RUĐER BOŠKOVIĆ INSTITUTE, CROATIA
JOŽEF STEFAN INSTITUTE, SLOVENIA
JOANNEUM RESEARCH, AUSTRIA

New Materials

BOOK OF ABSTRACTS

in Industry & Medicine

Zagreb, 25 – 26 November 2008

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CONTENT

WORKSHOP ON NEW MATERIALS
IN INDUSTRY & MEDICINE:
RTD POTENTIAL FOR COLLABORATIVE PROJECTS

Within the scope of the European Association of Research and Technology Organisations

EARTO

Special Interest Group

Novel bioactive substances for industrial and biomedical use

Conclusions

(accepted by participants at the end of the meeting)

The Workshop was successful and developed into international conference, which included:

- presentations of the partner institutes Joanneum Research Institutes (JR, Austria), Jozef Stefan Institute (JSI, Slovenia) and Ruder Boskovic Institute (RBI, Croatia) done by respective Directors,
- 27 research presentations done by equally presented experts from partner institutes and
- parallel session of the 3 directors and administrative officers of the institutes devoted to the future interaction activities.

The success of the meeting includes also intensive discussions on collaboration perspectives among experts, interest of the public media and decision to continue with similar activities in spring 2009 devoted to the next topic – *Biosensors*.

On November 26th participants of the meeting agreed on following conclusions to be used for public dissemination of results and reporting to EARTO and other relevant institutions:

1. R&D on New Materials can initiate and support industrial development in particular of modern industry based on micro and nano technologies, which we find necessary in current socio-economic situation.
2. R&D of New Materials is also important for development of modern medicine, especially for drug development and development and functionalisation of novel materials for medical implants, which is of broad socio-economic relevance.
3. Sophisticated equipment and methods available at RTOs are open for potential partners and should promote collaboration between RTOs, other research institutions and industry.
4. Material Sciences could be strong link to join R&D activities of RTOs and other R&D oriented partners (industry, research institutions, etc.), therefore EARTO should push this topic further involving other RTOs, organising similar further workshops and informing industry and European Commission on EARTO's initiative.

On behalf of the participants the Conclusions were prepared by
Neven Žarković, RBI,
Zagreb, November 2008.

Perovskite dielectrics for tunable applications

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Most of the investigations of tunable materials by the scientific community have focused mainly on paraelectric modifications near ferroelectric transitions of the displacive type, in particular on $(Ba_{1-x}Sr_x)TiO_3$-based compounds. However, their high losses, dielectric constant and the temperature dependence of the dielectric constant limit their widespread use, leading us to search for novel materials. We focused our investigation of tunable materials on ferroelectrics of the relaxor type, in particular on $Na_{0.5}Bi_{0.5}TiO_3$. The temperatures of the $Na_{0.5}Bi_{0.5}TiO_3$ phase transitions and thus the intensities of the dielectric relaxations were modified by the addition of various incipient-type ferroelectric compounds. We observed that samples with the highest tunability also exhibit the highest dielectric relaxations and have a morphotropic phase composition. However, these samples also show increased dielectric losses. Improved figures of merit were obtained for samples with increased additive concentrations and paraelectric polar order. We determined that this improvement relates to the low-temperature dielectric relaxations and to the dynamics of nanosized polar regions. In addition, it might be expressed by the exceptionally high nonlinear coefficients b.

Organic photodiodes – 3 key features

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Organic semiconductors have obtained considerable interest in the fields of electronic and photonic devices due to a wide range of applications as low-cost, large-area and disposable or throwaway electronics on thin and flexible substrates. In particular organic photodiodes have improved to a level which is sufficient for many applications. The ease of processing, based on layer-by-layer vacuum deposition, and the possibility to deposit these devices basically on any substrate as well as the possibility to tune the spectral response make organic photodiodes attractive for integrated systems, especially allowing facile integration with planar chip-based systems. The presented photodiodes are based upon Tang-type pn-heterojunction devices, which consist of thin layers of p-type conducting copper phthalocyanine (CuPc) and n-type perylene tetracarboxylic bisbenzimidazole (PTCBI). As a first key feature we present the possibility to manufacture organic devices on nearly every kind of substrate. In order to demonstrate this we fabricated organic photodiodes on conventional newspaper. As a second key feature we point out that organic photodiodes can be monolithically integrated into different application areas. As an example for this we demonstrate the monolithic integration of a microstructured organic photodiodes with a planar optical stripe waveguide. The manufacturing of this waveguide-integrated organic photodiode is based on an UV photolithography process. As a third key feature we point out that, due to the great variability of organic semiconducting materials, it is possible to create new functions compared to inorganic photodiodes. As an example for this spectral selective organic photodiodes are presented. The spectral sensitivity is achieved either by choosing organic semiconductors with the appropriate photoresponse or by utilizing adequate device architectures with integrated optical filters. The results demonstrate the great flexibility of organic semiconductor materials.

Metal oxide nano-particles and nano-composite polymer electrolytes - electrodes and electrolytes in solar and galvanic cells of the second generation

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Nanocomposite polymer electrolytes and nanophased metal oxide films are tailored and used as electrodes and electrolytes in galvanic and solar cells of second generation.

