2\textsuperscript{nd} International Workshop
on Functional Nanostructured Materials

October 11th – 12th, 2018, Kraków, Poland

Faculty of Chemistry
Jagiellonian University
2nd International Workshop
on Functional Nanostructured Materials
October 11th – 12th, 2018, Kraków, Poland

BOOK OF ABSTRACTS

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Welcome

On behalf of the Organizing Committee, I would like to welcome you to the 2nd International Workshop on Functional Nanostructured Materials (FuNaM-2) that will take place from 11th to 12th October 2018 in Kraków.

Kraków is one of the most beautiful cities in Poland, having many historical spots that are worth seeing. Besides its historical values, Kraków is also a students’ city with more than 20 universities with the oldest one in Poland – Jagiellonian University, our alma mater. The Department of Chemistry, where the conference will take place, has a new and modern facility, which favors scientific creativity and allows for the development of research. I strongly believe that this will also be a great and inspiring place for our conference.

The aim of this year’s workshop is to bring together both young and experienced scientists working in the field of functional nanomaterials to present and exchange their knowledge and experience. The conference topic meets worldwide trends in science, which are focused on health protection (e.g., implants, biosensors, drug delivery systems), energy conversion and storage, and environment protection (e.g., electrocatalysis, water purification, renewable energy sources). Therefore, the proposed session’s topics cover all aspects of the synthesis, characterization, and applications of functional nanostructured materials that may be used as biomaterials, materials for energy purposes and materials applied in electrochemistry. Finally, electrochemistry can also be a very useful tool allowing the fabrication of various nanostructured materials. Therefore, some attention will also be focused on this aspect during the conference.

It should be emphasized, that this year’s edition of the conference will also be focused on the development of other useful scientific skills, like writing good quality research papers, spreading scientific achievements or writing a proper research proposal. I hope that such workshops will be a great possibility to learn new things and to exchange knowledge and share experience between scientists on different career levels.

I am confident that our Workshop will provide an excellent opportunity for many inspiring discussions, sharing experience and tightening scientific cooperations between young and experienced scientists, both during intensive sessions and less formal activities in the city of Kraków.

Finally, I would like to thank our Honorary Patrons - Rector of the Jagiellonian University, prof. Wojciech Nowak, the President of the City of Kraków - prof. Jacek Majchrowski, and the Marshal of the Małopolska region – Jacek Krupa. I would also like to thank our sponsors for their support: ABL&E-JASCO POLSKA Sp. Z O.O., ATEST Sp. Z O.O, LAMBDA SYSTEM - Kreft Barszczewski Sp.J., and Consulate General of Federal Republic of Germany in Kraków.

One more time, I would like to welcome all of you, and I hope that you will have a great time in Kraków.

Grzegorz D. Sulka
Chair of the 2nd International Workshop on Functional Nanostructured Materials
Head of the Nanostructured Materials Group
ORGANIZER

Faculty of Chemistry
at the Jagiellonian University

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Session 1 - Nanostructured biomaterials

Prof. Charles James Kirkpatrick

Charles James Kirkpatrick has a triple doctorate in science and medicine (MD, PhD, DSc) from the Queen's University of Belfast (N. Ireland) and is emeritus Professor of Pathology at the Johannes Gutenberg University Medical Center in Mainz, Germany, where he directed the Institute of Pathology from 1993 to 2015. He holds honorary and visiting professorships at universities in Sweden, China, Singapore, and Cuba. He is a former President of both the German Society for Biomaterials (2001-2005) and the European Society for Biomaterials (ESB, 2002-2007). His principal research interests are in the fields of biomaterials in tissue engineering and regenerative medicine, with special focus on human co-culture systems. During the past years his work has involved bone vascularization, the development of barrier models (e.g. air-blood barrier, blood-brain barrier) to study nanoparticle interactions with cellular systems, as well as co-culture models for upper respiratory tract regeneration. He is author/coauthor of 533 publications in peer reviewed journals, and has given more than 500 invited lectures worldwide. Kirkpatrick has an h-index of 59 (Scopus) & 74 (Google Scholar) and has been cited > 20,000 times. In 2008 he received the ESB’s George Winter Award, and in 2010 he was awarded the Chapman Medal from the Institute of Materials, Minerals & Mining, London, UK for “distinguished research in the field of biomedical materials”. In 2014 he received the TERMIS-EU Career Achievement Award (awarded at the TERMIS congress in Genova, Italy). His current research is being carried out at the Goethe University of Frankfurt, where he holds a senior professorship.
Challenges for Nanomaterials in Bioengineering: A Life Science View

Charles James Kirkpatrick\textsuperscript{1,2,3}

\textsuperscript{1}Emeritus Professor of Pathology, Johannes Gutenberg University, Mainz, Germany
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\textsuperscript{3}Department of Biomaterials, Sahlgrenska Academy, University of Gothenburg, Sweden

Progress in nanotechnology has opened up new avenues for bioengineering. As in many fields, novel ideas and technologies can lead to new applications, which can benefit society, but also to new challenges, which need to be addressed if these innovations are to be of lasting significance. Functional nanomaterials are a prime example of biomaterial developments with enormous potential. Thus, for example, there is the possibility to modify the surface of a bulk material to create a specific nanotopography. Alternatively, a nanocoating on the material could be employed to deliver medication or other biological agents. Together with massive strides in polymer chemistry, the renaissance of electrospinning has enabled extracellular matrix (ECM)-like, biodegradable fibre matrices and hydrogels to be synthesized. Thus, the typical membrane-like products could be used as wound dressings with interactive properties for the release of growth factors or anti-infective agents. A final example of nanomaterials for bioengineering are the rapid developments in engineered nanoparticles. These offer great promise for diagnostics, but also for the delivery of drugs and / or genes. Here the possibilities are legion and range from growth and differentiating factors, via angiogenic factors to anti-inflammatory drugs and chemotherapeutics, as well as various species of nucleic acids (DNA, miRNA etc.). Among the challenges are the modes of nanoparticle (NP) access to the human body, this ranging from skin contact, ingestion, and inhalation, to injection. This raises the need to understand how NPs interact with the various barrier systems in the human body. Much of our work in the life science aspects of NPs has involved establishing complex human co-culture systems to simulate these barriers with a view to unravelling how NP size, shape, surface physicochemistry etc. influence cellular uptake, transport, storage and exocytosis. In addition, further complexity is found in the type of biological microenvironment encountered by the NPs. Among the complex co-culture models established are those for the respiratory tract, e.g. the air-blood barrier, which is of interest for NP transport into the body by an inhalational route. The most complex of these air-blood barrier models involves the incorporation of surfactant and macrophages, as these features are also present in the alveoli in vivo. Other co-culture models based on cellular self-organization have been developed to simulate the blood-brain and skin barriers. Finally, a major challenge prior to any clinical translation is the testing of functional nanomaterials in relevant animal models. This is particularly complex not just by the choice of animal, but also on account of the exact methodology for nanoparticle delivery.
Session 1 - Nanostructured biomaterials

Dr. Eng. Ewa Kijeńska

Ph.D. in Materials Science and Engineering from Faculty of Materials Science and Engineering, Master Degree in Industrial Biotechnology from Faculty of Chemical and Process Engineering at Warsaw University of Technology. She is coordinating electrospinning related research within Biomaterials Group at Faculty of Materials Science and Engineering at Warsaw University of Technology. Her research focuses mainly on fabrication, physicochemical and mechanical characterization along with in vitro and in vivo studies of electrospun fibers for tissue engineering application.
Electrospun nano- and sub-microfibrous constructs and their application in tissue engineering

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Versatile method of electrospinning allows of obtaining of numerous fibrous structures with fibers in range from nanometers to micrometers. By varying the process parameters and by modifications of utilized set-ups, it is possible to fabricate not only constructs with different patterns of fibers (e.g. random, aligned), but also with diverse dimensions and shapes (mats, multilayer systems, cylinders, fluffy foams etc.) and different structures of fibers itself (core-shell fibers, hollow fibers) [1]. High similarity of electrospun nanofibers to natural fibrous structure of native extracellular matrix (ECM) make them promising substrate to be applied in tissue engineering (TE).

Electrospun nanofibers can be fabricated from both natural and synthetic polymers, or their blends [2]. Additionally, they can be easily functionalized or enriched with, among others, nanoparticles, biomolecules, growth factors or drugs [3-5]. Presented study will describe how electrospun fibers in the form of scaffolds could be used in peripheral nerve, tendon or bone tissue engineering. The influence of their morphology and physico-chemical properties on cell behavior will be discussed.

Acknowledgements
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Session 1 - Nanostructured biomaterials

Dr Eng. Alicja Kazek-Kęsik

Alicja Kazek-Kęsik is working at the position of Adjunct in the Department of Inorganic Chemistry, Analytical Chemistry and Electrochemistry at Silesian University of Technology in Gliwice, Poland. She received her diploma and PhD in Chemical Technology at Silesian University of Technology. Her research interests range from biomaterials to bone tissue reconstruction, biological investigations, as well as various electrochemical surface treatments. She has laboratory experience with biological characterization of biomaterials, especially with regard to their cytocompatibility and anti-bacterial properties. She is focused on plasma electrolytic oxidation of various metallic materials, especially titanium and titanium alloys. She has also improved her knowledge of X-ray techniques at Institute for Nanoscience and Cryogenics in France. She is an author of over 30 scientific articles as well as patents about anodization processes and one patent application about formation of hybrid oxide-polymer coatings. Her research is supported by Polish National Science Centre and she was awarded by Polish Electroplating Society.
Formation of functional coatings on metal surfaces

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INTRODUCTION
Titanium and its alloy titanium are mainly used in dental prosthetics. Requirements of the materials must be met to provide its application in medicine, especially when their surface is modified. The surface treatment of the material should be relatively simple to obtain an implant with the required dimensions. The surface modification of metals by the plasma electrolytic oxidation (PEO) caused the formation functional coatings which might be post-treated using e.g. polymers or ceramic particles.

EXPERIMENTAL
Surface of the Ti alloy was anodized in 0.1M Ca(H₂PO₄) solution according to the procedure presented in paper [1]. Fast-degradable layers of poly(sebacic anhydride) (PSBA) or poly(lactide-co-glycolide) (PLGA) with loaded drugs were formed on the anodized surface. Surface morphology, chemical composition, drug released and its stability, degradation of the polymers, as well as biological analysis of the materials were examined.

RESULTS AND DISCUSSION, CONCLUSIONS
After 7 days of the material immersion in artificial saliva, the layers were degraded by 20.7 mol.% and 77.8 mol.%, when the PSBA and PLGA were used. The polymeric layers might be loaded with amoxicillin, cefazolin, vancomycin, doxycycline or clindamycin. The concentration drugs in coatings is between 20-100 μg, however it is enough to inhibit bacteria adhesion, bacteria growing and the surfaces are still cytocompatible. Fig. 1. presents representative morphology of the hybrid layer, and determined surface roughness. The anodized Ti alloy surface is favorable for post-treatment and the formation of a hybrid, oxide-polymer layer loaded with selected drugs.

Fig.1. Morphology of the anodized Ti alloy with PSBA layers loaded with vancomycin.

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Dr. Lifeng Liu

Lifeng Liu (Researcher ID: A-2522-2012, Orcid ID: 0000-0003-2732-7399) is currently Senior Staffer Researcher (tenured), Principal Investigator and Group Leader at the International Iberian Nanotechnology Laboratory (INL) – the first international research organization in the field of nanoscience and nanotechnology. He obtained his B. S. degree in Applied Physics from Beijing Jiaotong University (2001), and both his MS (2004) and PhD (2007) degrees in Condensed Matter Physics from the Institute of Physics, Chinese Academy of Sciences (IOP-CAS). He joined Max Planck Institute of Microstructure Physics – Halle (MPI-Halle), Germany in 2007, first working as a postdoctoral researcher and then as a staff scientist. He started his independent research career in 2008 and became the head of group “Porous Alumina” in 2009. In 2011, he moved to the International Iberian Nanotechnology Laboratory (INL) and set up a research group there. Lifeng Liu has been actively working on nanomaterials and nanostructures since 2002, with particular emphases on fabrication and characterization of complex nanostructures, nano-magnetism, nanoscale solid-state reactions, ferroelectric nanostructures and nano-electrocatalysts. His present interest mainly focuses on nanomaterials for renewable energy generation, storage, and conversion. So far, he has filed 2 PCT patents and authored/coauthored more than 120 peer-reviewed papers in major international journals, which have been collectively cited 4600+ times, leading to an h-index of 40 (Web of Science, as of Dec 2017). In addition, Lifeng Liu has delivered 30+ oral presentations at different international conferences/workshops/universities including 1 plenary talk, 5 keynote speeches, and 14 invited talks. Besides, he has offered extensive professional services to the community. He actively serves as a reviewer for 60+ scientific journals and for grant applications of several funding agencies from North America, Europe and Asia. He was a member of organizing/scientific committee of a number of national/international conferences. Honors and awards he was granted recently include: FCT Investigator Grant 2014, Young Researcher Award 2015 by the Portuguese Electrochemical Society, INL Award for Professional Services 2016, and Prof. Ruldoph A Marcus Award 2017.
Compositional and microstructural engineering of transition metal phosphides for improved electrocatalytic performance

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Water splitting has been proposed to be a promising approach to renewable energy storage through converting the off-peak solar or wind energy to hydrogen fuels. Presently, one of major challenges facing widespread deployment of water splitting devices is their high cost, which primarily results from the use of precious and scarce noble metal catalysts.

In this talk, I will present our recent efforts towards compositional and microstructural engineering of transition metal phosphide (TMP) electrocatalysts, with an aim to improve their electrocatalytic performance for hydrogen and/or oxygen evolution reactions (HER & OER). I will showcase three examples: 1) Trends in the OER activity of TMP nanoparticles [1]. We have investigated the alkaline OER electrolysis of a series of TMP catalysts and observed a notable trend in OER activity which follows the order of FeP < NiP < CoP < FeNiP < FeCoP < CoNiP < FeCoNiP. Our results show that the introduction of a secondary metal(s) to a mono-metallic TMP can remarkably boost the OER performance. This promotional effect can be ascribed to the enhanced oxidizing power of bi- and tri-metallic TMPs. 2) RuCoP nanoclusters showing superior HER performance in alkaline solution [2]. The RuCoP clusters were prepared by wet chemical reduction of metal cations followed by a low-temperature phosphorization treatment. When used to catalyze the HER, they show exceptional activity with a very low overpotential (η) of 23 mV to reach -10 mA cm⁻² and a high turnover frequency (TOF) value of 3.85 s⁻¹ at η = 100 mV. The superior HER performance can be attributed to the partial electron transfer from CoP to Ru, which substantially improves the HER kinetics on active Ru sites. Theoretical calculations also show that the adsorption energy of –OH on RuCoP is lower than that on pristine Ru clusters and that water dissociation happens on RuCoP more easily, both contributing to the improvement of HER activity. 3) Hollow CoP octahedron (OCH) nanostructures with well-defined exposed crystal facets [3]. The hollow CoP OCH NPs were prepared by solution phase synthesis of CoO OCH precursors, followed by a post-phosphorization treatment and subsequent chemical etching process. They show excellent intrinsic electrocatalytic performance for the OER, substantially outperforming CoP nanospheres without any preferentially exposed facets.

Acknowledgements

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Session 2 - Nanomaterials for energy conversion and storage

Dr. Sigita Trabesinger

Dr. Trabesinger is currently a Project Leader at Paul Scherrer Institute (PSI), Switzerland. She completed her undergraduate studies at Vilnius University, Lithuania, and obtained in 2008 a PhD degree in Structural Chemistry from Stockholm University, Sweden, where she studied nanoporous carbons, their synthesis and properties, with an emphasis on versatile characterization methods for amorphous materials. Her first step into electrochemical energy storage was during her postdoctoral studies at Uppsala University, Sweden, which led to a scientist position at PSI in 2011. Since then she is working on various aspects of rechargeable Li-ion and post-Li-ion batteries, with a focus on various characteristics of Li–S batteries, NCM-based cathodes, negative Si-enhanced graphite electrodes and the performance of battery materials on electrode and cell levels.
Materials Choices for Viable Lithium–Sulphur Batteries

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The rapidly increasing integration of renewable energy into the global energy scheme demands rechargeable batteries with high gravimetric and volumetric energy densities at reasonable costs. The prospect of a readily available, low-cost, environmentally friendly battery with high theoretical specific charge (1672 mAh/g) and high theoretical energy density (2500 Wh/kg) outweighs the challenges encountered on the way to full-scale commercialization [1, 2]. Some of these challenges are materials related, such as insulating nature of sulphur and of its lithiation end-product, lithium sulphide, but also challenges inherently related to the cell chemistry, such as polysulphide formation upon lithiation of sulphur and consequent polysulphide-shuttle onset. Besides these inherent challenges, Li–S cell’s performance is very sensitive to large number of parameters, such as electrolyte amount (Figure 1), salt concentration, electrolyte additives, binder, and conductive matrix [3].

![Figure 1](attachment:image.png)

Figure 1. Sensitivity of Li–S cell performance to the amount of electrolyte.

The sensitivity of the Li–S system to many experimental parameters and material properties speaks to the importance of directing future research towards the entire Li–S-battery set-up. In addition, commercial viability study of novel cell components, such as interlayers and membranes, designed to alleviate one of the most challenging issues of Li–S batteries, — polysulphide shuttle, — will be presented [4].

