparticles synthesis is based on the reaction of active carbonyl groups in oxidised amylopectin and amino groups in amino acids. In water, due to hydrophobic – hydrophilic forces amphiphilic molecules forms



nanoparticles. Nanoparticles formation was verified by using light scattering technique (NanoSight LM 10). The measurements were repeated at least triplicate. Optimal combination of polysaccharide and reagents concentration, their modification and component ratio were adjusted and defined.

Results and discussion

4 amino acids were examined as coiling agent (valine, glycine, leucine, phenylalanine) for 3 amylopectin oxidation degree (5, 7 and 10%). Also 4 substitution degree of aldehyde group was tested (10, 25, 50 and 100%). Based on these results, it can be concluded that properties of amino acids have important influence on nanoparticles formation. Nanoparticles diameter is decreasing with oxidation degree while no change of nanoparticles diameter was observed with change of substitution degree for given type of amino acids. Impact of the freeze-drying process on the nanoparticles diameter also was conducted. For all examined nanoparticles after lyophilization and rehydration obtained nanoparticles were slightly larger. Measured diameter errors are larger but the diameter distribution of nanoparticles is narrower. That leads to the conclusion that received nanoparticles have diameters similar but with more uniform size distribution as a result of the staidly going process of rehydration.

Conclusion

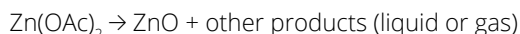
Obtained nanoparticles are very stable, biocompatible and homogeneous in size. Nanoparticles can be dried to the powder form and easily get dispersed again when immersed in water. Conducted studies show that the number of substituted aldehyde groups by amino acids and its properties defined formation of nanoparticles. The best results were obtained using phenylalanine as cooling agent for all substitution degree. Nanoparticles prepared as described synthesis method have potential use in drug delivery systems with a particular orientation to the therapy and diagnosis of tumors.

Size-dependent density of zinc oxide nanoparticles obtained by microwave solvothermal synthesis

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Laboratory Nanostructures IHPP PAS is an expert in the synthesis of nanoparticles (NPs) with small size distribution using technology microwave solvothermal synthesis (MSS). MSS technology allows precise control parameters of NPs synthesis such as reaction time, temperature and pressure. The authors obtain the zinc oxide particle with narrow size distribution in microwave solvothermal synthesis which can be expressed as follows:



The developed method enables precisely control of the average particle size and chemical composition of the obtained ZnO NPs by regulating composition of precursor and synthesis parameters. Increase in the average particle size of the ZnO NPs from 22 to 115 nm which resulted and a decrease in the specific surface area from 53 to 9 m²/g and at the same time, the density increased from 5.20 g/m³ to 5.57 g/m³. The authors synthesized a pure, fully crystalline hexagonal ZnO NPs (Fig. 1).

Research directions of the Laboratory of Nanostructures IHPP PAS are focused on the characteristics of nanomaterials according to ISO/IEC 17025 and the possibility of their application in medicine, optics, optoelectronics pharmacy and cosmetics. Laboratory of Nanostructures IHPP PAS deals with the characteristics of nanomaterials obtained by our team, project partners (e.g. Shyman), as well as provides research services such as analysis of density, surface area, morphology, phase composition, thermogravity of nanomaterials, surface tension, viscosity, stability and the size of nanoparticles in colloidal solutions and suspensions.

Name	Average crystallite size from Scherer's formula (XRD) [d _c ±σ.nm]	Average grain size calculated from SSA BET [d±σ.nm]	Specific Surface Area (BET) [a _s ±σ.m ² /g]	Density [ρ±σ.g/cm ³]
ZnO Type 1	21 ± 4	22 ± 3	53 ± 3	5,20 ± 0,05
ZnO Type 2	25 ± 4	28 ± 4	40 ± 3	5,24 ± 0,05
ZnO Type 3	33 ± 7	33 ± 4	34 ± 3	5,33 ± 0,05
ZnO Type 4	50 ± 17	48 ± 4	23 ± 3	5,48 ± 0,05
ZnO Type 5	58 ± 18	78 ± 4	13 ± 3	5,52 ± 0,05
ZnO Type 6	52 ± 10	115 ± 4	9 ± 3	5,57 ± 0,05

Fig.1 Properties of ZnO nanopowders synthesized by Laboratory Nanostructures IHPP PAS.