$(PEO)_8ZnCl_2$ polymer electrolytes and nano-composites were prepared using PEO γ-irradiated to selected doses and TiO_2 nanograins. The influence of added nanosize TiO_2 grains to polymer electrolytes and the effect of γ-radiation from a Co-60 source were studied by small-angle X-ray scattering (SAXS) simultaneously recorded with differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD) at synchrotron ELETTRA. Infrared (IR) and impedance spectroscopy (IS) were also performed (1). We observed changes between 293 K and 373 K for treated and as prepared polymer electrolyte in SAXS/DSC/WAXS spectra and during the phase transition to the superionic phase at 335 K. Above-mentioned treatments largely enhanced the conductivity of polymer electrolyte. Room temperature conductivity increase up to two orders of magnitude was achieved.

Metal oxide nanostructured thin films were studied as electrodes for dye-sensitized solar cells and charge-discharge second generation batteries. We have studied materials based on titanium, cerium and vanadium (2). Materials based on titanium are nanocrystalline TiO_2 thin films, which play an important role in new generation of photochemical solar cells. Dye-sensitised cell differ from the semiconductor devices that they separate the function of light absorption from charge carrier transport. This cell was made of relatively non pure material with a cheap preparation procedure and energy conversion efficiencies ranging from 7 to 12%. Average grain sizes and specific surface areas as a function of temperature for TiO_2 samples annealed in oxydizing and non-oxydizing atmosphere were obtained by GISAXS measurements at synchrotron ELETTRA.

Vanadium oxide, such as V_2O_5, has been extensively studied because it tends to form layered structure that allows the intercalation/de-intercalation of different ions between its layers. It can be used as catalysts, in electrochromic device, in an advanced electrochemical cell concept, especially in lithium batteries. We have also studied V/Ce films intercalated with Li^+-ions. 2D-GISAXS measurements revealed morphology change upon the intercalation of Li^+ ions. GIXR (grazing-incidence X-ray reflectivity) was used for determination of layer thickness.

The conductivity of $(PEO)_8ZnCl_2$ polyelectrolytes films can be significantly increased by radiation processing of poly(ethylene oxide) and addition of TiO_2 nano-grains. These treatments significantly increased conductivity of polyelectrolytes and lowered temperature of the phase transition.The results are stimulating for further research of PEO polyelectrolytes and nanocomposites and also gather information on underlying conductivity mechanisms.

GISAXS at ELETTRA could be applied for determining grain size and porosity in TiO_2, CeO_2, V_2O_5 and V/Ce oxides on glass substrate as well as for following the process of intercalation of cations into the porous nanostructured films. The morphology obtained by modifying and choosing particular preparation is suitable for application in advanced electrochemical and efficient new solar cells.

By means of electrical measurements, we have shown that polymer electrolyte $(PEO)_8ZnCl_2$ can be combined with V_2O_5-CeO_2 at 38 at.% of V as intercalation cathode in order to obtain all solid-state rechargeable galvanic cell. Further optimisations of electrolyte and electrodes properties are in progress.

References

1. A.Turković, M. Pavlović, P. Dubček, M. Lučić-Lavčević, B. Etlinger, S. Bernstorff, SAXS/DSC Study of Polymer Electrolyte for Zn Rechargeable Nanostructured Galvanic Cells, J. of Electrochemical Society 154 (6) (2007) 554-560. and ibid. Virtual Journal of Nanoscale Science & Technology **15** (2007), 17; 554-560.
2. A. Turković, SAXS Characterization of Mesoporous Thin Films: A Solar Energy Point, Chapter 11 in the Book: Solar Energy Research Technology and Applications, Editors William L. Olafsson, V.I. Bengsson, Nova Science Publishers, Inc. (2008).1-29.

Electro-deposition of ferromagnetic (shape memory) materials with reduced dimensionality

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Equiatomic ordered $L1_0$ Co-Pt and Fe-Pd systems are very promising as magnetic storage media and for MEMS devices. A part of MEMS and NEMS devices include the build in of actuators with high performances. Ferromagnetic Shape memory Alloys ($Fe_{70}Pd_{30}$) represent interesting candidates since reversible strains of several percents can be achieved in moderate fields of below 1T.

Electro-deposition represents a low-cost alternative for preparing nano-engineered materials, without extensive loss of material. One dimensional or two dimensional nanostructures could easily be obtained with the template assisted electrodeposition into a high aspect ratio polycarbonate template. Co-Pt based thin films and tubular nanostructures were successfully synthesized, and high coercivities of μ_0H_C=1.2T were achieved in thin films. One-dimensional Co-Pt-based nanostructures were prepared via template-assisted electro-deposition into high-aspect-ratio track-etched polycarbonate membranes. Tubular nanostructures with a diameter of 200 nm and lengths of 1000−8000 nm were obtained directly, without any pore-wall functionalization, as was previously reported in the literature. The mechanism of direct tube formation was attributed to the appropriate relative rates of the deposition and the diffusion of the Co^{2+} and Pt^{2+} ions into partially Au-covered pores. We found that diffusion is the rate-determining step of the electro-deposition process; therefore, the stoichiometry and the related properties can be controlled via the electrolyte composition. The highest obtained coercivity was μ_0H_C=0.85 T, which makes these materials interesting for advanced electronic and magnetic devices, as media for high-density magnetic recording or as a potential drug- delivery agent. Furthermore, their large surface-to-volume ratio and Pt content would make them interesting for catalytically driven processes. Another ferromagnetic system, Fe-Pd, was successfully synthesized via the electro-deposition method and thin films as well as one-dimensional nanostuctures were obtained. The reaction regime was found to be kinetically controlled; therefore, the stoichiometry and the related properties can be influenced via the applied voltage. This knowledge is extremely important since the $Fe_{50}Pd_{50}$ composition gives high coercivities, while $Fe_{70}Pd_{30}$ composition is a magnetic shape-memory alloy capable of producing strains of 6-10 % in moderate magnetic fields.