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Session 2 - Nanomaterials for energy conversion and storage

Dr. Krzysztof Fic

Krzysztof Fic graduated in Chemical Process Engineering at the Faculty of Chemical Technology, Poznan University of Technology on 5th June 2008. On 10th June 2008, he was accepted for the position of research assistant in the Department of Applied Electrochemistry. On the 1st October 2008, he began his Ph.D. study with a major interest in electrochemistry. His research activities focused mainly on the electrochemical systems for the energy conversion and storage, in particular on phenomena occurring at the electrode/electrolyte interface. In 2011, he was awarded by ‘Ventures’ program, funded by the Foundation for Polish Science. Project ‘High-energy electrochemical capacitor operating in redox active electrolytes as an innovative source of power’. The work was further continued within the INTER project financed by the Foundation for Polish Science. In April 2011, he visited the Centre National de la Recherche Scientifique, Centre de Recherche sur la Matière Divisée, Orléans (France) under the supervision of Prof. François Béguin. This visit was devoted to the training in Thermal Programmed Desorption (TPD) method conjugated with Mass Spectroscopy (MS). In October 2011, he took a research internship at Heyrovsky Institute in Prague, supervised by Prof. Ladislav Kavan. The major goal of this stay was the training in spectroelectrochemistry of carbon materials, particularly for Raman spectroscopy. Ph.D. dissertation of Krzysztof Fic was defended on 5th June 2012. Since 1st October 2012, he is employed as an academic teacher at the Institute of Chemistry and Technical Electrochemistry of Poznan University of Technology. In 2013 – 2015 he spent six months in Solvay company (Brussels, Belgium) serving as an Experienced Researcher in the Energy Caps project within IAPP Marie Curie Action. In 2013-2015, he managed two scientific projects founded by Polish Ministry of Science and Higher Education and National Centre for Research and Development with a total budget more than 270.000 EUR devoted for young scientists, namely IUVENTUS PLUS and LIDER. At the same time, he was the manager and researcher in two European Projects (EU FP-7 Marie Curie Action: Industry Academia Partnership and Pathways called ENERGY CAPS and FP7-Energy pillar: Nanowires for energy storage). In October 2013, he was awarded by the City Council in Poznan by a stipend for young scientists. In October 2014, he was honoured by Ministry of Science and Higher Education receiving the stipend for outstanding young scientists, recognized as the noblest award for starting-career researchers. In July 2015 he was selected by French Embassy in Warsaw for a one-month research stay in France as an award for his scientific achievements; then, in February 2016, he visited the Institut de Science des Matériaux de Mulhouse, where under the supervision of Dr. Camelia Ghimbeu he was trained in the advanced characterization of carbon materials. Krzysztof Fic is the co-author of 39 papers indexed in ISI Master Journal List with total Impact Factor over 170. His H-index is 11, and citation number approaches 1000 records (excl. self-citations). He is also co-author of 12 patents and 19 patent applications. In 2009-2018, he presented 45 oral communications and 16 posters during national and international conferences, in Europe, U.S., Mexico, Brazil, Japan, South Korea, Hong Kong, Taiwan, China and Australia.
A number of oral communications and posters he has co-authored is even greater. Krzysztof Fic is an active member of national and international organizations including the Polish Carbon Society, the International Society of Electrochemistry, American Chemical Society, the Electrochemical Society and Material Research Society. Besides, he served as Associate Editor of the “Central European Journal of Chemistry” until June 2012. Since December 2016 he serves as a Member of Polish Young Academy at Polish Academy of Sciences. He serves as a scientific supervisor in two projects funded by National Science Centre. Moreover, he serves as researcher and an executive manager of the Polish-Swiss Research Programme (PSPB 107/2010) realized in cooperation between Institute of Chemistry and Technical Electrochemistry (Poznan University of Technology) and Paul Scherrer Institute (Villigen, Switzerland) concerning in-situ investigations of next generation electrochemical capacitors. Recently, he is a Principal Investigator in Starting Grant, founded by European Research Council (2017-2022).
Electrode/electrolyte interface in capacitive energy storage – operando study

Krzysztof Fic\textsuperscript{1}, Anetta Platek\textsuperscript{1}, Jakub Menzel\textsuperscript{1}, Mikolaj Meller\textsuperscript{1}, Elzbieta Frackowiak\textsuperscript{1}
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This paper will provide comprehensive insight on the application of the \textit{in-situ} and \textit{operando} techniques such as Raman spectroscopy, Quartz Crystal Microbalance (EQCM) or Scanning Electrochemical Microscopy (SECM) for determination of charge storage phenomena and ageing factors in activated carbon-based supercapacitors.

\textit{In-situ} Raman investigation for activated carbon electrodes operating in neutral aqueous media like Li\textsubscript{2}SO\textsubscript{4} or LiNO\textsubscript{3} solutions indicated that there is a mild oxidation of positive electrode during cycling (vibration modes from oxygen-based functionalities found) whereas the surface chemistry of negative electrode appears to be stable. EQCM study confirmed significant frequency/mass variation on the positive side, whereas negative electrode remained stable. However, SECM demonstrated that during positive and negative polarization, the thickness (and volume) of the electrode changed remarkably.

Interesting results were obtained for carbon electrodes operating in KI solutions. It has been confirmed that iodide anion undergoes several redox processes and strongly interacts with activated carbon surface. An oxidation of carbon surface has been identified near the iodide/iodine redox activity potentials. EQCM study confirmed the presence of various iodine species in the electrolyte. Carbon ‘corrosion’ has been observed especially for more concentrated iodide solution. However, we proved that IO\textsubscript{3}\textsuperscript{-} anion does not contribute significantly to this process.

Finally, operando studies allowed for elucidation on the charge storage mechanisms in water-based capacitive systems and identification of the tentative reasons for their performance fade.

\textbf{Acknowledgements}

European Research Council is acknowledged for financial support within the Starting Grant project (GA 759603) under European Unions’ Horizon 2020 research and innovation programme.
Session 3 - Electrochemistry for nanomaterials and nanomaterials for electrochemistry

Dr. Ivan Buijnsters

Dr. Ivan Buijnsters has a PhD degree in applied physics from Radboud University Nijmegen, The Netherlands. During his PhD research he focused on the deposition of wear and corrosion-resistant diamond coatings on steels, which was followed by postdoctoral research on the surface engineering and vapour phase growth of carbonaceous nanomaterials. Since 2014, he is an assistant professor at Delft University of Technology, specializing in the development of functionalised synthetic diamond nanomaterials for application in precision engineering, advanced chemical engineering, and sensor devices.
Application of diamond nanomaterials in electrochemistry

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Diamond is often considered an ideal engineering material since it combines various extreme physical and chemical properties compared to other materials. The development of synthetic diamond films and nanoparticles over the past few decades has enabled a wide range of applications based on the combination of these unique properties of diamond, and the variety of material properties obtainable through tuning of the microstructure, surface, morphology, and impurity/doping levels. Interest in the use of electrically conductive diamond electrodes has steadily grown since the first publications on the basic electrochemical properties of diamond in the late 1980s and early 1990s [1]. Boron-doped diamond (BDD) electrodes are nowadays widely applied in (waste)water treatment, electroanalysis, and biosensing [2]. They offer excellent electrochemical properties [3], including widest working potential window of all electrode materials, low background and capacitive currents, weak molecular adsorption, self-cleaning features, and the ability to withstand extreme potentials, corrosive and high temperature/pressure environments.

However, BDD is not a standard electrode material and its material properties highly depend on how the material has been synthesized and treated prior to application. As a result, measured electrochemical characteristics can vary quite significantly among different research groups. In particular, with the rapid advances in the production of nano-sized diamond, both as particles and in thin film form, joint research efforts by materials scientists, physicists and chemists are needed to aid understanding of how to work with nanodiamond from an electrochemical viewpoint, improve electrode quality [3] and successfully explore new application fields.

In this talk, I will present the current status and latest trends in diamond electrochemistry. Synthesis and functionalization of BDD thin-film materials and diamond nanoparticles for application in electrochemical (bio)sensing will be reviewed. Specific focus will be given to the wide range of diamond materials and electrode architectures (from bulk down to the nanoscale) that have been reported in the scientific literature. Some recent electroanalytical applications will be discussed with special emphasis on the interplay between boron dopant level, microstructure, non-diamond carbon content, and surface chemistry. Furthermore, I will show novel results from our group on the microfabrication of thin-film nanodiamond and electrochemical characteristics of femtosecond laser textured BDD electrode surfaces [4].

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Session 3 - Electrochemistry for nanomaterials and nanomaterials for electrochemistry

Dr. Anton Lytvynenko

Dr. Anton Lytvynenko is a postdoctoral researcher at Faculty of Chemistry, Jagiellonian University, and a junior research scientist in DL. V. Pisarzhevsky Institute of Physical Chemistry of the National Academy of Sciences of Ukraine. He graduated from Taras Shevchenko National University of Kyiv (Chair of Inorganic Chemistry, Chemical faculty). He performed scientific research for his bachelor and master diploma in L.V.Pisarzhevsky Institute of Physical Chemistry and earned PhD degree (2016) in Physical Chemistry in the Institute. His work was mainly devoted to synthesis and characterization of polynuclear complexes and coordination polymers (especially porous) of 3D metals as well as to experimental study and quantum chemical prediction of their various properties (magnetochemical, catalytic, electrocatalytic etc.). After defense of the PhD thesis on electrocatalytic properties of porous coordination polymers in organic halides reductive dehalogenation he started to study nanostructured metals (nanoporous metal foams as well as metal nanoparticles confined in coordination polymers) for electrocatalytic and catalytic applications. He is an author of 16 scientific papers and 3 patents of Ukraine; awardee (2017) of Ukrainian Parliament’s award “For the most talented young scientists in fundamental and applied research and scientific-technical developments”. The work of Dr. Lytvynenko is supported by the National Academy of Sciences of Ukraine (Stipend for young scientists, awarded in 2017), and his postdoctoral research in Poland is supported by the International Visegrad Fund.
Nanoporous silver foam: electrodeposition, structure and electrocatalytic activity in reductive dehalogenation

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INTRODUCTION

Nanoporous metal foams can be described as a result of aggregation of metal nanorods and/or nanoparticles in a way that implies formation of substantial nanoscale porosity. Such materials are promising for a number of applications, especially as electrocatalysts. Electrochemical reductive dehalogenation of organic halides attracts interest as a tool for detection and remediation of persistent organic pollutants. The aim of this work was to compare the electrocatalytic activity of nanoporous silver foam and bulk silver in reduction of various organic halides.

RESULTS AND DISCUSSION

Nanoporous silver foam samples (AgNF/GC) were prepared by cathodic electrodeposition of silver onto glassy carbon (GC) support from aqueous AgBF₄ acidified by HBF₄ under high current densities. The resulting matt grey coating possessed 2-level hierarchical structure: 1. Cavities ca. 20 μm mean diameter (Fig.1 a) separated by silver walls ca. 7 μm mean thick (the sizes didn’t depend on the applied current density within 1.5–9 A/cm² range); 2. Aggregated filaments 70–300 nm thick that formed the walls. AgNF/GC exhibited superior electrocatalytic activity compared to bulk Ag in debromination of a range of organic halides: CF₂Br₂, CF₃CHClBr; bromobenzene and its derivatives with redox-inactive (F⁻, CH₃O⁻, CH₃⁻) as well as redox-active (–CN, –NO₂, CH₃C(O)⁻) substituents. The superior activity manifested as anodic shift (up to +345 mV, bromobenzene) of the CV peaks (Fig. 1 b) attributed to dehalogenation. Formation of active sites on AgNF/GC surface facilitating the reduction was hypothesized. Less than 1 mg of AgNF revealed performance comparable to ca. 0.5 g of Ag wire in electrolysis of 1-fluoro-4-bromobenzene.

Fig. 1 a) A photo of AgNF/GC sample through optical microscope (reflected light); b) Cyclic voltammograms of bromobenzene (5.5 mM, 100 mV/s) on AgNF/GC, bulk Ag and GC.

Acknowledgements

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Session 3 - Electrochemistry for nanomaterials and nanomaterials for electrochemistry

Dr. Tomasz Rębiś

Tomasz Rębiś received a Ph.D. at Poznan University of Technology in 2015. Currently, he is holding an assistant professor position in the Institute of Chemistry and Technical Electrochemistry at Poznan University of Technology. He also spent one year at Faculty of Physics, Chemistry and Biology at Linkoping University (Sweden). In the network science arena, he has focused on the studies on the electrochemistry of novel lignin-based conducting polymers and nanomaterials. His current research and scientific interests include electrochemistry, analytical chemistry, synthesis of nanoparticles, nanostructured and hybrid materials for energy storage and chemical sensors.
Advanced Redox - Active Biomaterials Based on Lignosulfonates

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Biopolymers with redox functions such as lignin derivatives are promising electroactive materials, which can be used in the development of chemically modified electrodes for electrocatalytic, electrochemical sensing and charge storage purposes [1-3]. The biopolymer lignin is found in green plants and makes up 20-30 % of the weight of wood while lignosulfonates arises from pulp and paper industry as a byproduct of paper manufacturing. From a chemical point of view lignosulfonates have no regular structure, however, they are mainly composed of phenylpropane segments (C₉ units) having hydrophilic sulfonic groups and electroactive methoxyphenol groups [4]. Being polyphenolic compounds lignin derivatives show substantial electroactivity especially in the range of anodic potentials. This is due to the fact of developing of quinone/hydroquinone redox couple during the oxidation process. Thus, they can be generally classified into quinone based redox polymers undergoing fast proton-coupled reversible redox transitions over wide pH range [2].

There are several types of hybrid nanomaterials and composite materials consisting of lignosulfonates or other technical lignins. These materials differ from each other with the physical interactions occurring between them, such as electrostatic interaction, intermolecular π–π interaction or Van der Waals interaction. Composites in which lignin was covalently bound to other components have also been synthesized; hydrogen bonds have also occurred [1-7]. Generally, the following types of lignin-based materials can be distinguished:

a) Lignin/conducting polymer materials;
b) Lignin/carbon nanomaterials;
c) Lignin/noble metals nanoparticles materials;
d) Lignin/transition metals (Fe, Co, Cu, Ni) hexacyanoferrates nanoparticles

Recently, a great interest of application of lignin derivatives in the development of charge storage devices can be observed. So far, the most promising results have proved that lignin derivatives can be considered as electroactive materials for the application in light and inexpensive organic batteries or supercapacitors [1,5]. Lignosulfonates were recently used as electroactive materials and showed remarkable electrocatalytic behavior toward biomolecules such as NADH [2]. In the course of our research, we also found that lignosulfonates are excellent materials for the development of conducting polymer-based hydrazine sensor [3]. Moreover, one of the most promising application of lignosulfonates is the synthesis of noble metal nanoparticles, were this biopolymer can play the role of both reducing and stabilizing agent [6]. Taking into account the relatively dense aromatic structure of lignosulfonates, they possess a tendency to adsorb on both insulating and conducting surfaces. Therefore, this biopolymers may be used to tune carbon surfaces due to strong π–π interactions and hydrophobic attraction of alkyl chains in lignosulfonate [7].

With this talk, the results regarding the synthesis and electrochemical performance of different lignin-based electroactive materials will be presented in order to allow a broad view of such materials nowadays.

ORAL PRESENTATIONS
Fancy shaped nanoparticles for fancy applications

Magdalena Parlinska-Wojtan, Elżbieta Drzymała, Grzegorz Grużel, Joanna Depciuch, Alexey Maximenko, Anna Pajor-Świerzy, Piotr Warszyński, Małgorzata Stec, Jarosław Baran and Andrzej Kowal

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INTRODUCTION

Nowadays, nanoparticles (NPs) with sizes varying from 5 – 100 nm find more and more applications in materials engineering, chemistry, catalysis, medical and biosciences. The surface atoms are the most active sites therefore NPs with fancy shapes, porous, hollow and hybrid are sought. We produce PtRhNi rhombic dodecahedra with a PtRh frame and a Ni core in a one pot synthesis and Pt/SnO₂ or Pt/Re/SnO₂ and NPs for ethanol oxidation reaction (EOR), Fig. 1(a) & (b). In the latter system we synthesize the metal and oxide NPs separately and subsequently assemble them using their opposite zeta potentials [1]. It was found, that the addition of Re enhances the EOR activity fivefold. For biomedical applications, in particular in photothermal anticancer therapy, we produce gold NPs with fancy shapes such as nanorods or nanostars, Fig. 1 (c, d) using seed mediated growth synthesis. Indeed, we found that the nanorods are more efficient in colon cancer cell killing compared to nanostars or nanospheres. Moreover, to control the NPs distribution in the cells, hybrid NPs with a SiO₂ or Au shells and a magnetic Fe₂O₄ core were synthesized using either thermal decomposition method, Fig.1 (e), or laser ablation Fig. 1(f). All NPs are imaged by scanning transmission electron microscopy (STEM) with the high angular annular dark field detector (HAADF) combined with energy dispersive X-ray spectroscopy (EDS) mapping for chemical characterization. Additionally electron and X-ray diffraction, as well as Fourier transform infrared spectroscopy (FTIR), were performed to assess the structure and chemistry of the NPs systems.

Fig. 1 STEM HAADF images of the fancy NPs (see text for details).

Acknowledgements

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Oxygen plasma functionalization of parylene C coating for metal implants: role of nanotopography

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INTRODUCTION

The challenges of metal implant engineering are to introduce specific properties which result in optimization of the metal-implant tissue interface. One of the most explored options is coating metal implants with a polymer which can be additionally functionalized for a long-term implantation success. In the study, we take an advantage of the synergistic effect of physical (nanotopography) and chemical (surface groups) modifications of parylene C by oxygen plasma to design and develop a multilayer coating for novel, functional implants.

EXPERIMENTAL

Parylene C films were prepared by CVD technique. The samples were modified using oxygen plasma. For the therapeutic layer preparation, the biodegradable D,L-lactide-co-glycolide copolymer (PLGA) was used. The coating was then thoroughly characterized using surface-dedicated (SEM, µFTIR, LDI-MS) and biological (in vitro cells and microbiological) tests.