Nanoparticle Dispersions of Polycyclic Aromatic Hydrocarbon Materials

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In the last few years research on different kinds of organic nanoparticles is steadily increasing. In the past, inorganic particles in the size range of a few nanometres were found to show size dependent optical and electronic properties. Recently, organic nanoparticles were also found to show some size dependent optical and nonlinear optical properties even in a rather big size range between 100 to 200 nm. Especially polycyclic aromatic hydrocarbons show a very broad range of interesting properties like intensive colour, fluorescence, photoconductivity, semiconducting properties and a very special chemical and photochemical behaviour. Therefore, these materials are often used for pigments and dyes, fluorescent probes, etc. and they are promising materials for sensors, bioprobes and organic electronic devices. While there is abundant literature on the preparation and applications of inorganic semiconductor particles, reports on organic nanoparticles are relatively scarce. A frequently used process to prepare pure organic nanoparticle dispersions is the so called re-precipitation method. [1]. Here, a solution of the organic material in a good solvent is added into an excess of a poor or non-solvent under vigorous stirring. The material precipitates and submicron sized particles are formed depending on temperature, concentration, stirring and other parameters. Another method, based on laser ablation of organic crystals dispersed in a liquid has recently been introduced by Tamaki [2]. In this case, intense laser light is irradiated onto a dispersion of a coarse powder or large crystals of organic material in a solvent or surfactant solution. Above a certain laser fluence threshold material evaporates from the surface of the crystals by a laser ablation mechanism and subsequently condenses in the surrounding liquid phase to form submicron or nanometre sized particles.

We report on different methods for the preparation of stable nanoparticle dispersions of polycyclic hydrocarbons such as pentacene, tetracene, rubrene, and perylenediimides. This includes the re-precipitation method from solution, laser ablation, and a novel direct condensation method. The direct condensation method allows the preparation of large volumes of stable, concentrated dispersions by avoiding most of the disadvantages of the other existing techniques. The particles were characterized regarding particle size and shape, dispersion stability and optical and spectroscopic properties. Particle size was usually about 100 nm, and the dispersions showed structured absorbance bands in the visible region typical for the respective substances. Rubrene and tetracene particles gave characteristic luminescence spectra. Many different film forming and structuring methods can be applied for further processing of the nanoparticle dispersions. They were shown to be compatible with spin coating, spray coating, dip coating, electrostatic self assembly and ink-jetting techniques.

References:

[1] H. Nakanishi, H. Oikawa: *Reprecipitation Method for Organic Nanocrystals*, in: H. Masuhara, H. Nakanishi, K. Sasaki (Eds.) *Single Organic Nanoparticles* (Springer, Heidelberg 2003).

[2] Tamaki Y., Asahi T., Masuhara H., Appl. Surf. Sci., **168** (2000) 85-88.

Inkjet Printing Technology

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Inkjet is a non-contact printing technology in which droplets of ink are jetted from a small nozzle directly to a specified position on a substrate. From the beginning of the 1960s this technology was patented and improved leading to the first commercially available Inkjet Printers. Whereas in the past decades simply graphic colored images where produced, Inkjet Printing undergoes a renaissance nowadays. Utilizing the ability of this additive technique to place picoliter sized droplets on different even flexible substrates has led to an expansion of possible Inkjet Printing applications. Efforts of materials developers worldwide focus now on structured deposition of advanced functional materials like metal nanoparticles, fluorescent dyes, functional polymers and biomolecules.

In this work we present the adaption of commercially available silver (Ag) inks to a Dimatix DMP 2800 Drop on Demand inkjet printing system. On the one hand the formulation and optimization of different jettable inks is depending on various parameters like viscosity, surface tension and fluid evaporation. On the other hand important parameters are the characteristics of the substrate. It is a major goal to optimize the characteristics of the jettable fluid to match the substrate's requirements.

Hydrothermal synthesis of multiferroic materials

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The class of materials, extremely important for computer and electronic industry, are the perovskite materials that typically possess so-called ‘ferroic’ properties: ferroelectricity, ferromagnetism and ferroelasticity. Only some of them are multiferroic materials that possess two – or all three – of the ‘ferroic’ properties. For this kind of materials both magnetization and polarization are coupled, and thus in principle permit data to be written electrically and read magnetically. This is attractive, given that it would exploit the best aspects of ferroelectric random access memory (FeRAM) and magnetic data storage, while avoiding the problems associated with reading FeRAM and generating the large local magnetic fields needed to write A part of already established collaboration of the groups in IRB and IJS is pointed toward the syntheses and the study of perovskite multiferroic materials as BiFeO3, BiMnO3, BiCoO3. Bismuth ferrite is commensurate ferroelectric and incommensurate antiferromagnetic at room temperature, BiMnO3 is ferromagnetic and ferroelectric below TM=105 K, while BiCoO3 have antiferromagnetic ordering and giant ferroelectric polarization leading to giant magneto-electric coupling.

We use the hidrothermal syntheses, that is crystallization of substances from high-temperature aqueous solutions at high vapor pressures, since it is simple and inexpensive method. Since it is hard to synthesized pure multiferroic, the optimization of hydrothermal conditions (pH, temp., time) is necessary to get pure materials with reduced dimensionality and nanometric sizes. The phases appearing during a hydrothermal reaction in the Fe–Bi–O system were investigated, with the aim to optimize the conditions for the syntheses of nanostructured multiferroic BiFeO3.

The prepared samples were analyzed by X-ray powder diffraction (XRD), while the morphology, nanostructure and chemical composition were determined using high-resolution transmission electron microscopy (HRTEM) and/or scanning electron microscopy (SEM). In situ temperature dependent Raman spectroscopy measurements were shown as a tool for observation of antiferromagnetic to paramagnetic transition in BiFeO3, since the antiferromagnetic behavior of BiFeO3 can not be straight forward observed by magnetic measurements.

We succeed in the syntheses of pure bismuth ferrite in the procedure where solutions containing both iron and bismuth ions were co-precipitated prior to hydrothermal processing. The phonon anomalies were observed by high temperature Raman spectroscopy around the magnetic Neél temperature (≈640 K), although this magnetic transition is not accompanied by a structural phase transition.

In the future we plan in situ high temperature Raman investigation of BiFeO3 at the ferroelectric Curie temperature (≈1100 K) where a first-order structural phase transition is expected. Further optimizations of hydrothermal conditions for syntheses of BiFeO3 with reduced dimensionality as well as hydrothermal synthesis of BiMnO3, BiCoO3 are also planed. Detailed Raman investigation of temperature phase transitions in synthesized multiferroics will clarify their ferroic properties. These measurements will be possible since first class Raman instrument in IRB is equipped with various cryostats and temperature cells for in situ temperature measurement from 10 to 2000 K.

Materials processing for application in ITER fusion reactor

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The activities of the Slovenian Fusion Association (SFA) are briefly presented. As a part of the European Fusion Development Agreement (EFDA), SFA performs research oriented towards solving technological problems for the future fusion reactor ITER currently under construction in Cadarache, France. The major problem of modern fusion reactors is interaction between hot fusion plasma and solid materials. Plasma is often at the temperature of about 100.000.000°C and causes degradation of the materials facing plasma. The most exposed part of the ITER divertor will be made from Carbon Fibre Composite (CFC) which interacts with hydrogen ions forming CH_x molecules that desorb from the CFC and condense in remote parts of the reactor. The deposited films represent an unpredictable source of hydrogen and are radioactive since tritium is used as fuel. The deposits should be removed occasionally. The IJS research group works on removal of deposits with neutral oxygen atoms. The principles of such cleaning procedure as well as technical considerations are presented.

Radiation modification of polymers and nanomaterials

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The research on influence of gamma- and electron beam radiation on polymers and nanocomposites is presented. Various applications of radiation modification of polymers are already in practice. Depending mainly on chemical nature of a polymer, crosslinking and/or degradation are possible outcomes of irradiation. The most important advantages of polymer radiation modification are:

- no initiators and/or catalyzers are necessary
- initiation is homogeneous and its rate is independent of temperature
- low temperature reactions are possible
- solid state reactions are easily initiated
- graft copolymerization is facilitated
- better overall properties of irradiated products can be obratined
- products are sterile, what is of special interest in biomedical applications

Disadvantages are few: relatively high cost of irradiation facilities and radiation protection, particularly for isotope sources.

To stress the possibilities offered by ionizing radiation, some examples in which results would not be obtained or would be misinterpreted without radiation are listed:

- Based on previous research, the influence of upper liquid-liquid transition (a third order phase transition caused by cleavage of intramolecular hydrogen bonding in polyester) on crosslinking of unsaturated polyester resin was expected. It has to be investigated by performing reactions on various temperatures including those below room temperature what cannot be achieved by chemical initiators while radiation initiation was very effective.
- While studying post-radiation crosslinking of various unsaturated polyester resins by DSC, differences in thermogram shapes were observed that are usually attributed to initiator(s), but in this case none were used. The explanation was found by NMR spectroscopy: the resin having a single peak in thermogram had polyester containing *iso*-phthalic units. Reaction induced phase separation due to presence of *ortho*-phthalic units in polyester resulted in thermograms with double peaks. By additional literature reviewing it was

found that *ortho*-phthalic units were present in almost all polyesters that showed DSC thermograms with double peaks.

- Poly(ethylene oxide), PEO, is semicrystalline polymer valuable for biomedical applications and polyelectrolytes. It is important to study the effects of radiation conditions on PEO since it can crosslink or degrade, depending on radiation conditions. If solid PEO is irradiated in air degradation of amorphous part produces short chains that form additional macroconformations and overall crystallinity increases. On the other hand, it seems that on irradiation in aqueous solutions crosslinking prevails reducing the crystallinity.

In the field of nanomaterials possibilities for radiation modification are even greater. At gamma source in our laboratory nanoparticles were prepared and modified. Polymeric nanoparticles can be made from soluble polymers. Radiation can be used to prepare nanocomposites by:

- polymerization or crosslinking of monomers or resins with nanoparticles
- simultaneous polymerization and production of nanoparticles
- intercalation of polymers to clays and zeolites.
- addition of nanoparticles to previously irradiated polymers

Some of our investigations on nanocomposites of irradiated PEO indicate possible synergism between irradiation and included nanoparticles. Offering our experience and wishing to enhance research and application possibilities we are open for cooperation.