RESULTS

Surface modification of parylene C resulted in changes in its chemical composition by generation of functional groups such as –COOH, –OH as well as nanotopography. Fluorescent staining of focal contacts of MG-63 cells together with SEM observations revealed improved biocompatibility of oxygen plasma modified parylene C. Generated nanotopography, effectively limited the surface area available for bacteria. SEM observations revealed, that early-stage biofilm formation on unmodified parylene C takes place after 4 h of incubation. After the same time interval, on the surface of oxygen plasma treated samples not agglomerated single bacteria cells dominated the picture. The drug–loaded PLGA results in prolonged in-site ibuprofen release up to targeted 21 days [1] and followed the Korsmeyer-Peppas kinetic model.

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Silicon oxycarbide – the novel bioactive amorphous material for medical applications

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Silicon oxycarbide (SiOC) is the amorphous material containing carbon ions bonded into the silica network and so-called free carbon. Presence of this second form causes black colour of the glass. The structure of the material binds structures of amorphous silica (ν-SiO₂) and silicon carbide. In the network, carbon is present as an anion and replaces some of the oxygen ions but it must be noted one carbon ion replaces two oxygens. That phenomenon causes densification and stiffening of the matrix and gives good mechanical properties durability, chemical and thermal stability, corrosion and oxidation resistibility [1,2]. Specific properties of the black glasses cause great interests from distant industries and technology branches, for example, catalysts, fuel cells, protective layers and primarily biomaterials.

Silicon oxycarbide was proposed in the 1950s but developed in the past years [3]. It is mainly due to the wide use of the sol-gel method. The hydrolysis and polycondensation reactions of organosilicon compounds containing Si-C bonds lead obtaining preceramic precursors. After high-temperature treatment, it is possible to obtain homogenous amorphous products of high purity and controlled amount of both bonded and free carbon [4]. For the synthesis also commercially available long-chain polymers might be used but they cause an increase of free carbon content and a decrease in the adhesion on the metallic substrates, what might be a fundamental problem in case of preparation of the coatings.

This work presents a study of the black glasses based coatings on titanium and steel substrates. The path of synthesis and detail examination is presented. Structural analysis of SiOC-based materials is presented along with microstructure and surface properties, such as topography, roughness, wettability and surface free energy, corrosion resistance and mechanical parameters examination. As the final stage, bioactivity of black glasses was tested with the use of the so-called Kokubo test [5]. Finally, the results of the cell integrity examinations are presented. Based on the research it might be concluded that the silicon oxycarbide based coatings are very promising material for the medical applications as the functional bioactive and biocompatible coatings on metallic implants.

Acknowledgements

This work has been supported by the National Science Centre project No.2017/25/B/ST8/02602.

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Anti-corrosive coatings based on SiOC glasses for interconnects in Solid Oxide Fuel Cells

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The increasing demand for the production of an energy is the main reason of a considerable increase in the importance of the research concerning the power engineering branch. Due to expected shortages in fossil fuels resources and rising environmental problems concerning their consumption, more environmentally-friendly alternatives are of a great interest. One of them are Solid Oxide Fuel Cells, which comprises both decrease in greenhouse gases emission and high electrical efficiency resulting from simple and modular construction. However, due to harsh working conditions combined of elevated temperature (600 - 800°C) and aggressive gaseous atmosphere, high temperature corrosion of particular elements (interconnects) seems to be the limiting problem, which significantly decrease the efficiency of the SOFC system. One of the possible remedy can be silicon oxycarbide glasses [1,2].

SiOC glasses, sometimes calles black glasses are ceramic materials, which possess the structure of an amorphous silica. Their general formula - SiCₓO₂(1-x), describes the fundamental rule of the process formation – the anionic substitution of the determined number of oxygen anions by two times lower quantity of carbon ones. The created structural carbon in the form of Si-C bonds provides with high corrosion and chemical resistance even at elevated temperatures. On the other hand, when the given threshold of carbon concentration in the glass structure is exceeded, so-called free carbon phase is formed. In comparison to structural one, it generates electrical conductivity of SiOC glasses, which is obligatory for interconnects’ materials [2]. Additionally, formation of SiOC glasses via sol-gel method, gives an outstanding possibility to modify the synthesis process and to dope the material with cations i.e. Al³⁺, which enhances the thermal stability of glasses even up to 1500°C [3].

The objective of this study was to apply the SiOC or SiAlOC glasses in the form of protective-conducting coatings in order to improve the corrosion resistance of the ferritic stainless steel dedicated for interconnects. Simultaneously, the proposed system has to meet the requirement concerning appropriate electrical conductivity. Coatings were prepared by means of sol-gel method with an application of the dip-coating technique. A set of structural studies (XRD, MIR) confirmed formation of appropriate coating material. Microscopic studies (SEM, Confocal) allowed for choosing samples of the most compacted and homogenous surface microstructure. Such specimens were evaluated taking into account corrosion behavior (Thermogravimetric analyses - 100h/800°C) and electrical conductivity (DC 2-point 2-probe technique). The first studies together with structural (XRD, Raman) and microstructural (SEM + EDS, Confocal) characterization of surface and cross sections of oxidized samples revealed the significant improvement in the resistance to oxidation, due to coatings application. The second studies showed an acceptable level of conductivity, stable in time.

Acknowledgements
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REFERENCES
Characterization of silane-based layers on amorphous metal surface for the power industry application

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INTRODUCTION
Low magnetic losses and high electrical resistivity are two desirable features that should characterize magnetic core of electrical transformer. Metallic glass foil is one of the newest material used in transformer manufacturing, which exhibit both these properties. As a result, transformer with laminated core made of metallic glass exhibit up to 70% lower core losses when it is compared with standard device [1]. Nevertheless, researches related to this material are still continued and one of the way is to achieve well-attached layer to metal surface [2]. A very promising compounds are silanes because of presence of reactive hydroxide groups when they are in the hydrolysed form. During reaction with metal surface they can easily form metal-oxane bonding (M-O-Si).

EXPERIMENTAL, RESULTS AND DISCUSSION, CONCLUSIONS
Presented work contains results of covering Metglas 2605 foil with layers based on different silane precursors. Two types of silanes were used: tetraethoxysilane (TEOS) and dipodal 1,2-Bis(triethoxysilyl)ethane (BTSE) and in both cases, they were hydrolysed with acid. Samples of Metglas 2605 foil were covered with one or two layers of obtained solutions and then were characterized with scanning electron microscopy, confocal microscopy and Raman spectroscopy.

Received samples were compared in order to select best system to obtain a smooth coating without cracks on amorphous metal foil. Moreover, chemistry of obtained layers was studied and differences were noted. As the result, the best preparation process was indicated and appropriate silane layer was chosen for further examination, where well attached and uniform layer is needed.

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REFERENCES
Synthesis and characterization of nickel-silver core-shell nanoparticles for conductive materials

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INTRODUCTION

During the last years, the growing interest in low-cost metallic inks and pastes for application in the field of electronics have been observed. The most popular metal in terms of conductive properties is silver. Although conductive nanomaterials based on Ag nanoparticles (NPs) have obvious advantages such as high conductivity and stability to oxidation, they are too expensive for large-scale commercial application in electronic devices. One of the suitable metals, which can be used as a replacement of silver is nickel, due to its much lower cost and good electrical conductivity. However, Ni NPs are easily oxidized in air, resulting in poor conductivity. Therefore, the protection of nickel from oxidation is an important challenge for implementing Ni NPs in conductive materials. As a suitable option to overcome the high cost of Ag and to prevent the spontaneous oxidation of nickel, Ni-Ag core-shell nanoparticles can be synthesized.

RESULTS AND DISCUSSION

In our research, Ni-Ag core-shell NPs were synthesized by using two methods. In the first, the three-step process of synthesis was used: (1) formation of a dispersion of Ni nanoparticles; (2) removing an excess of reducing agent; and (3) transmetalation (galvanic displacement) reaction, where the surface of Ni NPs acted as a reducing agent of silver ions. In the second method of fabrication of Ni-Ag core-shell NPs, the nickel NPs were first synthesized in the presence of the excess of the nickel ions and deficiency of the reducing agent to avoid the process of washing of nanoparticles. After that, the silver shell was formed by the addition of silver ions. The Ni-Ag NPs with optimal size 70 and 250 nm were obtained in the first and second method, respectively.

The Ni-Ag NPs obtained in the second approach, because of the higher percentage of metallic nickel, were used for the preparation of conductive ink. To obtain conductive metallic structures, we used thermal sintering by heating the metallic patterns deposited on a glass substrate. After sintering at 350°C for 30 min the conductivity was found to be 11% of bulk nickel.

CONCLUSIONS

The obtained conductive properties of ink coatings based on Ni-Ag NPs are promising for their application in the fabrication of electronic circuits or devices.

Acknowledgements

The „Development of methodology of synthesis and stabilization of metal nanoparticles for conductive materials” project is carried out within the Homing programme of the Foundation for Polish Science co-financed by the European Union under the European Regional Development Fund.
TiO$_2$ nanotubes with Pt and Pd nanoparticles as catalysts for electrooxidation of formic acid

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This work demonstrates a successful application of titania nanotubes in preparation of effective electrocatalysts supports. TiO$_2$ nanotubes (TiO$_2$ NTs) with strictly defined geometry were produced by anodization of Ti substrate [1]. The catalysts were obtained by decoration of the TiO$_2$ NTs with Pt or Pd nanoparticles (NPs) by magnetron sputtering. Morphological features, and/or peculiarities, as well as surface composition of the resulting catalysts have been studied by scanning electron microscopy (SEM), scanning transmission electron microscopy (STEM) and chemical surface analysis via X-ray photoelectron spectroscopy (XPS). The electrocatalytic activity of the TiO$_2$ NTs, decorated by Pt, Pd and/or Pd+Pt NPs was investigated by cyclic voltammetry (CV) and the Pd on TiO$_2$ NTs catalyst was additionally tested in a direct formic acid fuel cell test [2,3]. The maximum of specific power (calculated in mW·mg$^{-1}$ of Pd) for 0.2 Pd/TiO$_2$ catalyst was 70% higher than that of the commercial, highly dispersed Pd/Vulcan, which demonstrates that TiO$_2$ NTs can find practical applications in fuel cells [4].

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References

Nanopatterning of the magnetic FePd and CoPd thin films by the perforated anodized oxide templates

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Nanopatterned magnetic films which are formed by creating an ordered network of nanopores are called antidot arrays or antidots. A simple way of antidots fabrication is to deposit magnetic films on the perforated oxide templates such as anodic aluminium and titanium oxides (Al\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2}) templates.

We investigated the morphology, structure and magnetism of the hard magnetic CoPd and FePd thin films deposited on the porous Al\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2} templates where pore diameters and interpore distances varied in the range of 10-180 nm and 20-420 nm, respectively. Special attention was dedicated to find the possibility to control the effective magnetic anisotropy constant, coercivity, remanence magnetization and the mechanism of magnetization reversal of the porous films by the corresponding selection of templates morphology. We elaborated on the role played by the crystalline structure of the porous and continuous films in their magnetic properties.

We found that CoPd nanoporous films deposited on both types of porous templates retain the perpendicular magnetic anisotropy observed for continuous film. Deteriorated values of effective anisotropy constant and remanence magnetization for the porous films with respect to the continuous films were explained by the partial deviation of magnetic moments from the direction normal to the sample plane. The increase of the values of the coercive field of the nanoporous films in comparison to the continuous films was related to the pinning of the magnetic moments on the nanopores. We observed the transition of the magnetization reversal mechanism from the domain wall motion described by the modified Kondorsky model for the continuous films, to coherent rotation mode described by the Stoner-Wolharth model for the nanoporous films.

Nanopatterned FePd films showed differences in the localization and the distribution of the FePd alloy on the substrate surface, which depended on the pore size of the Al\textsubscript{2}O\textsubscript{3} templates. Additionally, the localization and the distribution of the FePd alloy changed with annealing. The annealing above 530°C induced the formation of the partially ordered L\textsubscript{1\textsubscript{0}} FePd alloy. Nanostructuring of the FePd film did not significantly change its magnetic properties. However, we observed isotropic properties of the nanopatterned FePd film annealed at 530°C which were explained by the hemispherical distribution of the material on the nanoporous template.

These results show that applied approach of nanostructuring allows us to tune the coercive field and the effective magnetic anisotropy constant of the CoPd and FePd films by engineering the porosity and/or pore size of the templates.

Acknowledgements

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INTRODUCTION

Low dimensional nanostructures from bulk layered materials can be obtained by mechanical delamination, like graphene flakes formation, and further shape modification using e.g. FIB lithography. Particularly the second step of the method proposed introduces structural defects into the crystal and thus it may strongly affect the functional properties resulting from the (near) surface effects. As such, controlled FIB processing may be crucial for controlling the functional properties of materials with an active surface states such as bismuth chalcogenides.

Bismuth chalcogenides belong to the group of materials that can make future electronic devices far more powerful than today. These layered materials, especially Bi₂Te₃, exhibit excellent thermoelectric properties associated with good electronic and low thermal conductivity. Single crystals of selected bismuth chalcogenides exhibit also the properties characteristic for Topological Insulators (TI), namely extraordinary robust electronic transport at the surface layer of a thickness of few nanometers only, while their interior is an insulator. Similar properties can be found in some semiconductors, but in TI the flow of electrons on the surface layer is not affected by impurities and dopants (except magnetic ones), which makes TI particularly promising for use in magnetoelectrics and spintronics.

EXPERIMENTAL RESULTS AND DISCUSSION

Our research is focused on systematic investigation of defects associated with nanostructurization of highest purity TI using caused focused ion and electron beams. Single crystals of bismuth chalcogenides (Bi₂Se₃ and Bi₂Te₃) synthesized using Bridgman method were probed depending on the parameters of nanofabrication processes (beam current, kinetic energy of particles, time of exposure, etc.). The atomic structure was observed using transmission electron microscopy (Fig. 1), while the chemical analysis of Ga diffusion was probed by means of X-ray micro-spectroscopy.

The ultimate goal of the study is to optimize the parameters of FIB lithography in order to keep the minimal desired size and shape of the nanostructures and preserve TI properties minimizing the damage in the surface state induced by the impinging ions.

Acknowledgements

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Fig. 1: TEM images of crossection of Bi₂Se₃ single crystals milled using focused beam of Ga ions.
POSTER

PRESENTATIONS
Nanostructured Biomaterials Session
One-step sonochemical fabrication and embedding of bioactive nanoparticles into nanorough parylene C implant coating

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INTRODUCTION
Although the progress in biomaterials research is dynamic, implantable medical devices still face two principal challenges regarding their extended use in vivo: biomaterial–associated infections (BCI) and the lack of native tissue integration. One of the strategies to prevent BCI is embedding nanoparticles of bioactive molecules, which can be obtained via sonochemical synthesis. The general aim of the study was to explore the approach employing the generation of antibiotic nanoparticles under ultrasound irradiation and their immediate embedment into the polymeric surface. For the proof of concept, we choose the antibiotic: gentamicin sulphate and the surface implant coating: oxygen plasma modified parylene C.

RESULTS AND DISCUSSION
The application of a strong acoustic field into an aqueous solution induces acoustic cavitation. The used ultrasound conditions resulted in the formation of gentamicin sulphate nanoparticles (GNPs) with an average size in the narrow range of 30-70 nm and their docking into the parylene C nanopores. The FTIR spectra confirmed the molecular structure of the antibiotic was preserved. The obtained surface morphology resulted in controlled elution of the drug up to 7 days.

CONCLUSIONS
The strategy allows obtaining, in a one-step process, an attractive NPs/polymer system with a function of prolonged bioactive substance release from the surface. Moreover, it can be straightforwardly implemented for other drug-polymeric coating couples, thus can be considered as very promising for the development of implant coatings with controlled drug release.

Fig. 1 The main subsequent steps leading to gentamicin nanoparticles formation and embedding into parylene C pores under ultrasonic radiation.

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Gold nanorods – synthesis, growth mechanism, characterization and cancer therapy application

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The shape of nanoparticles influences their electronic and optical properties thus finding potential application in anticancer therapy [1]. However, it is desirable to use agents, which minimize light extinction by intrinsic chromophores in native tissue. Therefore, these materials should be active in the near-infrared region (NIR) of the radiation spectrum. Gold nanorods (Au NRs) can absorb and scatter strongly in the NIR region (650-900 nm) [2]. These unique properties provide the potential of using Au NRs in photothermal cancer therapy. In the present work, we study the influence of reducer concentration, synthesis time and temperature on the formation of Au NRs and their optical and anticancer properties. We found, that too high concentration of reducer leads to the creation of gold nanostars (Au NSs). Moreover, increasing the synthesis temperature causes porosity and distortion of Au NRs, while extended synthesis time leads to creation of gold nanopeanuts (Au NPes) (Fig. 1). Furthermore, changes in the synthesis factors leads to shift of the plasmon resonance peak to shorter wavelengths. It was found that after exposure to continuous red laser at 808 nm, colon cancer cells (SW480 and SW620 cell lines) with Au NRs added to the cell culture, the viability of cells was lower than without Au NRs in cells culture.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{STEM HAADF overview images of Au NRs synthesized at different reaction conditions.}
\end{figure}

REFERENCES
Tuning the surface properties of carbon nanotubes and graphenic materials via oxygen plasma treatment

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One of the essential advantages of carbon materials consists in their facile surface functionalization. Among the proposed methods for surface modification, cold plasma has been proven as an efficient and universal technique for introduction of various chemical moieties, in particular oxygen [1,2].