Extremely acidic organic molecules – computationally predicted superacids awaiting experimental synthesis

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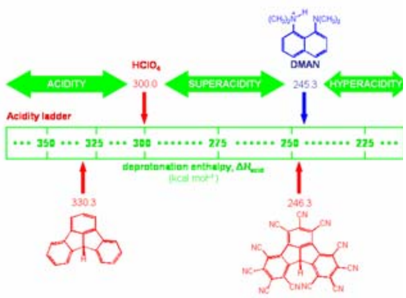
We developed a useful and efficient strategy in designing exceptionally acidic organic molecules consisting of polycyanation of known organic skeletons. It has led us to theoretically predict many molecules exhibiting superacidity and the very first neutral organic hyperacid, undecacyanofluoradene. Apart from unprecedented acidity, these molecules and their deprotonated anions should possess many useful properties promoting them as candidates for new materials.



Superacid is any acid stronger than 100% sulfuric acid.[1] There is an ongoing interest in chemistry for compounds exhibiting extreme acidity, since neutral superacids are the most important catalysts in chemical transformations.[2] In a majority of acid-catalyzed chemical reactions stronger acids provide better catalyst. Nowadays, chemistry and industry predominantly make use of strong inorganic acids although their application is associated with a number of drawbacks and environmentally intolerable solutions. Replacing these acids with exceptionally active organic superacids would reduce waste and energy needs, cut down the process time and make the overall process safer and more economical. Having all in mind, design of novel neutral organic superacids is vital from both practical and scientific points of view.

Our strategy[3] in tailoring remarkably acidic molecules has enabled us to predict several classes of superacids and the very first hyperacid, namely undecacyanofluoradene.[4] As evidenced by their gas-phase deprotonation enthalpies

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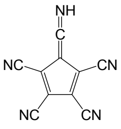
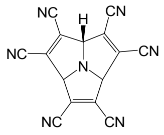
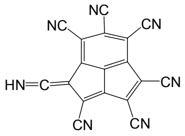
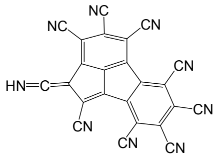
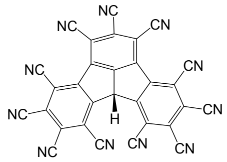
[1] R. J. Gillespie and T. E. Peel, *J. Am. Chem. Soc.* **1973**, *95*, 5173–5178.

[2] G. A. Olah, G. K. S. Prakash and J. Sommer, *Superacids*, Wiley-Interscience, New York, 1985.

[3] R. Vianello and Z. B. Maksić, *Chem. Commun.* **2005**, 3412–3414; *Tetrahedron*. **2005**, *61*, 9381–9390; *Eur. J. Org. Chem.* **2004**, 5003–5010.

[4] R. Vianello and Z. B. Maksić, *New J. Chem.* **2008**, *32*, 413–427, **Hot Article**.

(ΔH_{acid}) or by pK_a values in DMSO, they surpass the acidity of sulfuric acid by 30–50 orders of magnitude. Some of the proposed systems are shown in Scheme 1.

system	H_2SO_4					
ΔH_{acid} (kcal mol^{-1})	306.3	263.9	255.1	261.8	251.9	246.3
p$K_{a,DMSO}$	1.99	–20.2	–26.5	–22.6	–16.8	–21.6

Scheme 1

Since the selected molecular skeletons are long-known in chemistry and the synthetic pathways of polycyanation are well-documented in the literature it is likely that some of the proposed molecules could be prepared. It is also expected that the conjugate base anions of these superacids would possess some useful properties like low nucleophilicity, low basicity, weak coordinating ability and high solubility in organic solvents, which should make them useful in everyday chemical applications.

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Semiconductor Nanostructures

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In this short presentation we shall discuss some aspects of research on semiconductor nanostructures. We shall illustrate some examples of our recent research on defects and defect engineering in the bulk semiconductors to show how defects and their engineering affects the bulk properties of matter.

Next we will demonstrate how nanosctuctured semiconductors affect the properties of matter, and illustrate the possible applications for memory devices of new generation and/or advanced solar cells of the third generation. We shall show few possible modes of semiconductor nanostructures production and illustrate several techniques we apply for their characterization.

Laser and plasma assisted coating techniques for industrial and medical applications

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Many of the presently used Physical Vapour Deposition techniques (PVD) like sputtering, arc evaporation, and PA-CVD are not able to provide coatings at temperatures < 100°C with properties of high- or medium-temperature deposited coatings. In the field of PVD the Pulsed Laser Deposition (PLD) coating technique stands out against nearly all others by its unique feature of pulsed high- and low-energetic plasma flux, enabling even coating at room temperature (~ 25-40°C) with properties known only for elevated deposition temperatures (> 250°C). Combining PLD and magnetron sputtering in so-called hybrid processes enables the realisation of excellent film adhesion, advanced film properties and high deposition rates. Potential fields of application are wear-resistant, low-friction, decorative and biocompatible coatings for temperature sensitive substrates.

The presentation will give an introduction in PVD and will show the principles of PLD and hybrid processes. Practical applications will be demonstrated based on the R&D activities of JOANNEUM RESEARCH.

Biomedical materials at IJS – from magnetic beads to vascular grafts

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Plasma (gaseous discharge) is often used for surface modification of materials, especially polymer materials. An exposure of a sample to a high flux of neutral atoms formed in plasma results in surface functionalization of the material and increased surface roughness, leading to changes in the surface energy and hydrophilicity. By this way biocompatibility of the materials like human implants can be enhanced. By plasma treatment we can also enhance surface adhesion of various bioactive coatings to the substrate. In medical applications usually oxygen or nitrogen plasma is used. Three different applications of plasma in biomedical field are presented including functionalization of organic composites of magnetic beads, surface modification of artificial blood vessels and sterilization of medical materials.