In this work the modification of multiwalled carbon nanotubes (MWCNTs) and graphenic surfaces by oxygen plasma towards controlled tuning of their electrodonor properties (work function) was investigated (Figure 1). The surface changes were monitored with spectroscopic (XPS, RS) and microscopic (TEM, SEM) methods. The work function (Φ) measurements experiments were carried out by the dynamic condenser method of Kelvin. For MWCNTs at the first stage of plasma treatment the significant increase of work function is observed (up to 1.4 eV) and after passing the maximum the work function decreases and finally stabilizes. The DFT results confirmed the experimentally observed formation of surface dipoles at initial stage of treatment (XPS) and breaking the C-C bond and insertion of oxygen into the structure which results in material surface amorphization (TEM, RS). For graphenic surfaces generation of surface oxygen groups leads to dramatic increase in the work function (from 4.4 eV to 6.0 eV) and decrease in the water contact angle (from 93.8° to 7.0°). The investigated surfaces were also evaluated in terms of bacterial colonization. The bacteria (S. aureus) coverage systematically increased with the plasma treatment from 3.2% (untreated graphenic surface) to 9.2% (60 W, 0.5 mbar, 20 min). The obtained results revealed that colonization of graphenic surfaces is strongly governed by the surface oxygen concentration, wettability, and electronic properties (Φ).

Figure 1. Changes in electronic properties of carbon surfaces upon oxygen plasma treatment.

Concluding, oxygen plasma treatment allows for precise control of the electronic properties of carbon materials. Such modifications in surface morphology and electrodonor properties pave the way for carbon materials applications as electrocatalysts, catalytic supports and graphenic-based biomaterials.

REFERENCES
Preparation and modification of SiOC amorphous layers via the sol-gel method

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Silicon oxycarbide (SiOC) based materials (known also as black glasses) are nowadays the point of interest of various industries and technology branches such as biomaterials, catalysts, fuel cells, protective layers for example. It is basically due to their unique features such as durability, good mechanical properties, chemical and thermal stability, corrosion and oxidation resistibility [1]. This properties significantly vary from the ones of amorphous silica (ν-SiO₂). It is caused by the denser and stiffer network – a result of the replacement of part of the oxygen ions by the carbon ions - due to the different valence one C⁴⁺ anion replaces two O²⁻. Although the properties of black glasses are magnificent, they might be enhanced by the modification with particular anions, cations or nanoparticles. Addition of anions such as carbon and nitrogen results in an increase of mechanical parameters. Modifications with aluminium, boron, zirconium may enhance respectively mechanical properties, stability and temperature capability. Also, some novel features might be added to the material, e.g. magnetic (by iron, cobalt or nickel ions) or catalytic properties (copper, palladium, platinum ions) [2].

The mentioned modifications are possible because the preparation of black glasses engages the so-called soft chemistry method. In most of the published articles, preparation of SiOC-based materials is based on the commercially available silicon resigns which undergo thermal treatment resulting in obtaining the ceramic material. The use of commercial polymers limits the possibility of modification on the elemental level. In this work, a slightly different path is proposed. However it is using the long-chain organosilicon compounds – ladder-like polysilsesquioxanes – the precursors are self-synthesized. They are synthesized from the alkoxides containing silicon-carbon bonds along with silicon-oxygen with the use of the sol-gel method. The process is basically based on hydrolysis and polycondensation of the monomers during which preceramic precursors might by further tailored and modified by the variety of organometallic compound as well as inorganic salts. The sol-gel process takes place in the solution (e.g. ethanol) making deposition via the dip coating technique effortless. However, the thermal treatment in the protective atmosphere of the inert or reducing gas is required as before [1,3].

This work will focus on the presentation of preparation and possibility of modification of black glasses with phosphorus and cerium ions as well as multiwalled carbon nanotubes. These particular modifications lead obtaining coatings of enhanced bioactivity and biocompatibility, antibacterial properties, controlled topography, improved mechanical parameters and conductivity. The study concerns structural and microstructural examination along with the particular functional properties testing confirming obtaining of the modified black glasses of desired characteristics.

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REFERENCES
Polysaccharide-based nanocapsules as drug delivery systems for anticancer treatment

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INTRODUCTION
An oleic acid’s (OA) anticancer properties are interesting both from the scientific and epidemiological point of view since years. It is known that the diet rich in oleic acid (OA) decreases the risk of cancer diseases. The OA molecule in an interaction with cells has a great influence on inhibition of proliferation of cancer cells. [1] From the physicochemical point of view, OA exhibits poor water solubility and various techniques are used for the enhancement of the solubility of lipophilic or hydrophobic drugs which include physical and chemical modifications of drug and encapsulation of those drugs in formulation in aqueous vehicles.

EXPERIMENTAL
Herein, research is focused on nanocapsules as oleic acid delivery system for potential anticancer therapy. The aim of the work was to obtain polysaccharide-based nanocapsules templated on liquid cores by using ultrasound-assisted emulsification. The hydrophobically modified polysaccharide was used to stabilize O/W emulsion by anchoring hydrophobic arms in an oil droplet without the need of using low molecular weight surfactants. [2] The morphology, sizes and stability of obtained nanocapsules were characterized. Stability studies are focused on monitoring zeta potential value in time. The basic biological research including cytotoxicity, cellular internalization and uptake was performed.

CONCLUSION
OA-based nanocapsules exhibit larger toxicity for cancer cells then non-cancer cell lines. They effectively deliver the cargo into cells and are able to release it inside them. In comparison with capsules made from another polysaccharide different ways of uptake are observed. The prepared nanostructured materials are still developed towards targeted drug delivery and encapsulation of variety of lipophilic active compounds

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REFERENCES
Methodology of preparation of biocompatible drug carriers based on proteins

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INTRODUCTION
Pharmacy is currently one of the most rapidly developing fields of science. Scientists conducted studies on the preparation of new drugs and in parallel on the materials that could act as drug carriers. One of the most interesting substances that can be used for synthesis of such carriers are proteins. Such protein based drug carriers after the release of the drug degrades to non-toxic products without a negative impact on the environment.

EXPERIMENTAL PART
For purpose of preparation of drug carriers based on albumin first step was to prepare its solution in Tris-HCl buffer. Next, the solution was mixed with the potassium phosphate. Process was conducted with different parameters to check their impact on the size and properties of protein spheres. In Fig. 1. an impact of the concentration of potassium phosphate on the size (diameter) of prepared spheres is shown.

As it was presented, the use of higher concentration of potassium phosphate resulted in a formation of spheres with a smaller diameter.

CONCLUSIONS
Parameters of the synthesis of protein spheres have an impact on their size. Prepared spheres based on protein, i.e. albumin, constitute an interesting materials that can be considered as innovative biodegradable and non-toxic drug carriers.

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REFERENCES
Characterization and anticancer properties of magnetic nanoparticles produced by different methods

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Magnetic iron oxide nanoparticles (IONPs) are widely applied in magnetic resonance imaging, magnetic thermoablation hyperthermia, cellular labeling and separation, gas sensors or as catalysts. We synthesized IONPs by three different methods: i) co-precipitation, which is a preferred route in terms of simplicity, ii) thermal decomposition, being the most developed route leading to proper control of size and morphology and iii) pulsed laser ablation in liquid, offering NPs obtained by a chemically clean route, which fulfills “green synthesis” requirements. The i) method resulted in platelet-like NPs, Fig. 1(a), while the second method allowed to control the shape of the NPs from spherical to nanocubes, Fig. 1(b,c). Subsequently, the spherical IONPs were functionalized by a porous SiO₂ shell, Fig. 1(d,e), while the laser obtained NPs were functionalized by Au, Fig. 1(f,g), which resulted in both cases in a decrease in their cytotoxicity. It was found that vacuum annealing at T below 300°C does not affect the superparamagnetic state of the IONPs, however it allows to tune their values of blocking temperature in a wide range. Moreover, vacuum annealing allows to change the saturation magnetization of the fabricated IONPs.

Figure 1. STEM HAADF images of NPs obtained by: i) co-precipitation (a); ii) thermal decomposition (b,c); functionalized Fe₃O₄ core/SiO₂ shell (d,e); iii) pulsed laser ablation in liquid FeOx core/Au shell (f,g)

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Anodization of titanium based alloys for biomedical applications

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INTRODUCTION

Pure titanium as well as its alloys are extensively used in various fields, such as chemical industries, military, and very often in medicine, where are a basic material for surgical instruments and implants. One of the most commonly used titanium alloy for biomedical purposes is Ti-6Al-4V. Besides its great qualities and applicability, it has several drawbacks. First of all, this alloy is characterized by quite high Young’s modulus in comparison to the compact bone. What is more, it is comprised of vanadium and aluminum, which ions may have a toxic effect on human body. In particular, aluminum ions may be responsible e.g., for Alzheimer’s disease. That is why scientists are still searching for new titanium materials that could replace those mentioned above. An example of such alloys may be Ti-15Mo and Ti-13Nb-13Zr, which are currently intensively investigated [1-2].

Another important problem that may be encountered in orthopedics is a danger of implant failure caused by an incomplete osseointegration. A connection between bone tissue and the implantable material occurs via formation of a native oxide layer on the metal’s surface. This process is time-consuming and the oxide layer is very thin. That is why, a material already with such layer – preferably thicker and of more complex morphology might be a good solution. Moreover, such layers may be obtained via a simple and cost-effective method such as electrochemical oxidation. It was already proven that formation of titanium oxide layer in the form of nanotubes significantly improves osseointegration process [3].

In the presented studies, one-step anodization process of Ti-15Mo and Ti-13Nb-13Zr alloys was conducted in an ethylene glycol based electrolyte containing fluoride ions (0.38 wt%) and water (1.79 wt%) under a constant temperature of 20 °C. An influence of applied potentials on the nanostructures of oxide layers were tested. The surface of samples was examined using a field emission scanning electron microscope (FE-SEM) with EDX analyses, work function and contact angle measurements. It was shown that by changing the applied potential, oxide layers with different surface parameters may be obtained, and thus different cell’s response may be suspected.

REFERENCES
Modified anodic titanium dioxide layers as potential drug delivery systems and scaffolds for cell culturing

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INTRODUCTION
Recently, nanoporous anodic titanium oxide (TiO₂) (ATO) layers are thoroughly investigated as drug delivery systems and scaffolds for cell culture. It is noted that the surface chemistry and topography play a crucial role. Therefore, the modification of ATO surface can improve the cells behavior.

EXPERIMENTAL, RESULTS AND DISCUSSION, CONCLUSIONS
Nanoporous TiO₂ layers were fabricated via a three-step anodization process. ATO layers were modified with 0.5 M sodium hydroxide (NaOH) for 15 min. In order to obtain anatase phase, TiO₂ samples were annealed in air for 2 h at 400 °C. The samples non-annealed and annealed NaOH-modified samples were immersed in 1% ethanolic solution of different silane derivatives ((3-aminopropyl)triethoxysilane (APTES), (3-glycidoxypropyl)trimethoxysilane (GPTMS) and (3-mercaptopropyl)-trimethoxysilane (MPTMS)) for 2 hours. Ibuprofen, a nonsteroidal anti-inflammatory drug, was loaded inside nanopores and, then, released in a 0.01 M phosphate buffer solution (PBS, pH = 7.4) at 37 °C. A desorption-desorption-diffusion (DDD) model was fitted to the obtained drug release profiles. In biological studies, the osteoblast-like cells line MG-63 were seeded on TiO₂ layers and incubated for 2, 24 or 72 h. MTS assay was carried out to examine cell viability and proliferation on different samples. The morphology of adhered osteoblast-like cells was investigated using a fluorescent microscope and scanning electron microscope. The data showed that the modification of nanoporous TiO₂ layers with small chemicals such as silane derivatives enhanced metabolic activity of adhered cells. In addition, the cells were well dispersed. It was demonstrated that modified with silane derivatives nanoporous TiO₂ layers could be successfully applied as drug delivery systems. In conclusion, both amorphous nanoporous TiO₂ anatase layers can be successfully modified with NaOH and silane derivatives (APTES, GPTMS, MPTMS) and the modified samples can be used as drug delivery systems and scaffolds for osteoblasts-like cells culturing.

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Chitosan-coated anodic nanoporous TiO$_2$ layers as potential drug delivery systems

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INTRODUCTION
Recently, anodic titanium dioxide (TiO$_2$) (ATO) layers are widely investigated as an implant material. In addition, nanoporous TiO$_2$ layers can be coated with biocompatible polymers, such as chitosan. Chitosan has antibacterial and osseointegration properties. The polymeric coating reduces the burst release of drugs and extends overall release.

EXPERIMENTAL, RESULTS AND DISCUSSION, CONCLUSIONS
Nanoporous TiO$_2$ layers were synthesized via a three-step anodization process. The samples were annealed in air at 400 and 600 °C in order to obtain anatase or mixture of anatase and rutile phases, respectively. The samples were coated with chitosan applying the dip-coating process. The modified TiO$_2$ layers were studied as potential drug delivery systems. Ibuprofen, a nonsteroidal anti-inflammatory drug, was used in drug release studies. The release studies were carried out in a 0.01 M phosphate buffer solution (PBS, pH = 7.4) at 37 °C. The drug concentration was determined using UV-Vis spectrophotometry. A desorption-desorption-diffusion model of the drug release was fitted to the resulting profiles. The apatite-forming ability of chitosan-coated nanoporous ATO layers was examined in simulated body fluid (SBF). In order to form calcium phosphate crystals on ATO surfaces, the samples were soaked in SBF for 1, 3, 5, 7, 14 and 21 days and, then, were characterized by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). Based on the results, it was demonstrated that coating of nanoporous TiO$_2$ samples with chitosan inhibited the process and reduced the fraction of the drug released in the first stage (“burst” effect). The desorption from the surface and nanopores was slower, however the diffusion process is faster, for polymer-coated samples than non-coated. It was noted that chitosan coated anatase and mixed anatase/rutile samples exhibited apatite forming ability. In conclusion, the nanoporous TiO$_2$ layers could be successfully coated with chitosan and the coated samples are a promising implant material.

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Impact of different morphology and crystalline structure for apatite-forming ability of anodic nanoporous titanium dioxide layers

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INTRODUCTION
Due to their good mechanical properties and great biocompatibility, titanium and its alloys are commonly used as bone implantable materials. However, Ti-based implants exhibit poor osseointegration and bioactivity. The process of chemical bonding between the biomaterial and surrounding bones is long-lasting because it occurs via an oxide layer formed on the material surface. In order to tackle this problem anodic titanium oxide (ATO) layers can be formed before implantation via anodization process. The length and diameter of nanopores/nanotubes can be easily controlled by anodizing voltage. In addition, it was reported that formation of hydroxyapatite on anodic TiO2 layers is accelerated by the presence of anatase or rutile phases. Typically, the samples are soaked in simulated body fluid (SBF).

EXPERIMENTAL, RESULTS AND DISCUSSION, CONCLUSIONS
Nanoporous TiO2 layers were synthesized via a three-step anodization process in an ethylene glycol electrolyte under a constant voltage ranging from 30 to 70 V. The duration of the first and second anodizing step was 3 h, while the third step lasted 10 min. The anatase and a mixture of anatase and rutile phases were obtained by annealing the as-prepared amorphous TiO2 layers in the air for 2 h at 400 and 600 °C, respectively. The samples were soaked in a simulated body fluid for 1, 3, 5, 7, 14 and 21 days. Then, they were washed gently with distilled water. ATO layers were characterized by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). Based on the results, it was demonstrated that annealed samples exhibited better apatite-forming abilities than amorphous ATO layers. Moreover, anodizing voltage had an impact on the formation of calcium phosphate crystals on ATO samples. Samples anodized at 60 and 70 V exhibited the best apatite-forming abilities. In conclusions, the anodization potential and crystalline structure have an influence of apatite-forming ability of anodic titanium dioxide layers.

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REFERENCES
Halloysite/alkaline phosphatase component of hydrogel scaffold for bone tissue regeneration

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Alkaline phosphatase (ALP) is an enzyme that actively participates in the biomineralization process, leading to the renewal of bone tissue. ALP catalyzes dephosphorylation processes leading to the formation of free phosphate groups, which in combination with calcium form hydroxyapatite, the main component of bone. Unfortunately ALP, being a protein and enzyme, is susceptible to deactivation and degradation. In order to improve its stability as a bioactive component of a hydrogel scaffold intended for bone tissue repair, the enzyme was first encapsulated in a halloysite nanocarrier. Halloysite, a nanoclay which occurs mainly in the form of nanotubes, was chosen as a carrier due to its high durability and thermal resistance, biocompatibility and unique tubular structure with negative external surface and positively charged interior. Halloysite nanotubes have the lumen, which is large enough to encapsulate ALP, and it is assumed that they should provide very good protection and stabilization for it. The presence of halloysite should also improve the mechanical properties of the subsequently formed hydrogels. The obtained composite material was subjected to physicochemical characterization using SEM, FTIR and XPS techniques. The activity of the entrapped protein was determined using the Bessey and Lowry colorimetric method. The protein was effectively introduced into the halloysite nanotubes and remains active. The enzymatic activity of the halloysite-entrapped ALP in a biomineralization process was also tested using calcium glycerophosphate as a substrate. SEM measurements confirmed the formation of crystallite on the surface of the nanotubes, while EDS analysis confirmed that hydroxyapatite was indeed produced. In the further studies, the methodology for preparing chitosan hydrogels cross-linked with a non-toxic genipin, and containing different amounts of halloysite nanotubes with entrapped ALP, was developed and optimized. Research was also conducted on the influence of the inorganic component on the swelling process of the hydrogel material. The new hybrid system has a potential as a scaffold for the treatment of bone defects.
Antimicrobial Supramolecular UPy-Based Biomaterials

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INTRODUCTION
The use of biomaterials inside the body always entails the risk of infection. This risk might even be higher in \textit{in situ} tissue engineering applications. Since the porous scaffold materials can form a niche for invading bacteria, the intended \textit{in situ} production of novel tissue may be severely compromised by infection. Therefore, we aim to develop a new polymeric supramolecular scaffold material, exerting two important functions: preventing microbial adhesion and thereby preventing biofilm formation, and inducing endogenous (eukaryotic) cells to repair the body.

EXPERIMENTAL
The antimicrobial polymers were prepared by simply mixing-and-matching of Ureido-Pyrimidinone (UPy) based supramolecular polymers \cite{Dankers2005} with the antimicrobial peptides (AMPs) SYM11KK, L9K6 and LASIO III modified with a supramolecular UPy moiety. The secondary structure of the UPy-AMPs was investigated by CD spectroscopy. Solid samples were prepared by drop-casting polycaprolactone (PCL2k)-diUPy with AMPs or UPy-AMPs on glass coverslips. The antimicrobial activity of the UPy-AMPs in solution and of the drop-casted samples against \textit{Escherichia coli}, and (methicillin-resistant) \textit{Staphylococcus aureus} was evaluated.

RESULTS AND DISCUSSION
The UPy-functionalization of the AMPs did not affect their secondary structure, as proved by circular dichroism spectroscopy, and the antimicrobial activity in solution was also retained. In addition, the incorporation of UPy-AMPs into a UPy-polymer (PCL2k-UPy) was stable and the resulting material was biocompatible. The addition of 4 mol\% UPy-AMPs in PCL2k-UPy polymer samples materials protected the material against colonization by \textit{E. coli} and (methicillin-resistant) \textit{S. aureus}. The modular approach enables a stable but dynamic incorporation of the antimicrobial agents, allowing the use of AMPs with broad range activity, like the promising novel Synthetic Antimicrobial and Anti-biofilm Peptide SAAP-148 \cite{deBreij2018}. Next, we aim to control cell adhesion by functionalizing UPy-units with the cell-adhesive peptide RGD sequence. Ultimately we aim to use such materials for \textit{in situ} infection-free tissue engineering of vascular tissues, such as vascular grafts and heart valves.

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Impregnation of TiO\textsubscript{2} surface by halogenated porphyrins derivatives for enhanced ROS generation

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Nanoparticle metal oxides represent a new class of important materials that are increasingly being developed for use in health-related applications and photooxidation. Titanium dioxide (TiO\textsubscript{2}) is a well-known nanometer-sized crystal material that indicates lack of toxicity, stability and versatile photocatalytic properties. Its photocatalytic activity is derived from the charges' separation processes occurring in a bulk and on its surface. Unfortunately, TiO\textsubscript{2} poorly absorbs in visible light, so it is not effective in the natural environment. However, the photosensitization of wide-bandgap TiO\textsubscript{2} with organic dyes immobilized at the surface extends the spectral range of TiO\textsubscript{2} photoactivity into the visible region of light. [1]

In the presented work, we demonstrate the efficient immobilization of 5,10,15,20-tetrakis(2,6-difluorosulfon furylophenyl) porphyrin (F\textsubscript{2}POH) and its zinc (II) complex (ZnF\textsubscript{2}POH) on the surface to TiO\textsubscript{2} that derived from the substitution of functional groups -SO\textsubscript{3}H as well as fluorine atoms. All of prepared materials were thoroughly characterized in terms of their morphological, spectroscopic, electrochemical, photochemical and functional properties by diffuse reflectance spectroscopy (DRS), scanning electron microscopy (SEM), cyclic voltamperometry as well as biological and photocatalytic tests. The photocatalytic activity in the degradation of model pollutants 4-chlorophenol as well as opioid drug - tramadol was investigated using polycrystalline TiO\textsubscript{2} impregnated with the free base-porphyrin and its metal-derivative. The photocurrent measurements have demonstrated that derivatives of fluorinated porphyrin, especially ZnF\textsubscript{2}POH, significantly improve photoactivity of titania within visible range of light. Moreover, materials based on fluorinated porphyrins exhibited a significantly higher antibacterial activity under visible light than those of TiO\textsubscript{2} modified with commercial tetraphenyl porphyrin (TPPS). Finally, TiO\textsubscript{2} alone is not active against bacteria at the same experimental conditions implying that material containing fluorinated and sulfonated porphyrins improve photochemical activity and efficiency of the reactive oxygen species generation upon visible light and thus are highly promising materials for biomedical applications.

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Nanomaterials for Energy Conversion and Storage Session
Synthesis of polypyrrole-nickel hydroxide hybrid nanowire arrays by pulse electrodeposition

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INTRODUCTION
Both, metal oxides and conducting polymers have been extensively studied in the past decades as a pseudo-capacitive materials. On the one hand, conducting polymers, such as polypyrrole (PPy), combine advantages of organic polymers with electronic properties of semiconductors, and hence, are attractive materials for the use in data storage devices and photovoltaic cells. On the other hand, Ni-based nanostructures and thin films have been extensively used as electrode materials for lithium-ion batteries and fuel cells, electrochromic films, gas sensors, and electrochemical supercapacitors. Hybrids play an important role since as a multicomponent system, can combine the properties of their constituents, which make it possible to overcome the drawbacks of individual components. Apart from new features and enhanced performance, such an approach quite often allows the drawbacks of single components to be diminished or reduced entirely. Therefore, the aim of this study was to prepare and characterize polymer–metal hydroxide (polypyrrole–nickel hydroxide, PPy-Ni(OH)₂) nanowire arrays by voltage pulse electrodeposition of polypyrrole and nickel oxide into nanoporous anodic alumina oxide (AAO) template.

EXPERIMENTAL, RESULTS AND DISCUSSION, CONCLUSIONS
The structural features of as obtained PPy-Ni(OH)₂ hybrid nanowires were characterized using FE-SEM and TEM analysis. Their chemical composition was confirmed by Energy-Dispersive X-ray Spectroscopy (EDS). The presence of nickel hydroxide in the synthesized PPy-Ni(OH)₂ nanowire array was confirmed by X-ray photoelectron spectroscopy (XPS). Both FE-SEM and TEM analyses confirmed that the obtained nanowires are composed of the polymer matrix with nanoparticles dispersed within. EDS and XPS techniques confirmed the presence of the PPy-Ni(OH)₂ in the nanowire array obtained. Optimal working potential range (i.e., available potential window), charge propagation and cyclic stability of the electrodes have been determined with cyclic voltammetry (CV) at various scan rates. Interestingly, the electrochemical stability window for the aqueous electrolyte at PPy-Ni(OH)₂ nanowire array electrode is remarkably wider (ca. 2 times) in comparison with the non-modified PPy electrode. The capacitance values, calculated from cyclic voltammetry performed at 20 mV s⁻¹, were 25 F cm⁻² for PPy and 75 F cm⁻² for PPy-Ni(OH)₂ array electrodes. The cyclic stability of the PPy nanowire array electrode up to 100 cycles shows the capacitance fade of about 13 %.
Electrochemical performance of supercapacitors with polysaccharide-derived carbon aerogel electrodes

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Rapidly growing market of electric/hybrid-electric vehicles (xEV) and higher energy consumption constantly increase modern society demands towards high-power energy systems. These changes are accompanied by growing concerns about environmental issues, including climate change and depleting of fossil fuels [1]. All points mentioned above force multitude of scientists to develop and improve electrical energy storage systems that meet requirements of swift technology evolution as well as ecology and economy matters.

Supercapacitors (SC) have become one of the most attractive power devices for increasing number of applications such as sustainable energy generation, transportation or power systems [2]. SC advantages including fast charging/discharging rate, very good cycling stability and outstanding power density allow them to play an important role in applications mentioned above [3].

Most widely used electrode materials for SC are carbon-based materials such as activated carbons [4], nanotubes [5] or carbon aerogels (CAG) [6]. The latter ones are ultralight materials built of an interconnected nanoparticle network structure. Their properties, such as well-defined porosity, large specific surface area, good conductivity and stability allow them to be implemented in a broad range of applications. Most common methods of creating carbon aerogels are connected with resorcinol-formaldehyde gel synthesis, connected with usage of toxic compounds and expensive synthesis routes [7].

In this work we present research on SC with electrodes made of activated carbon aerogels obtained by alternative and novel route that is based on sol-gel synthesis of natural polysaccharides (different types of starch) [8]. This inexpensive, energy-saving and environmentally friendly process results in obtaining electrode materials that exhibit good electrochemical performance (rate capability, capacitance retention) in SC. Following experimental methods have been used to characterize performance of polysaccharide-derived SC with CAG electrodes: voltammetric-charge-discharge tests (CELL TEST), cyclic voltammetry (CV), electrical conductivity tests (EC) and electrochemical impedance spectroscopy (EIS).

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REFERENCES
Spinel-based materials for high-performance Li-ion batteries

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The rapid development of lithium-ion battery (Li-ion, LIB) technology requires a great deal of emphasis on improving all components of the cell. The trade-off between the cell’s operating parameters, its cost and environmental issues is forced by a sharp increase in the demand for effective energy storage systems in electric and hybrid-electric vehicles [1]. A crucial component of the cell is a cathode material. Its most important properties are specific capacity, working voltage, structural stability, durability in numerous charge-discharge cycles and rate capability. There are not many materials that meets these requirements at the same time with being cheap and environmentally-friendly. Nonetheless, LiMn₂O₄ (LMO) and its derivatives are attractive solution which to some extent combine all the above-mentioned advantages [2].

One of the most important requirement for today’s LIBs is ability to being charged or discharged with very high rates. With the development of technology and the proliferation of electric vehicles, charging times comparable to those of petrol-powered vehicles will be required. Forcing such conditions on currently used commercial Li-ion cells would cause a dramatic drop in the capacity, life of the cell and could lead to a dangerous increase in temperature and ignition of the cell or even the entire battery pack. The above-mentioned problems necessitate the development of modifications of Li-ion technology at all levels, in particular modification of electrode materials.

This work presents the latest achievements in the modification of lithium-manganese spinel materials for high-power LIB applications. A review of research on the modification of lithium-manganese spinels by doping with various elements and its surface modifications was performed.

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Electrochemical performance of carbon coated LiMn$_{2}$O$_{3.99}$S$_{0.01}$

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Constant increase of fossil fuels use and galloping environment pollution forces mankind to search for most effective and environmentally benign solutions of developing safe and clean energy storage systems and power sources. One of the solutions of contamination problems is moving away from fuel combustion powered vehicles towards electric and hybrid-electric vehicles (xEV), powered with safe and clean powers sources, such as Li-ion batteries [1]. One of the most promising cathode materials used in this technology is lithium manganese oxide spinel (LMO).

LMO based materials perfectly fits the market requirements in terms of economy and ecology, due to its negligible toxicity and low cost and high abundance of manganese. Although, LMO has some flaws that needs to be overcome to make them as effective as it is possible. One of them is its structural instability and phase transition that takes place in around room temperature [2], Mn$^{3+}$ ions dissolution into liquid electrolyte [3], which leads to electrochemical properties deterioration [4]. These flaws can be overcome by doping material with sulphur, which leads to improved structural stability and capacity retention due to reduction of unfavourable phase transition of spinel in room temperatures [5,6]. The other approach to enhance LMO performance is surface modification. Carbon coated spinel exhibits improved conductivity, rate capability, capacity retention and diffusion coefficient [7].

In this work carbon coating on S doped LMO was fabricated using method similar to Conducting Carbon Layer coating [8]. The effect of CCL coating on LMO has been examined. The effective procedure of coating LMO based material with conducting carbon layer has been developed. The methods used in the study are x-ray diffractometry (XRD), transmission electron microscopy (TEM), galvanostatic charge-discharge tests (CELL TESTS), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS).

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Ethanol oxidation reaction on Pt/Re/SnO\(_2\) catalyst supported on carbon substrate: Effect of the synthesis method

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Nanoparticles due to their reduced size show specific physical, chemical and often also catalytic properties [1]. This is due to the drastic increase in the percentage of surface atoms along with the decrease of nanoparticle size, what is extremely important in catalysis, as surface atoms play a crucial role [2]. Platinum NPs are commonly used as catalysts in alcohol oxidation reactions in DEFCs, but their catalytic efficiency may be enhanced by adding Rh or SnO\(_2\) [3,4]. So far, the best catalysts for ethanol oxidation (EOR) seem to be PtRh/SnO\(_2\) NPs designed by Adzic group [4]. The size and chemical composition control is critical as well as physical contact between the NPs, as it directly affects catalytic properties. Kowal et al showed that the ethanol molecule is completely oxidized only when it is in contact with all three components of the catalyst [5].

Fig.1 Scheme of controlled assembling of positively charged SnO\(_2\) NPs with negatively charged metallic Pt and Re NPs into ternary catalysts by adjusting their pH values.

The aim of this study was to compare the electrocatalytic activity towards EOR of SnO\(_2\) NPs decorated by Pt and Re NPs produced by three different synthesis methods. The first method was based on mixing Pt, Re and Sn containing precursors and reducing them together. In the second method, first SnO\(_2\) NPs were produced and then Pt and Re precursors were added to the solution and reduced. The third approach was based on the zeta potential theory allowing assembling the individually synthesized NPs (Pt, Re and SnO\(_2\)) in a controlled way, leading to the formation of the desired ternary NPs arrangement with physical contact between them [6]. The Pt/Re/SnO\(_2\) nanoparticles were deposited on carbon Vulcan XC-72R and characterized by Transmission Electron Microscopy (TEM), EDS analysis, X-ray diffraction (XRD) and cyclic voltammetry.

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Design and synthesis of effective electrocatalysts for the oxygen reduction reaction (ORR) based on carbon-supported manganese-cobalt spinel

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Design and synthesis of new potential catalysts for electrode reactions, such as ORR is one of the most important purpose of research in the context of full commercialization of fuel cells [1]. A great deal of research has been devoted to upgrading the catalysts for ORR in order to avoid the main limitations of commercial Pt catalyst such as the high cost and scarcity. The cost reduction can be accomplished by reducing Pt loadings or by designing efficient non-noble-metal-materials, such as transition metal oxides catalysts [2]. It is known that better dispersion of nanoparticles provide more available active sites for oxygen reduction, therefore it is important to apply the appropriate carbon carrier that provide uniform dispersion of the spinel particles. The aim of this research is the development of an effective electrocatalysts of the oxygen reduction reaction (ORR), which will be exhibited catalytic activity comparable to the commercial Pt catalysts. The proposed materials are based on the Mn-Co spinel deposited on different type of carbon matrix. Our research focus on determine the influence of the carbon support nature on the catalytic activity and the mechanism of oxygen reduction. The catalytic properties of well-characterized materials were studied by rotating disk electrode method (RDE) and rotating ring-disk electrode method (RRDE).

Figure 1. LSV curves Mn-Co spinel deposited on selected carbon supports in O₂-saturated 0.1 M KOH solution recorded at 1600 rpm.

The catalytic performance of Mn-Co spinel is found to depend strongly on properties of carbon supports, which plays a triple role in the ORR activity, determining dispersion and faceting of the spinel nanoparticles as well as the extent of the undesired 2e⁻ reduction pathway, controlled by the fraction of an amorphous component.

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REFERENCES
Electrochemical and structural properties of bio-derived carbon nanostructures as Li-ion anode materials with regard to source of precursor and preparation conditions

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INTRODUCTION

The nanostructured carbons are a relatively new class of electrode materials that exhibit many desirable features for energy storage applications. Among them, there are carbon aerogels which become more and more popular due to their specific structure and attractive properties such as: well-defined porosity, large surface area, chemical and thermal stability, high electrical conductivity and high capacitance. However, the commonly used carbon aerogels precursors are frequently poisonous and expensive which leads to i.a. the restrictions in a large scale production. Therefore, actual studies have been largely focused on carbon precursors that are easily accessible, renewable, low-cost, as well as environmentally friendly. One of the representatives is the most abundant, non-toxic, naturally occurring polysaccharide - starch [1-4].

In the present work nanostructured carbon materials (CAGs) obtained from the starch, were successfully synthesized via sol-gel polymerization followed by the carbonization process [5-7]. The aerogel materials were characterized concerning structural and textural properties by using X-ray powder diffraction (XRD), elemental analysis (EA), Raman spectroscopy (RS), nitrogen adsorption/desorption method (N₂-BET), and scanning electron microscopy (SEM). The galvanostatic charge/discharge tests (GCDT), cyclic voltammetry (CV) as well as electrochemical impedance spectroscopy (EIS) measurements were carried out to analyse electrochemical behaviour of the CAG materials.

The results show the influence of different carbon precursors and synthesis parameters on the aerogels morphology and electrochemical properties. Defining the proper composition of the precursors and changing the preparation conditions allow to functionalize nanostructured carbon material depending on the purpose of use.

ACKNOWLEDGEMENTS

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Structural evolution of CCL/Li$_2$MnSiO$_4$ in lithium-ion cell

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The rapid development of industry and technology is one of the reasons for the continuously growing worldwide energy demand. Moreover the last decades have seen that there is a need for dynamic progress in the field of energy storage systems. Because of these even the most popular Li-ion technology, which is nowadays prevailing portable energy source, is constantly being optimized by using new, more efficient materials [1].

Li$_2$MnSiO$_4$ (LMS) is one of the novel cathode material that seems to be worth a closer look. High operating voltage, high thermal and chemical stability (resulting from the strong covalent Si-O bonding in the lithium silicate structure), potentially low cost of production and environmentally friendliness make this material attractive, especially for the application in Li-ion batteries [2-4]. Furthermore, due to the theoretical possibility of reversible intercalation of two lithium ions per formula unit, Li$_2$MnSiO$_4$ can reach very high theoretical capacity up to 333 mAh/g [3-6]. However the main drawback of this material is its low electrical conductivity (~10$^{-16}$ S/cm at room temperature) which is related to the structural limitations. Another problems are poor cyclability and very low ionic conductivity. These obstacles cause that pristine LMS is completely ineffective as cathode material [5-6].

One of the possibilities to handle all these problems is to form the nanometric conductive carbon layers (CCL) directly on the active material grains [7-8]. The carbon layer stabilizes the surface, but it is not sufficient for structure stabilization. During the first cycle of working in Li-ion cell, there is still observed the amorphization of the Li$_2$MnSiO$_4$ structure. Although amorphous LMS can still provide the capacity of 185 mAh/g, the reversibility is really low in subsequent cycles [9].