Zirconia based ceramics for dental applications

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The growing demand for esthetic restorations in dentistry has led to the development of tooth-colored, metal-free systems. In most cases, yttria partially stabilized tetragonal zirconia (Y-TZP) is used as the core material, owing to its superior mechanical properties, chemical stability and biocompatibility. These zirconia-based all-ceramic dental restorations are manufactured to serve in the aggressive environment of the oral cavity for a certain period of time, which normally spans 7-10 years. For the material's selection and microstructure design the following two criteria should taken into consideration: the damage tolerance upon mechanical surface treatment and the aging behaviour in an aqueous environment. Based on the results of our extensive research work conducted to evaluate the effects of dental grinding, sandblasting, fatigue and ageing on performance of several Y-TZP ceramics, differing in their chemical composition and mean grain size, the coarse-grained bio-medical grade Y-TZP ceramics also containing 0,25 % of alumina was suggested for dental applications. This material was used in the production of newly developed dental root posts with a core for affixing the prosthetic crown that were subjected to preclinical testing and clinical trials.

In order to improve the adhesion, the interior (cementation) surface of the fixed partial denture was modified by applying an alumina coating exhibiting a large surface area. For fabricating the coating, a relatively simple process was developed that exploits the dissolution/precipitation of aluminum hydroxides, which originate from the hydrolysis of AlN powder in an aqueous suspension. A uniformly thin nano-crystaline coating consisting of gamma-AlOOH in the form of 6 nm thick and 250 nm long interconnected lamellas can be formed this way. By a heat treatment at 600 - 1200 ^{0}C these lamellas will be transformed to a transient alumina without any noticeable change in the morphology, but their bonding to the substrate will be significantly improved. This coating has a potential of improving the adhesion of dental cements to sintered ceramic substrate by a factor of 2-4, depending on the surface roughness of the substrate and dental cement used.

More recently, zirconia based full-ceramic dental implants were also introduced to replace the traditionally used metals. Since these implants do not bond to living bone, a bioactive coating was deposited onto the surface of sintered Y-TZP ceramics, using a biomimetic method. After just two hours of immersion using a supersaturated solution containing Ca^{2+} and PO_4^{3-} ions, the ceramic substrates were covered with a thin layer of poorly crystallized calcium phosphate nanocrystals. Initially, the adhesion was poor, but it improved substantially during an additional heat treatment at 1050 ^{0}C for 1 hour. During this heat treatment, the platelet-shaped Ca phosphate particles deposited from a supersaturated solution onto the surface of the substrates grew into larger and more isotropic grains forming a dense coating also exhibiting bioactivity in the simulated body fluid (SBF).

Potential Use of Crystalline Aluminosilicatesin Medicine and Pharmacology

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Zeolites are hydrated natural and synthetic three-dimensional microporous crystalline solids with well-defined structures containing AlO_4 and SiO_4 tetrahedra linked through the common oxygen atoms in a regular framework. The properties of zeolites such as ion-exchange, inter-crystalline pores that discriminate between molecules of different dimension, strong acidic sites and active hosts for metal catalyzed reactions have earned them extensive industrial uses, and fundamental zeolite research has also become an area of great interest. Besides, there is abundant evidence that zeolites (molecular sieves) possess positive biological activity as a basis for their present and potential application in medicine and pharmacology.

To better understanding the interactions between inorganic microcrystalline materials (zeolites) and biological systems, fundamental chemical, physical and structural properties of zeolites are presented. Although most of studies of the interaction of zeolites and living systems include natural zeolites (most frequently clinoptilolite), the latest studies showed a great potential of the synthestic ones. Hence the advantage of synthetic zeolites over natural ones, based on a great number of structural entities (mere than 300), purity, defined cationic forms and possibility of their controlled modification and controlling of particulate properties (crystal shape and size from micro to nano) are critically evaluated. Finally, some of results of the latest studies concerning the interactions of synthetic zeolites performed at the Ruđer Bošković Institute are presented.

Functionalized magnetic nanoparticles for biomedical applications

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In biomedical applications involving magnetic nanoparticles, their ability to be manipulated or detected from a distance using an external magnetic field is an important factor. In diagnostics, the nanoparticles are targeted to specific tissue with a selective targeting ligand (for example, with a monoclonal antibody) attached to their surfaces. The nanoparticles concentrated in the targeted tissue (for example, in a tumor) can act as a contrast-enhancement agent for MR imaging, or alternatively, they can be detected through their magnetic properties. In therapy, the magnetic nanoparticles are used for targeting bonded therapeutic agents to a certain part of the human body using an external magnetic field. The magnetic nanoparticles can even be used to overheat a malignant tissue. In magnetic hyperthermia, the magnetic nanoparticles are concentrated inside the tumor and the malignant cells are then overheated by exciting the nanoparticles with RF alternating magnetic fields.

For biomedical applications, the magnetic nanoparticles have to be non-toxic, biocompatible, they have to be retained in the blood’s circulation system for a long time, they have to stay in stable colloidal suspensions without agglomeration, and they have to be functionalized, e. g., coated with a layer of functionalization molecules, providing specific functional groups for the further selective bonding of the different molecules needed for specific applications. The functionalization molecules usually also provides colloidal stability of the nanoparticles in aqueous suspensions. To avoid magnetic agglomeration, the nanoparticles usually need to be small enough to be superparamagnetic (i.e., below approximately 15 nm).

At the Department for Materials Synthesis, Jožef Stefan Institute, we study the synthesis of magnetic nanoparticles. Primarily, nanoparticles of both magnetic iron oxides (maghemite and magnetite) are synthesized. Iron oxide is today practically the only magnetic material used for the nanoparticles in biomedical applications, since it was already registered for in-vivo applications. For specific applications, for example, in magnetic hyperthermia, we also synthesize the nanoparticles of other spinel ferrites ($CoFe_2O_4$), hexaferrites ($SrFe_{12}O_{19}$) and perovskites ($Sr_{1-X}La_XMnO_3$). We used several different synthesis methods, ranging from simple co-precipitation from aqueous solutions, to methods that enable the closer control of particle size: the microemulsion method, the thermal decomposition of organo-metallic complexes, and the hydrothermal method.

Recently, our research has been primarily focused in the functionalization of the nanoparticles by grafting different silane molecules, for example, 3-aminopropil silane, to their surfaces directly, or over a thin surface layer of silica. The control of the functionalization process enables us to tune the nanoparticles' surface properties, for example, their surface concentration of amino groups and, consequently, their surface charge.

Another approach in the nanoparticles' functionalization is the coating of nanoparticles with functional polymers. We synthesize superparamagnetic nanocomposites containing large amounts of magnetic nanoparticles dispersed in a polymer matrix of PMMA. The nanocomposites are prepared by the precipitation polymerization of MMA in the presence of a concentrated ferrofluid. When the polymerization takes place in a mini-emulsion system, round nanocomposite particles with sizes of approximately 100 nm are obtained, which can be used as magnetic beads.

Amino-beta-Lactams - Synthons for Biologically Interesting Compounds

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Azetidin-2-one, a four membered cyclic lactam (beta-lactam) skeleton has been recognized as a useful building block for the synthesis of a large number of organic molecules by exploiting the strain energy associated with it. The skeleton has been extensively used as a template on which to build the heterocyclic structures fused to the four-membered ring using the chirality and functionalisation of the beta-lactam nucleus as a stereocontrolling element. Efforts have been made in exploring such new aspects of beta-lactam chemistry using enantiomerically pure beta-lactams as versatile intermediates for the synthesis of aromatic beta-amino acids, and their derivatives, peptides, polyamines, polyamino alcohols, amino sugars, and poly-amino ethers. The development of methodologies based on beta-lactam nucleus is now referred as "beta-lactam synthon method". Homochiral amino-beta-lactams (synthons) will be prepared applying the chiral ester enolate-imine condensation strategy, synthetic methodology based on the azetidin-2-one nucleus: the "beta-lactam synthon method". Thus obtained amino-beta-lactams will be transferred into chiral imines and as such employed in Diels-Alder and aldol reactions. Furthermore, the amino-beta-lactams will be employed in the reactions with isocyanates and isothiocyanates to form the corresponding ureas and thioureas that will serve as building blocks for the synthesis of imino-thiazolidinone, imino-oxazolidinone, tetrahydro-triazinone, and oxadiazinone ring connected to the beta-lactam ring via C-N bond. Beside evident biological activity of the above mentioned compounds, there is a constant need for the development of novel and efficient methodologies of stereo- and enantioselective synthesis that will result in the development of novel organic synthetic methods and reaction mechanisms which in combination with combinatorial chemistry methods may result with new and pharmacologically potential candidates. The analytical techniques (RP-HPLC - UV/VIS and ELSD, LC-MS) in combination with spectroscopic methods will be employed for the analysis of complex reaction mixtures and product identifications. The compound structures will be determined in combination of CHNS elemental, spectroscopic (UV/VIS, FT-IR, NMR, LC-MS) and X-ray crystallographic analysis.

Bioactive glasses in medicine

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The surface charges of biomaterials are recognized to be the most important factors in determining biological responses. However, the mechanism for the nucleation and growth of these hydroxyapatite (HA) layers on the surface of the bioglasses is still not clear.

This study was focused on the structural and electrical processes produced when the electrical polarization was applied on the surface of bioactive glasses, namely 13-93 glasses. It was of interest to investigate the polarization/depolarization mechanism and effect of charge carriers formed during positive or negative electrical polarization. It is important to clarify the mechanisms for polarization and depolarization of bioactive glasses in relation to the mobility of sodium ions (Na^+) and formation of Na^+-NBO (non-bridging oxygen) dipoles that can be reoriented by the applied electrical field. The structural aspect of electrical depolarization was investigated in relation to the ionic migration and transport distance. The systematic study of the electrical processes of bioactive glasses was analyzed by two complementary techniques: thermally simulated depolarization/polarization current (TSDC/TSPC) and impedance spectroscopy (IS).

Various polarized voltages up to 200 V were applied for a different time t_p at a higher temperature T_p. As a consequence it was found that the maximum current density increases with increasing polarization voltage and the stored charges/current density are 2.5 times larger for 13-93 glass polarized with higher voltage. Also, the SEM images of negatively polarized surface soaked in SBF for 2 days shows the agglomeration of HAP.

In conclusion it seems that the increase in charge density induced by electrical polarization is sufficient for an enhancement of surface activity.

Novel composite bone implant materials

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Investigations in our groups deal with design, preparation and physical-chemical characterization of biomimetic, organic-inorganic materials for hard tissue replacement or repair. These materials are based on different calcium phosphate phases *in-situ* precipitated or transformed within different organic matrix.