The aim of this research is to examine the structural changes of lithium-manganese silicate in lithium-ion cell.

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Effect of doping on electrochemical and structural stability of lithium-manganese oxide spinel

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INTRODUCTION

The last decades have seen the rapid development of new technology in many industry sectors which have heightened the need for reliable energy storage solutions. Rechargeable lithium-ion batteries are the dominant power source for consumer electronics and electric cars because of their energy density and efficiency. The main drawbacks of Li-ion cells are the cost of their production and safety exploitation problem. This obstacles might be overcome by improving the properties of well-known cathode materials or finding new ones [1].

LiMn\textsubscript{2}O\textsubscript{4} is an alternative cathode material to the layered oxides which are the most common in commercial systems. Notwithstanding its specific capacity, high operating voltage, low cost and environmentally friendliness, LiMn\textsubscript{2}O\textsubscript{4} is limited in a large scale applications due to its structural instability [2]. At around room temperature, it is observed a reversible adverse phase transition which is related to Jahn-Teller distortion of high-spin Mn\textsuperscript{3+} ions. Moreover, LiMn\textsubscript{2}O\textsubscript{4} has limited stability towards organic solvents in liquid electrolytes, which results in its partial dissolution and its decomposition in the Li-ion cell. These phenomena lead to decrease in the capacity during the charge/discharge cycles [3].

In the present work partial and synergetic substitution of the cationic and the anionic sublattice were investigated as one of the possible strategies to deal with the aforementioned problems. The structural stability of the cathode materials based on the lithium-manganese spinel doped with potassium, nickel and sulphur was analyzed. The structural properties and the stability of the materials vs. liquid electrolytes were examined using the X-ray diffraction (XRD) and thermal analysis (TGA/DTG/SDTA/DSC). The cathode materials morphology was studied by the transmission electron microscopy (TEM-EDS). Structural changes of these materials before and after cell tests were investigated by the scanning electron microscopy (SEM) as well as the X-ray photoelectron spectroscopy (XPS). To analyze electrochemical behavior of the obtained materials the galvanostatic charge/discharge tests (GCDT) as well as cyclic voltammetry (CV) were carried out.

The research shows the influence of doping various ions into the different sublattice on the structural and electrochemical stability of the obtained nanomaterials.

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Hierarchically porous carbogels derived from starch as new high performance anode materials for lithium-ion batteries

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INTRODUCTION
The anode materials in lithium-ion cells should meet the following requirements:
low first cycle irreversible loss, excellent porosity and conductivity, minimum structural changes upon charge and discharge, high specific capacity (mAh/g) and low cost. In according to this features our investigation was focused on on bio-derived carbon materials for the sake of high specific capacity, controlled microstructure and morphology. The promising precursor is starch because it is renewable raw material, characterized by low production cost. In this work we present carbon anode materials derived from diverse types of starch: maize MS, potato PS and rice RS. Main goal of this research was: how the origin of starch influence on physicochemical and electrochemical properties of new carbogel materials [1-2].

EXPERIMENTAL
At the first step, raw materials were dispersed in water (10% w/v), placed in a water bath, stirred and heated up to the gelatinization temperature. The starch suspension was removed from water bath, then water was exchanged into ethanol in during few days process. The last step was pyrolysis at different temperatures (700°C and 900°C) to obtain carbogel active anode materials (CBG). The effect of the carbon sources on the structure, morphology and electrochemical properties of obtained anode materials were investigated. To investigate the electrochemical performance of the carbon electrodes Li/Li+(CBG) cells were used. The galvanostatic charge-discharge tests (GCDT) and cyclic voltammetry (CV).

CONCLUSION
Proposed technology may find an application in obtaining anode materials for lithium-ion batteries. The synthesized materials have a hierarchically porous carbon microstructure with a large surface area and good electronic conductivity.

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CCL/LiFePO₄ - high performance positive electrode materials for electrochemical energy-storage devices

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INTRODUCTION

The improvement of Li-ion batteries performance depends on the development of new and more efficient electrode materials as well as the development of improved manufacturing processes of nanomaterials of already commercially used systems. The use of nanomaterials as electrode materials in Li-ion batteries results in achieving the operating parameters close to the theoretical values and increasing cells power.

Lithium iron phosphate (LiFePO₄, LFP) is regarded as one of the most promising cathode material for to the large scale energy storage systems (ESS) as well as hybrid and electric vehicles (xEV) thanks to its low price, non-toxicity, high thermal and chemical stability and good theoretical capacity (170 mAh/g). The key drawback for the commercial application is its low electrical conductivity [1].

EXPERIMENTAL AND CONCLUSION

The idea of cathode nanocomposite based on formation of nanometric conductive carbon layers (CCL) directly on the active material particles [2-4]. The developed process uses the aqueous deposition of polymer precursor and assures possibility to control the morphology and electrical properties of carbon layers CCL.

The CCL nanocoating significantly enhanced capacity retention and overall electrochemical and thermal cells performance.

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Iron-promoted Nickel-containing Hydrotalcite-derived Catalysts For CO$_2$ Methanation

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INTRODUCTION

Rising levels of CO$_2$ in the atmosphere increased concerns and social awareness about the climate change caused by the emission of GHG originating from combustion of fossil fuels for power generation and other industrial activities. Lowering the emissions of carbon dioxide from anthropogenic sources into the atmosphere includes the transition to carbon free sources of electricity, such as renewables or utilizing biomass as a feedstock for valuable chemicals, as well as CO$_2$ capture from stationary sources and direct capture of CO$_2$ from the atmosphere. The transition to renewable energy sources, one of the proposed solutions, creates an additional important problem, which is the energy availability on demand. This requires the storage of excess renewable energy e.g. in the form of chemical compounds. Methanation of carbon dioxide offers the possibility of storing excess energy in the form of methane assuming hydrogen will be provided via water electrolysis using excess energy [1].

EXPERIMENTAL, RESULTS AND DISCUSSION, CONCLUSIONS

Nickel-containing iron promoted catalysts were obtained using co-precipitation method at constant pH (9.5-10) at 65°C. The solution was aged for 1h and dried overnight at 80°C. The obtained materials were calcined at 500°C for 5h in air. The catalytic tests were performed in a fixed bed reactor using a mixture of H$_2$/CO$_2$/Ar = 12/3/5, with GHSV=12 000 h$^{-1}$. The products of the reaction were analyzed using a micro-chromatograph (Varian GC4900). Prior to the reaction the catalysts were reduced in-situ at 900°C (10%H$_2$/Ar).

The increased activity of the sample containing low amount of Fe (1 wt.%) may be explained by both increased reducibility of NiO and enhanced CO$_2$ adsorption capacity. However, the incorporation of higher amounts of iron (2 and 4 wt.%) resulted in activity decrease. As reported in literature CO$_2$ methanation is favored on catalysts with smaller metallic nickel particle size [2], thus bigger Ni$_0$ crystallites for samples containing 2 and 4 wt.% of Fe might be the reason of lower activity. The addition of low amounts of Fe effectively enhanced the catalytic activity in CO$_2$ methanation. Which may be explained by both increased reducibility and enhanced CO$_2$ adsorption capacity.

FIGURES AND TABLES

<table>
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<th>Ni15</th>
<th>Ni15Fe1</th>
<th>Ni15Fe2</th>
<th>Ni15Fe4</th>
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<td>72</td>
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Electrochemistry for Nanomaterials
and
Nanomaterials for Electrochemistry Session
The electrocatalytic properties of the silver nanowire array electrodes in aqueous solutions of chloroform

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The electroreduction of chloroform, a well-known toxic water pollutant [1], generally occurs at very negative potentials at non-catalytic electrode surfaces (e.g., glassy carbon) in aprotic media [2]. At electrocatalytic materials, like Ag, the potential threshold of chloroform is shifted toward less negative values. In our previous studies we have proven, that the electrocatalytic reduction of chloroform occurs at less negative potentials at the Ag nanowire array electrode in the NaOH aqueous electrolyte, as compared with the Ag bulk electrode [3]. In this work, the electrocatalytic properties of nanostructured Ag and bulk Ag electrodes were investigated by voltammetric techniques in other supporting electrolytes, such as: KClO₄, NaClO₄, Na₂HPO₄, and NaH₂PO₄ aqueous solutions.

The electrochemical characterization of the Ag electrodes was performed using the Gamry Instrument Reference 3000 potentiostat in a conventional three-electrode cell. For Cyclic Voltammetry (CV) measurements the Ag bulk electrode or the Ag nanowire array electrode was used as a working electrode. All measured values of the potential were referred to the Ag/AgCl electrode. The electrochemical experiments were carried out at room temperature in a 0.05 M aqueous solution. The CV curves were recorded in the potential range between −0.4 V and −1.4 V vs. Ag/AgCl at the scan rate of 20-200 mV s⁻¹.

A significant shift of the chloroform reduction potential threshold was observed for all studied electrolytes when nanowire and bulk electrodes were compared, however the most significant shift was observed for KClO₄ (Fig. 1). For all studied electrolytes, a linear correlation of the square root of the scan rate vs. the current density was observed, what suggests that the chloroform reduction reaction is controlled by diffusion.

![Fig. 1. Cyclic voltammetry (CV) measurements obtained in 0.05 M KClO₄ during electrocatalytic reduction of chloroform at silver electrodes: nanowire array (left) and bulk (right). Measurements were performed at a constant chloroform concentration of 8.26 mM and selected scan rates.](image)

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REFERENCES
Anodization of copper foil in sodium hydroxide solution

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INTRODUCTION
Apart from aluminum [1], such materials as titanium [2], zirconium [3], tin [4], zinc [5], copper [6], nickel [7], and stainless steel [8] are anodized. The structural parameters and chemical composition of formed oxides/hydroxides are influenced by anodization conditions [9], thus their change results in the different morphology, and chemical composition of obtained materials. The possibility of control both structure and composition at the synthesis stage is very interesting and desirable, especially in the context of future applications. Anodic oxidation of copper foil is usually conducted in an aqueous alkali solution which leads to the formation of Cu₂O or Cu(OH)₂ structures. Further thermal annealing of Cu(OH)₂ can lead to the formation of more desirable CuO [10], without any morphological changes. CuO as a p-type semiconductor with relatively narrow band gap (i.e., 1.2 eV) can be applied as an anode in lithium-ion batteries, catalytic material, high-temperature semiconductor or as an optical switch [11]. Therefore, one-step synthesis of CuO with different morphologies by a simple anodization method seems to be very desirable.

EXPERIMENTAL, RESULTS AND DISCUSSION
Anodization of copper foil was conducted in a conventional three-electrode cell using a Reference 3000 potentiostat (Gamry Instruments). As electrodes, a Cu foil (working electrode), a platinum grid (counter electrode), and a mercury–mercury oxide electrode (Hg/HgO, 3 M KOH) (reference electrode) were used. All anodization were performed in an aqueous NaOH solution in the concentration range of 0.2 – 1 M at two different temperatures of 20 and 30 °C, at different current densities ranging from 0.1 to 5.0 mA cm⁻², and also, at different anodization durations, from 5 min to 1 h. The morphology of obtained products was examined by using field-emission scanning electron microscopy (FE-SEM), while the chemical composition and crystallinity of the these materials were studied with EDS, XPS, and XRD techniques. The conducted research allowed to state that Cu₂O, CuO, and Cu(OH)₂ nanostructures can be obtained by simply changing the conditions during the anodization of copper in the alkali solution. The morphology, structure, and chemical composition of obtained nanostructures are influenced by anodization conditions, especially temperature, current density, and electrolyte concentration.

REFERENCES
Formation of anodic oxides on the surface of Fe-Al intermetallic alloys

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INTRODUCTION
Self-organized anodizing allows to form nanoporous oxides on the surface of valve metals and their alloys. Morphology of the oxides is usually controlled by the operating conditions like type, concentration and temperature of the electrolyte, anodizing voltage and duration of the process [1,2].

EXPERIMENTAL
FeAl intermetallic alloy was cut into samples (6 mm x 16 mm x 0.8 mm) from a casted FeAl ingot, degreased and electrochemically polished. Anodization was carried out in tree variants A) 20% H₂SO₄ in the voltage range 10 V – 25, 0°C, B) 20% H₃PO₄ in the voltage range 10 V – 25, 0°C C) 20% C₂H₂O₄ in the voltage range 10 V – 25, 0°C. After the oxide removal, the re-anodization was conducted at the same set of experimental conditions.

RESULTS AND DISCUSSION
Figure1 shows top-view images of nanoporous oxides formed by FeAl anodizing in three different electrolytes. It is apparent, that the oxides are still poorly-ordered, like in the case of Ni₃Al anodizing in aqueous solution of citric acid [3]. However it is noticeable that the pore diameter and interpore distance increase with anodizing voltage.

CONCLUSIONS
It is possible to create on the surface of the FeAl alloy anodic nanoporous oxides which morphology differs from one another depending on the use of various type of electrolyte.

Fig.1 Anode oxide was formed on the surface of the FeAl alloy in the anodising process in the electrolyte: A) 20% H₂SO₄, B) 20% H₃PO₄, C) 20% C₂H₂O₄.

REFERENCES
The Effect Of Annealing Conditions On The Photoelectrochemical Properties Of Anodic Tin Oxide Layers

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Nanostructured materials based on tin oxides have recently become very promising candidates for photoanodes for photoelectrochemical (PEC) water splitting. However, their relatively wide band gap is the most important drawback that should be overcome to achieve satisfactory efficiencies of the photoelectrochemical process under the visible light.

It should be mentioned that like in the case of other anodic semiconducting oxides (e.g., titanium oxide or tungsten oxide), a suitable thermal treatment of as synthesized porous layers is necessary to obtain effectively working photoanode. However, the composition of anodic tin oxide is a very interesting issue. For instance, it was proved, that conditions applied during annealing are crucial factor affecting the composition of anodic film [1]. Moreover, at the temperature higher than 400 °C, nanoporous morphology of such kind of layers is completely damaged and the material is converted in to crystalline SnO\textsubscript{2}. On the other hand, controlled annealing under optimal conditions can result in the formation of porous tin oxide layer with a significant content Sn\textsuperscript{2+} ions being responsible for the much lower band-gap of as-synthesized product [2–3].

Crack-free anodic tin oxide layers were obtained on the surface of Sn foil by anodic oxidation in a sodium hydroxide solution at two different potentials: 2 V and 4 V. Furthermore, as-received samples were annealed in various sets of conditions, including temperature, duration of the process, and composition of the atmosphere. The morphology and composition of synthesized nanostructured photoanodes were investigated by various techniques (e.g., FE-SEM, Raman spectroscopy) and correlated with the conditions applied during fabrication and annealing process. In every case, the band gap values were estimated from the photoelectrochemical measurements.

Acknowledgements

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REFERENCES

Photoelectrochemical Properties Of Nanoporous Tin Oxide Layers With Complex Internal Morphology Obtained By Anodic Oxidation of Tin

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Due to many advantages like stability in aqueous environment, resistance to corrosion and photocorrosion, as well as nontoxicity and environmental friendliness, tin oxide materials are commonly used as photoanodes for photoelectrochemical water splitting (PEC) [1–2], which is an effective strategy for production of hydrogen from water on a large scale. Among various methods used for the synthesis of these materials, anodic oxidation of tin seems to be very interesting strategy. Recently, we proved that it is possible to obtain crack-free porous anodic tin oxide layers by simple anodic oxidation of Sn in alkaline electrolyte at low applied voltages [3]. Moreover, the developed method allowed for the first time to obtain nanoporous structures with various pore diameters. It was already reported that anodic oxide layers with a complex internal morphology, e.g., TiO₂ nanotubes with periodically modulated channel diameters can offer better photoelectrochemical performance due to unique optical properties [4].

Therefore, here we present some recent results on anodic formation of crack–free nanoporous tin oxide layers with a complex internal morphology by simple one-step anodic oxidation of Sn foil. The alkaline electrolytes were used, and various anodizing conditions such as potential and electrolyte concentration were applied. This approach was based on differences between average pore diameters within the anodic tin oxide grown at the potential of 2 V and 4 V. This phenomenon allows obtaining SnOₓ layers with a precisely designed internal morphology [2]. The morphology of as synthesized nanostructured photoanodes were verified by FE-SEM. Correlations between conditions applied during the fabrication process and thicknesses of the resulting product were established. Finally, photoelectrochemical characterization of samples was performed using a photoelectric spectrometer.

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Electrochemical behavior of InSb thin films with different crystallographic structure in alkaline solution

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INTRODUCTION

Indium antimonide is a semiconductor widely used as a material for many applications including thermoelectric generators, infrared detectors, sensors and others. It should be noted that among III-V semiconducting materials, InSb has one of the most reactive surface. The cleaning the InSb surface from oxides is also reported in the literature [1]. Oxidation products on the surface can be formed during wet chemical processes and, consequently, their presence may be problematic from the point of view of further applications of InSb-based materials. Therefore, it is essential to know, how InSb behaves in various wet conditions. It creates an opportunity to determine in which case the material is more stable and from which factors should be protected. In the literature there are only a few studies attempting to explain reactivity of InSb [2,3].

EXPERIMENTAL, RESULTS AND DISCUSSION, CONCLUSIONS

In the present research, we studied thin InSb films electrodeposited on a graphite foil. The electrochemical synthesis was carried out in a citrate bath containing 0.06 M In^{3+} and 0.045 M Sb^{3+}. The pulse electrodepositions were conducted in a conventional three-electrode cell with a platinum counter electrode and SCE as a reference electrode. The electrodeposition was performed at room temperature using E_{on} = -2.3 V and E_{off} = -0.5 V vs. SCE. The duration of pulse ‘on’ was in the range from 1 to 1000 ms, and the ratio t_{on} : t_{off} was constant (1:5). The synthesis of all thin films lasted 15 min. The obtained InSb films were tested in a 0.5 M NaOH solution using electrochemical technics. Among the InSb films, those with the largest crystallite size (synthesized using t_{on} = 1 ms and 10 ms) are the most susceptible to corrosion in 0.5 M NaOH, what has been confirmed by the highest corrosion rate of 1.45 and 1.29 mm per year, respectively. The InSb thin films with a nanocrystalline/amorphous structure (t_{on} = 100 ms and 1 s) are more resistant to the corrosion than the crystalline and metallic films.

Figure 1. SEM microphotograph of InSb thin films obtained by pulse electrodeposition on graphite (A) (t_{on} = 1 ms, E_{on} = -2.3 V vs. SCE, t_{off} = 5 ms, E_{off} = -0.5 V vs. SCE), SEM image of the InSb film after 2 h OCP measurements (B) in 0.5 M NaOH. CV curves recorded after 2 h OCP measurements for the mentioned InSb sample, scan speed 5 mV/s (C).

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REFERENCES

**INTRODUCTION**

In recent years, tin oxide has attracted much attention due to its wide range of applications including solar cells, photocatalysts, gas sensors or Li-ion batteries [1, 2]. Among various methods of fabrication nanostructured oxide layers on metallic substrate, anodic oxidation of metals seems to be particularly promising, effective and low-cost method. However, as obtained nanoporous anodic layers (SnO$_x$) are stacked and filled with discontinuities as a result of intensive oxygen evolution during the process. Herein, we present some results on the effect of anodizing conditions, including applied potential and electrolyte concentration on the growth, morphology and composition of nanoporous tin oxide layers.

The morphology and composition of samples were confirmed by FE-SEM, XRD and XPS. The band gap of synthesized materials was estimated based on photoelectrochemical measurements (Figure 1) and UV-Vis reflectance spectra. It was confirmed that the samples anodized at higher potentials (4 V) exhibit the greater Sn$^{2+}$ ion contents and, in consequence, a red-shifted absorption edge as well as the lower optical band gap in comparison to the samples synthesized at 2 V [1, 2].

![Figure 1. Photocurrent (A) and IPCE (B) as a function of the incident wavelength together with (IPCE × hν)$^2$ vs. (hν) plot (C) for the samples anodized at different potentials.](image)

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**REFERENCES**

The electrochemical immunosensor based on the 4,4-thiobisbenzenethiol and gold nanoparticles for the detection of the collagen type I

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INTRODUCTION

Electrochemical immunosensors play a pivotal role in the specific detection between the antibodies and complementary to them antigens. These kinds of sensors are highly effective to recognize the target analyte, because of their significant sensitivity and selectivity. [1] However, the major challenge is related to the successful immobilization of antibodies on the surface of the applied transducer. [2] For this purpose, it is essential to modify the surface of the conductive working electrode in order to enhance the connection with the antibody receptor. [3] In presented study, we constructed the immunosensor based on the self-assembled monolayer (SAM) of the 4,4-thiobisbenzenethiol and gold nanoparticles for the verification of the collagen type I concentration.

EXPERIMENTAL, RESULTS AND DISCUSSION, CONCLUSIONS

The preparation method for the modification of the gold surface working electrode (Au) included four different stages. Firstly, 1 mM solution of 4,4-thiobisbenzenethiol (TBBT) was applied for 0.5h to obtain covalent bonding with the gold surface. The next step consisted of deposition of the nanocolloidal gold (AuNPs, 10 nm diameter) for 2h. The electrostatic interaction of the Collagen I monoclonal antibody (Ab COLI) and the sensor was acquired by implementation of 10 ug/ml solution of the Collagen type I antibody. Finally, the 1% solution of the albumin bovine serum (BSA) was used for the blocking of any unspecific binding. The sensitivity of the sensor was examined by the Electrochemical Impedance Spectroscopy (EIS) and the Cyclic Voltammetry (CV) in the presence of the [Fe (CN)₆]³⁻/⁴⁻ as an electroactive marker. The measurements were conducted for the 5 different concentrations: 1,2,3,4 and 5 pg/ml of the analyte. According to the obtained results, increasing values of the electron transfer resistance and the potential between the cathodic and anodic current through the higher concentrations of the analyte were observed. Therefore, we can conclude, that the self-assembled monolayer (SAM) of the 4,4-thiobisbenzenethiol and gold nanoparticles has a potential application for the effectively and precisely detection of the Collagen type I.

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The effect of anodizing conditions on the morphology and properties of nanostructured tin oxide layers

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Recently, SnO₂–based materials are extensively investigated due to their various promising properties and many possible applications including photovoltaics, solid-state gas sensors, catalysts, batteries and many others.

Nanostructured tin oxide layers can be easily obtained via simple anodic oxidation (anodization) of tin in sodium hydroxide electrolyte. In a typical anodic tin oxide film, pores are randomly distributed and the layers are stacked and full of discontinuities. The formation of such kind of cracks, being a result of relatively fast oxide growth accompanied by vigorous oxygen gas evolution at the anode, can significantly affect the properties of oxide layers and dramatically decrease their mechanical stability and integrity [1]. Several strategies have been developed that allow obtaining porous anodic layers of tin oxide without internal cracks. For example, the amount of internal cracks in the oxide film can be significantly reduced by using strongly alkaline electrolyte [3] and by reducing the anodizing potential [2]. Moreover, the temperature of the process and purity of substrate are other important parameters affecting the morphology of anodic tin oxide layers and their properties.

In this work we present a detailed investigation of the effect of anodizing conditions, especially the temperature of electrolyte, applied potential and purity of the substrate, on the morphology and structure of anodic oxide layers. A Sn foil with two different compositions was used as a starting material for anodizing. Tin samples were electrochemically oxidized in a typical 2-electrode system in a 1 M NaOH solution. The morphology of synthesized nanostructured SnOₓ was investigated by FE-SEM. Our preliminary studies showed that the temperature of the process significantly affects the porosity, thickness of the obtained oxide layers, as well as the amount of internal cracks within the anodic film. Finally, the photoelectrochemical performance of as prepared electrodes was determined using photoelectric spectrometer in a typical 3-electrode system.

REFERENCES
Electrocatalytic reduction of hydrogen peroxide at glassy carbon electrodes decorated with silver particles

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Over the past decade, a significant interest in the development of non-enzymatic sensors for the detection and determination of hydrogen peroxide (H₂O₂) increases due to its crucial role in many fields including food and agricultural products, cosmetics and pharmaceutical components, chemical and biological chemistry, clinical control, chemical and biochemical industry, and fuel cells[1]. For hydrogen peroxide sensing many different materials have been used including metals, metal oxides, hydroxides, and sulfides, composite materials, enzymes-, organic dyes- and protein-modified electrodes. Unfortunately, most of them cannot provide a long-term performance due to a low chemical and mechanical stability and low selectivity. To overcome these problems metal electrodes are frequently used. The most important advantage of using metal electrodes as sensors is that those electrodes can be used for cathodic determination of H₂O₂ without interference from other electroactive compound that could be present in the sample solution.

Among different metal cathodes that have been used as a sensing material for H₂O₂ detection and determination, silver structures seem to be the most promising due to a low absolute value of reduction potential, wide detection concentration range, high sensitivity and stability. The most simple and low-cost electrodes for H₂O₂ sensing seem to be glassy carbon electrodes decorated with silver particles. On the one hand, it is widely recognized that glassy carbon does not show electrocatalytic activity toward hydrogen peroxide. On the other hand, silver structures are great and powerful materials for H₂O₂ reduction.

In this work a comparative study of silver particle electrodeposition in a water-glycerine solution containing silver ions and sodium dodecyl sulfate (SDS) is presented. The morphology of silver particles (Ag-Ps) was characterized using scanning electron microscopy (SEM). Glassy carbon (GC) electrodes were decorated with synthesized silver particles and then protected by the Nafion® layer. The Ag-Ps@GC electrodes were used as a working electrode for detection and determination of hydrogen peroxide by chronoamperometry (ChA). Prepared electrodes showed a good electrocatalytic activity towards H₂O₂ reduction when compared to a pure glassy carbon electrode. Moreover, the Ag-Ps@GC electrode exhibited electrocatalytic response toward the reduction of H₂O₂ over a very wide range of H₂O₂ concentrations.

REFERENCES
One-step electrochemical synthesis of copper oxide for glucose sensing

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INTRODUCTION

Anodic oxidation of metal foils is a common method for the preparation of metallic oxides and hydroxides. The structural parameters and chemical composition of formed oxides/hydroxides are influenced by anodization conditions [1], thus their change results in the different morphology, and chemical composition of obtained materials. The possibility of control both structure and composition at the synthesis stage is very interesting and desirable, especially in the context of future applications. Anodic oxidation of copper foil is usually conducted in an aqueous alkali solution which leads to the formation of Cu$_2$O or Cu(OH)$_2$ structures. Further thermal annealing of Cu(OH)$_2$ can lead to the formation of more desirable CuO [2], without any morphological changes. CuO as a p-type semiconductor with relatively narrow band gap (i.e., 1.2 eV) can be applied as an anode in lithium-ion batteries, catalytic material, high-temperature semiconductor or as an optical switch [3]. Therefore, one-step synthesis of CuO with different morphologies by a simple anodization method seems to be very desirable.

The aim of this studies was a one-step synthesis of anodic copper(II) oxide and investigation of its electrocatalytic activity towards electrooxidation of glucose. The copper oxidation was performed in an aqueous NaOH solution in the concentration range of 0.25 – 1 M at 30 °C, and at a constant current density (1 mA cm$^{-2}$). The anodization duration was 40 min. The morphology of obtained product was examined by using field-emission scanning electron microscopy (FE-SEM), while the chemical composition and crystallinity of the obtained materials were confirmed with EDS, XPS, and XRD techniques. The as-obtained CuO electrodes were tested as a working electrode for detection and determination of glucose by cyclic voltammetry (CV), linear sweep voltammetry (LSV), and chronoamperometry (ChA). The preliminary results indicate that obtained electrodes can be applied as a reliable glucose sensor.

REFERENCES

Dark nanoporous zinc oxide layers obtained by anodization at strongly alkaline solutions

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Semiconducting metal oxides are especially interesting from the point of view of their photocatalytic and photoelectrochemical applications. One of the most promising examples of this kind of materials is zinc oxide. Due to the wide band gap (3.37 eV) this oxide absorbs mainly UV light, what makes the efficiency of visible light conversion quite low. Normally, ZnO is white in color, but it is possible to obtain black zinc oxides layers by simple anodic oxidation. Up to now, dark ZnO was only investigated in terms of zinc corrosion and there are only few papers about using this material as an antireflective coating [1–2].

Anodic oxidation (anodization) give a huge possibilities of the design of anodic film morphology by tuning the process parameters like applied potential, electrolyte concentration and duration of the electrolysis. What is more, this method is extremely simple and easy to scale-up. Additionally, it can also be eco-friendly, when non-toxic electrolyte is used what is very important in field of green chemistry.

Anodic oxidation of zinc foil was carried out in a 1 M sodium hydroxide electrolyte at the potential of 2 V and 4 V for 30 min. After the process, some samples were annealed in air at 200°C for 2 h with a heating rate of 2°C/min. The morphology of obtained zinc oxide was investigated by Scanning Electron Microscopy. The phase composition and crystallinity of as-obtained product, as well as the thermally treated layers were examined by XRD measurements. XPS spectra were recorded to confirm the product composition. Band gap values were estimated from UV-Vis reflectance spectra.

It was found that nanoporous oxide layers are obtained directly during anodization and there are no changes in the film morphology after the thermal treatment. XRD and XPS measurements confirmed that the main product of the synthesis is crystalline ZnO. Annealing only improves the crystallinity of oxide. What is very interesting, it was confirmed that the band gap value of dark oxide layers is dependent on the conditions applied during the synthesis.

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REFERENCES
Synthesis of TiO$_2$@Cu$_x$O (x = 1, 2) and TiO$_2$@PEDOT composites for photoelectrochemical applications

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INTRODUCTION

Nanoporous titanium dioxide is a promising material for photoelectrochemical applications, due to its beneficial properties such as low toxicity, photostability and high photocatalytic activity under UV illumination. Unfortunately, its usage is limited because of the wide band gap, which allows only small amount of radiation other than UV to be absorbed. Therefore, various modifications are introduced to overcome these obstacles [1-3]. All of them are based on the modification of electronic band structure of TiO$_2$ and include doping with metal or non-metal ions such as C, S, and N, sensitization by organic molecules, formation of heterojunctions either with other semiconductors with lower band-gaps, such as metal oxides, or deposition of conducting polymers. This research describes the effect of two types of modifications – creating TiO$_2$/Cu$_x$O (x = 1, 2) heterojunctions and coating the oxide with poly(3,4-ethylenedioxythiophene) (PEDOT) – on the photoactivity of tested material.

EXPERIMENTAL

Nanoporous TiO$_2$ was synthesised in a two-step anodization process followed by annealing and electrochemical reduction. Chosen modifications were then introduced to the oxide: Cu$_x$O was obtained by sputtering of metallic copper and its electrochemical oxidation in NaOH solution, PEDOT by electropolymerization from an aqueous solution containing the monomer (EDOT). Morphology of obtained materials was analysed by scanning electron microscopy (SEM), their chemical composition by energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD), and their photoelectrochemical properties by measuring photocurrents under sequential irradiation with light of various wavelengths. Experiments showed that both modifications improved photocurrent densities registered in the examined light range.

REFERENCES

Visible-light driven nanotubes formed from TiRE alloys: characterization and photoactivity

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Application of solar light to drive pollutants degradation over semiconductor surface is one of the green approaches proposed for air, water and wastewater treatment. Thus, a lot of attention is paid to different methodologies improve TiO2 properties in visible range of electromagnetic spectrum because it allows obtaining photocatalysts active under solar light.

In view of this, a series of TiO2/RE2O3 nanotubes (NTs) were prepared by the anodization of Ti90RE10 (RE= Ho, Er, Nd, Y, Ce, Tm) alloys and their properties were discussed in detail. The as-prepared NTs were characterized by scanning electron microscopy (SEM), diffuse reflectance spectroscopy (DRS), luminescence spectroscopy, and X-ray photoelectron spectroscopy (XPS). The photocatalytic activity and stability of all of obtained photocatalysts were evaluated by monitoring the degradation of phenol and toluene as water and air pollution models, respectively. The influence of the RE metals on the photoelectrochemical performance of modified TiO2 NTs was investigated as well.

The SEM micrograph analysis showed formation of uniform and vertically oriented NTs structures with an open tube top and smooth walls, characterized by high-surface-area geometries, several times bigger (approximately 2.2 times) than pristine TiO2 NTs. The results of XPS analysis proved that RE ions exist as surface compounds (RE3+ oxides). It was observed that modification with RE caused higher photoresponse (both photocatalytic and photoelectrochemical) in the visible-light region. The highest photoactivity were observed for the sample obtained from Ti90Ho10.

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Various morphologies of nanostructured zinc oxide obtained by anodization in sodium carbonate solutions

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Zinc oxide (ZnO) is an n-type semiconductor with a wide band gap and a large exciton binding energy. It has also higher electron mobility compared to titanium dioxide (TiO₂). In view of the above, ZnO can find many potential applications e.g. in photocatalysis, solar cells, light emitting diodes or gas sensors [1]. Furthermore, one-dimensional nanostructures like nanowires seem to be the most promising morphologies. They are offering enhanced electron transport efficiency, and what is important, an extremely high surface to volume ratio [2]. Among many electrolytes that have been proposed for the anodic formation of ZnO nanowires the most interesting are solutions of bicarbonates [1]. Here we present, that using slightly more basic carbonate solution it is possible to obtain nanowires of different morphologies.

Herein we present the most recent research regarding electrochemical formation of ZnO nanostructures via anodic oxidation in sodium carbonate. Anodization was carried out for the first time using sodium carbonate. The effect of anodizing conditions was investigated in details. Special attention was paid to the electrolyte concentration, applied potential, duration of the process and post-treatment procedures (annealing). It was noticed, that these factors have a big influence on the obtained morphology, as well as, the oxide growth rate.

The morphology of obtained ZnO samples before and after thermal treatment were investigated by Scanning Electron Microscope (SEM). Current density vs. time curves during anodization were also recorded.

Figure 1. FE-SEM images of ZnO nanostructures obtain by anodization: A) in 0.1M Na₂CO₃ at 15 V for 10 min, B) in 1 M Na₂CO₃ at 20 V for 10 min.

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REFERENCES

Synthesis and electrocatalytic properties of AgPd nanowire array electrodes

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Silver is the most commonly used metal for electrocatalytic reduction of organic halides. On the one hand, palladium was reported as a promising material for the synthesis of electrocatalytic electrodes \cite{1}. On the other hand, An et al. \cite{2} reported the use of bimetallic AgPd nanoparticles for reduction of benzyl chloride in acetonitrile. They showed that such materials showed much better electrocatalytic properties than the Ag bulk electrode. In order to use nanoparticles in electrocatalysis, they have to be immobilized on some supporting material. This issue can be addressed by the use of the nanowire array, which is much more stable and requires no additional support. Anodic aluminum oxide (AAO) membranes are widely used as templates for synthesis of various nano-sized materials, including nanowire arrays. Additionally, the size of the pores of the AAO can be easily modified. The use of the AAO allows to simplify the synthesis of nanomaterials. Yue et al. \cite{3} reported synthesis of AgPd alloy nanowire arrays by electrochemical deposition in nanoporous anodic alumina templates, commercially available from Whatman®. In this work, the synthesis of bimetallic AgPd nanowire array electrodes with a well-known composition was optimized, and the possibility of utilizing such electrodes for reduction of chloroform in an aqueous solution was explored.