We are currently developing several materials:

- *organic/inorganic composite coatings containing poly-L-lisine / poly-L-glutamic acid multilayer (PLL/PGA ML) as organic component and OCP/apatite as inorganic component.* The PE multilayers provide a polymer matrix, which may be designed to increase cell activity. The "*in situ*" grown calcium phosphate component additionally increases the osteoinductive properties of the system. The good correlation of *in-vitro* and *in-vivo* tests indicates that this organic/inorganic nanocomposite is a very promising surface coating with wide medical applications.
- *injectable bone repaire materials based on calcium phosphate in situ precipitated within gel of polymer wit reversible thermal gelation properties*. Amorphous calcium phosphate (ACP) was precipitated by rapid mixing of two aqueous solutions of the polymer, containing calcium and phosphate ions respectively. At 37^{o}C the polymer formed a gel within which ACP particles transformed into crystalline material.
- *amorphous calcium phosphate modified with different surfactants*. ACP cements and ceramics still exhibit problems of mechanical strength, injectability, and application techniques. Coating ACP with surfactants could be the solution to some of these problems. In this work we have compared the influence on the transformation of ACP of monomeric dodecyltrimethlyammonium bromide, DTAB, with corresponding dimeric dimethylene-1,2-bis (dodecyldimethlyammonium bromide), 12-2-12.

Preparation of hybrid organic/inorganic materials for drug delivery

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Hybrid organic/inorganic materials are group of compounds that can be used for a controlled introduce and/or release of active organic substances in living organisms and tissues. Two groups of hybrid materials (calcium carbonate ($CaCO_3$) or layered double hydroxide(s) ($Mg_{(1-x)}M^{3+}_x(OH)_2(A^{m-})_{x/m}\cdot nH_2O$)), into which model organic molecules (anti-inflammatory drugs) are absorbed/intercalated, will be prepared by precipitation from aqueous solutions.

The chemical-physical properties of such materials (morphology, specific surface area, porosity, chemical and mineralogical composition, kinetics and extent of release of organic molecules and particularly particle size) will be correlated with the preparation conditions.

However, in vitro testing under conditions similar to physiological will enable an estimation of the importance of a particular incorporation mechanism (absorption or intercalation) in the overall efficiency of the controlled release. Namely, in distinction from the porous calcium carbonates, in which the organic component is absorbed in the pores of carrier or adsorbed at the particle surface, in the case of layered double hydroxides, the organic molecules are in the form of anions and are bound electrostatically to the mineral layer, so that their release is a consequence of ionic exchange with counter ions from the surrounding media.

Subsequent treatment of surfaces of nanosized hybrid particles with appropriate compounds (e.g. polyethylene glycol) will be also done in order to test the biocompatibility of such materials and their potential to avoid phagocytosis by the reticuloendothelial system or cells.

New catheters for monitoring metabolic pathways and drug delivery in muscle tissue, fat tissue, skin and brain

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Institute of Medical Technologies and Health Management

Three different departments – Health Management, Medical Technologies, and Bioanalytics – cooperate on an interdisciplinary basis to forge the institute into a whole that is greater than the sum of its parts. We share not only a dedication to improving the quality of life of people suffering from chronic diseases, but also a sense of personal commitment, information technology state-of-the-art knowledge, and constant communication between the different departments. Experts in medicine, medical technology, biology, business management, information technology, and nursing work side by side in the institute, which covers all areas from basic research through testing and evaluation to the application stage – depending on the client's requirements. In this way patients, doctors, businesses, and public partners are assured of practical results that are tailored to meet the needs of everyone involved. We stand for transparency, cooperation and efficiency – to ensure that patients receive the best possible treatment.

INFORMATION TECHNOLOGY & DATA MANAGEMENT

We develop software for clients and health care projects to improve work flows in health services. Electronic documentation and data analysis allow doctors to objectively evaluate their own actions and serve as the basis for improving efficiency and creating transparency in integrated health care projects. A high degree of data security – one of the most important issues of our time – is a must when administrating sensitive medical data. We have extensive expertise and the infrastructure that is needed for developing and running secure information systems. Based on this high standard of development, we cooperate with specialists to continue actively developing the IT infrastructure of the entire institute. For example, we have designed a special application for data management in clinical studies. This software meets the requirements of all stages of the study, from the design phase to data management in an analytical laboratory.

IN-VIVO MONITORING OF METABOLIC PROCESSES AND TRANSPORT OF DRUGS INTO SKIN, BRAIN AND BONE

The departments of ‘Medical Technologies’ and ‘Bioanalytics’ have specific expertise in the field of continuous monitoring and automated metabolic control for diabetic and critically-ill patients (‘Closed-Loop’, ‘Artifical pancreas’) as well as expertise with minimally-invasive technologies for the direct access to body tissues/compartments for medical/pharmaceutical research purposes (‘tissue specific drug testing’, ‘PK-PD’, ‘skin penetration’). ‘Medical Technologies’ focuses on the development of novel technical solutions for patient care, clinical basic research and pharmaceutical research and realizes clinically applicable prototypes for use in trials according to medical device manufacturing standards (EN ISO 13485). ‘Bioanalytics’ laboratory is focused on cutting-edge bioanalytical methods for basic and industry/pharmaceutical research, and fulfils the international quality standards of Good Laboratory Practice (GLP). Together comprehensive high-quality services (technical- in vitro- bioanalytical- pre/clinical) for product evaluation and market release are provided to the medical device and pharmaceutical industry. These complex services are facilitated by close collaborations with several highly experienced partners, such as the Medical University of Graz with its up-to-date preclinical and clinical research facilities. All researchers are used to contribute Know-How, technology and specific research services to international collaborative projects.