The AgPd nanowire array electrodes were prepared by template-assisted electrodeposition in the AAO. The AgPd nanowire arrays were electrodeposited from a freshly prepared solution of 15 mM Pd(NO\textsubscript{3})\textsubscript{2} + 1.0 mM AgNO\textsubscript{3} + 0.5 M NH\textsubscript{4}NO\textsubscript{3}. The pH value of solution was adjusted to 8.0 by addition of NH\textsubscript{3}·H\textsubscript{2}O. The electrodeposition was performed in a three-electrode cell at 5 different potential values: -0.4 V, -0.6 V, -0.8 V, -1.0 V and -1.2 V. The electrochemical characterization of AgPd nanowire array electrodes was performed using a Reference 3000 (Gamry Instrument) potentiostat in a conventional three-electrode cell. All measured potential values were referred to the Ag/AgCl electrode. The electrochemical experiments were carried out at room temperature in a 0.05 M KClO\textsubscript{4} and 8.26 mM chloroform aqueous solution.

From the current vs. time curves and cross-sectional SEM micrographs of AgPd nanowires, the passed charge and length of bimetallic nanowires were estimated, respectively. It was found that the length of nanowires linearly increased with increasing the potential of deposition, however, the passed charge increased exponentially. The Pd/Ag weight % and atom % increased for depositions at the potential in the range of -0.4 and -0.8 V, and for higher potentials remained almost constant. The XRD measurements showed peaks corresponding to Ag and Pd. The LSV measurements showed that the bimetallic AgPd nanowire array electrode exhibited the electrocatalytic properties toward the reduction of chloroform in water.

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Electrocatalytic properties of palladium-decorated cobalt coatings obtained by electrodeposition and galvanic displacement

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Hydrogen, which electrochemical production is getting less expensive among the years and more ecological, is one of the alternative carrier of energy. The best electrode materials using in this process contain platinum group elements which are expensive very often. Platinum can be replaced by cobalt and its alloys in the production of electrodes for hydrogen evolution process. Electrochemical deposition of Co-Pd coatings was studied by K. Mech and co-workers [1,2]. The ability of this alloy for the four-electron oxygen reduction reaction is better than the pure palladium and similar to pure platinum. The surface of the electrode can be easily modified by formation of alloy to decrease of the hydrogen or oxygen evolution reaction overpotential. Cementation based on the spontaneous reaction of metallic surface layer M with a more noble metal, Mnoble, when the metal surface is treated with a solution containing the other metal in ionic form [3,4]. This method allows to obtain bimetallic materials and to change its properties by the substitution of underlying metal M using a small amount of Mnoble metal.

The aim of this work was to optimize the electrodeposition process of cobalt coatings, their modification with palladium ions, and the measurement of electrocatalytic properties of the formed Co-Pd alloys. Thick and smooth cobalt coatings were prepared via galvanostatic electrodeposition from acidic bath. Phase composition of obtained cobalt coatings were analyzed by X-ray diffraction. Smooth and compact Pd layer were obtained by modification of prepared cobalt by the galvanic displacement method in PdCl₂. The impact of palladium presence in cathodic deposits on the hydrogen evolution process was determined by the comparison of electrocatalytic properties of Co coatings with Co/Pd ones.

REFERENCES
Preparation and characterization of anodic TiO$_2$ impregnated with transition metal ions

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INTRODUCTION

Titanium oxide (TiO$_2$) is one of the semiconductors which possesses a wide range of properties such as: good chemical stability, biocompatibility and non-toxicity [1], and for this reason, it offers a lot of possibilities for using in photocatalysis and medicine [2,3]. However, from the point of view of photoelectrochemical applications, the main disadvantage of TiO$_2$ is absorption of the light from the UV range, which significantly limits its use as e.g., catalysts [4]. To solve this problem and to increase the range of absorbed radiation, applying different modifications of this semiconductor such as electrochemical deposition and impregnation with the solution containing transition metal ions is very often used [5].

EXPERIMENTAL, RESULTS AND DISCUSSION, CONCLUSIONS

In this study, in order to obtain nanoporous titanium dioxide layers, a three-step anodization in an ethylene glycol based electrolyte containing 0.38% wt. NH$_4$F and 1.79% wt. H$_2$O at a constant potential of 40 V was used. The modification method was based on impregnation of anodic TiO$_2$ samples with solutions containing various concentrations of cobalt, copper and iron ions followed by their annealing at different temperatures. The morphology and chemical composition of synthesized materials were investigated by using a field emission scanning electron microscope (FE-SEM/EDS), and their structure was determined by X-ray diffraction (XRD). The photoelectrochemical properties were characterized by UV-Vis spectroscopy.

The data showed that the structure of anodic TiO$_2$ samples impregnated with cobalt, copper and iron ions was changed depending on the concentration of transition metal ion used. Anodic TiO$_2$ samples showed a maximum absorption at 350 nm which shift depending on the modification of used ion. The modified TiO$_2$ samples exhibited different photoelectrochemical properties from those observed for unmodified TiO$_2$ samples. In conclusion, the obtained material can be a promising nanomaterial with improved photocatalytic performance.

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The interaction between photoactive anodic titanium oxide layers and ferrocene-based redox active polymers

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INTRODUCTION

Interest in photocatalytic properties of TiO₂ is constantly growing, and recently, new ideas to increase the efficiency of photocatalytic reactions are searched intensively. Very promising approach is to combine the unique geometry of nanoporous TiO₂ with unique redox properties of polymers, especially ferrocene-based redox active colloid (PAF-RAC) (Fig.1) [1].

EXPERIMENTAL, RESULTS AND DISCUSSION, CONCLUSIONS

Benzyl(ferrocenylmethyl)dimethylammoniumhexafluorophoshate (BAF), ammonium ferrocenylmethyl redox active polymer (PAF), and its redox active colloid (PAF-RAC) were synthesized according to reported protocols [1]. Anodic TiO₂ layers were prepared by two-step anodization carried out at the constant voltage of 70 V and 20 °C. The electrolyte was based on an ethylene glycol solution containing NH₄F (0.38 wt.%.) and water (2.1 wt.%). Afterwards, ATO samples were subjected to annealing at 400 °C for 2 h (2 °C/min) in a tube furnace [2]. For modified anodes, solutions of 5 mM BAF, PAF, and PAF-RAC were prepared in acetonitrile and sonicated for 3 minutes. Then 5 µL of the solution was dropcast onto previously annealed ATO samples with an exposed area of 0.0707 cm² in a custom Teflon cell. All electrochemical and photoelectrochemical measurements were performed using a CHI920D workstation (CH Instruments, Inc.) in 0.1 M NaOH using a three-electrode setup with the ATO as a working electrode. The reference electrode was a Ag/AgCl (sat. KCl) with a NaClO₄ agar salt bridge. The counter electrode was a 1 mm diameter Pt wire. Photocurrents were generated under illumination from a 6258 Oriel 300 W Xe lamp.

Fig.1. SEM images of ferrocene RACs particles (A) deposited into the ATO surface (B).

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The key role of anodic titanium oxide morphology on its photoelectrochemical properties

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INTRODUCTION
It is widely recognized that the morphology of semiconductor affects its photoactivity. Studies have shown that when the top morphology changes, very often photochemical properties of TiO₂ changed as well. This aspect has great impact on its photoelectrochemical applications in dye sensitized solar cells (DSSCs), where the efficiency of the process depends on the top surface reflection [1]. The morphology of anodic titanium dioxide is also affected by: an electrolyte type and its composition (e.g., water content and the presence of fluoride anions), pH, previous usage of electrolyte, voltage, time of anodization, temperature, and hydrodynamic conditions [2].

EXPERIMENTAL, RESULTS AND DISCUSSION, CONCLUSIONS
In this study, the effect of TiO₂ morphology (oxide thickness and pore diameter) on photoelectrochemical properties was investigated. Nanoporous anodic titanium dioxide layers were synthesized at 20 °C by a three-step anodization carried out at the constant voltages of 30 - 100 V in electrolyte based on ethylene glycol containing NH₄F (0.38 wt.%) and water (1.79 wt.%). The duration of the process was adjusted to obtain a series of materials of varying (2 - 8 µm) and similar oxide thickness (2 µm) (Fig.1). Afterwards, ATO samples were subjected to annealing in air at 400 °C for 2 h (2°C/min). Samples were characterized by SEM, XRD, Mott-Schottky and EIS measurements. Photoelectrochemical tests were performed using a three-electrode cell with a quartz window, where nanoporous TiO₂ was used as a working electrode (WE), a platinum foil as a counter electrode (CE), and a Luggin capillary with a saturated calomel electrode (SCE) as the reference electrode. The generated photocurrents were measured using a photoelectric spectrometer equipped with the 150 W xenon arc lamp and combined with a potentiostat. The photoelectrochemical characterization was performed in 0.1 M KNO₃ at the potential range of 0 - 1 V and wavelengths ranging from 300 to 400 nm.

Fig.1. SEM cross-sectional view of anodic TiO₂ obtained by anodization at a potential of 30 V (A), 60 V (B), and 100 V (C).

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REFERENCES
Fabrication of diameter modulated anodic aluminum oxide by pulse anodization of aluminum in phosphoric acid

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Nanoporous anodic aluminum oxide (AAO) films formed by electrochemical oxidation of metallic substrates have been extensively investigated and used in numerous applications. The most popular application of nanoporous AAO is its use as a template for the synthesis of various functional nanostructures [1–3]. The advantages of the template synthesis, as compared with other methods for nanowire fabrication, are: low cost of processing, easy materials handling, and relatively simply equipment requirement. A great benefit of electrochemical deposition is also its simplicity, and ability to tailor size, chemical composition, and microstructure with desired properties. Apart of plain nanowires segmented or multilayered structures, heterostructures of different compositions along the cylindrical axis of the nanowire, were successfully fabricated in porous membranes by electrodeposition. The main problem in fabrication of diameter-modulated nanowires is the precise control over the shape and size of segments periodically repeated along the nanowire axis. Therefore, fabrication and only a few techniques allow to synthesize them successfully.

A new anodization approach to synthesize periodically modulated nanochannels along the pore axis have been applied. The approach is based on employing a series of potential waves that consists of two or more different pulses with designated periods and amplitudes, and provides unique tailoring capability of the internal pore structure of anodic alumina. The fabrication of the desired product by using relatively low voltages has already been mostly developed, but the growing demand for nanopore arrays with diameters of more than 150 nm is one of the reasons why high voltage pulse anodization of aluminum is still developed. This is because the diameter of produced nanopores and the distance between them is proportional to the used anodizing voltage. On the other hand, the higher anodizing voltage the more likely uncontrolled oxidation of the sample and burning phenomena can occur. The goal of this work was to fabricate nanoporous aluminum oxide by high voltage pulse anodization in phosphoric acid and to optimize the process conditions. Aluminum oxide was synthesized by a pulse anodization of aluminum in a 1 wt.% phosphoric acid solution. The pores of resulting AAOs exhibit modulated diameters along the pore axes. In particular, both the pore diameter and length of modulated segments increase with the amplitude and period of current oscillations, respectively. Moreover, the current peak profile determines the internal geometry of nanopores. The key parameters such as the diameter of nanopores, density of nanopores, and distance between nanopores were estimated from Scanning Electron Microscope (SEM) images. Additionally, the analysis of nanopores shape was performed through accurate observation of cross-sections of resulting alumina layers.

REFERENCES
Optimization of modification and thermal treatment conditions of anodic WO$_3$ with enhanced photoelectrochemical properties

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INTRODUCTION
Nanostructured tungsten oxide possesses very interesting chemical, physical and catalytic properties. WO$_3$ can find promising applications as sensors, in photoelectrochemical cells or in photocatalytic degradation of organic dyes. It is widely recognized, that photoelectrochemical properties of nanostructured metal oxides can be enhanced by doping with transition metal ions [1–4].

EXPERIMENTAL, RESULTS AND DISCUSSION, CONCLUSIONS
Anodic WO$_3$ photoanodes were prepared by electrochemical anodization of tungsten foil in 1 M (NH$_4$)$_2$SO$_4$ + 0.075 M NH$_4$F at 50 V. Furthermore, a wet impregnation of anodic oxide with transition metal (Fe and Cu) ions was performed. In order to obtain a photoactive phase, the samples were subjected to annealing. A complex characterization of received materials was performed by using SEM, EDS, and XRD measurements. Photoelectrochemical tests were carried out in a three-electrode system, where nanoporous WO$_3$ was used as a working electrode, a Pt foil as a counter electrode, and an Ag/AgCl electrode as a reference electrode. The generated photocurrents were measured using a photoelectric spectrometer equipped with the 150 W xenon arc lamp and combined with a potentiostat.

It has been shown that semiconducting properties such as band gap, valence band and conduction band edge values have been changed for Cu-WO$_3$ and Fe-WO$_3$ compared with nonmodified WO$_3$. In the next step, optimization of wet impregnation conditions of anodic WO$_3$ with enhanced photoelectrochemical properties is planned to be performed.

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General Session
Chemical synthesis of silver cubic nanoparticles and characterization of Ag/TiO$_2$ nanotubes hybrid materials for SERS applications

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A SERS (Surface Enhanced Raman Spectroscopy) substrates fabrication is now a fast developing branch of nanotechnology, because the SERS method is an attractive tool for sensing molecules in trace amounts within the field of chemical and biochemical analytics, but the design and optimization of efficient platforms is still challenging [1,2]. In this work SERS platforms were prepared using a silver cubic nanoparticles (CNPs) with diameters around 40-60 nm deposited onto titanium oxide nanotubes (TiO$_2$ NT) that enabled obtaining reproducible spectra of pyridine 0.05M [3]. Such substrates ensure formation of suitable gaps and cavities serving as surface plasmon resonators significantly increasing the intensity of the electromagnetic field (so-called highly active places - "hot spots" [1]). Ag CNPs were synthesized by Skrabalak [4] method and deposited on nanotubes. Scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), UV-vis spectroscopy and SERS spectroscopy were applied to characterize the as-prepared Ag-NPs/TiO$_2$ NTs samples.

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REFERENCES

Studies on the corrosion behavior of TiAlCr alloy coated with black glasses in cyclic oxidation conditions

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Due to a combination of interesting properties such as low density, high Elastic modulus and specific strength in elevated temperatures and satisfactory corrosion resistance up to 700°C, TiAl alloys seem to be very promising candidate for construction materials used in the automotive industry. However, in order to broaden the spectrum of applications, problems such as low hot deformability and plasticity at room temperature and unsatisfactory corrosion behavior over 700°C have to be solved [1,2]. Amongst the proposed solutions, there are surface modifications i.e. with an application of protective coatings [3]. One of the materials which may act as a diffusive barrier against aggressive gases (O₂, N₂, steam) in elevated temperatures, are so-called black glasses.

These ceramic materials of α-SiO₂ structure exhibit a set of prominent properties such as high mechanical strength, chemical and corrosion resistance even at elevated temperatures, due to an introduction of Si-C bonds into the glass network. The sol-gel method, perceived as the most popular one to form black glasses, allows for tailoring the resultant material’s properties within very broad range, depending on its dedicated application. That is why, outstanding thermomechanical stability, crucial during oxidation tests, can be even more improved by means of cationic substitution i.e. replacing Si⁴⁺ cations with Al³⁺ ones [4].

The main aim of this work was to investigate the corrosion behavior of the proposed SiAlOC coating/Ti-48Al-2Cr alloy system in the cyclic oxidation conditions.

The coating material was obtained by using the sol-gel method. Then, layers were deposited on polished or grinded substrate by means of the dip-coating technique and subsequently given under the thermal treatment resulting in the formation of SiAlOC coatings. Both as-received and coated samples were used during oxidation tests in cyclic oxidation conditions (100 cycles for 1h) in the laboratory air atmosphere in 800°C. After that, the number of structural (XRD, Raman) and microstructural (SEM,EDS) studies were performed to evaluate the impact of applied coatings. Despite the promising results from oxidation kinetics, the rest of executed studies revealed that black glasses coatings partially did not suppressed the diffusive processes.

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REFERENCES
Sonochemically Prepared Zeolite Catalysts in the Reduction of NO\textsubscript{x} by NH\textsubscript{3} in Lean Gas Conditions: Catalyst Characterization and Activity Study

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INTRODUCTION

The issue of removal of nitrogen oxides (NO\textsubscript{x}) is still a current topic in the research. The emission of NO\textsubscript{x} by stationary and mobile sources as diesel engines, although regulated by low should continuously be minimalised. The nitrogen oxides have a negative impact on the environment, thus they may cause acid rain, photochemical smog and contribute to the ozone hole. As the main solution and the most efficient one the application of ammonia-selective catalytic reduction process (NH\textsubscript{3}-SCR) to NO\textsubscript{x} elimination is used in the industry. Many zeolitic and other oxides systems have been used as catalysts in this reaction over the last years, and among them, most of the zeolitic materials have been prepared by the classical ion-exchange method. However, the searching for the alternatives is not done yet. Much research is still carrying out on the development of new (zeolitic) catalysts that will have highly desired parameters and the high activity in the removal of nitrogen oxides.

EXPERIMENTAL, RESULTS AND DISCUSSION, CONCLUSIONS

The aim of this study was to provide the new synthesis route of iron substituted sonochemically prepared zeolite’s catalysts. The zeolites engaged in this study include zeolite Y, USY and MFI. The catalytic activity was established for deNOx SCR process in lean conditions. The activity of catalysts was compared for those prepared with the standard method and with ultrasound irritation. The properties of catalysts materials has been determined by micro-Raman spectroscopy, X-ray diffraction (XRD), scanning electron microscope (SEM), and UV/Visible diffuse reflectance spectroscopy (UV/Vis DRS). As it was shown in the study both catalysts method leads to decreasing of the porosity and specific surface area of catalysts, however the differences has been found between the Fe-loading depending on used zeolite support. The iron substituted catalysts shown great activity in deNOx process with selectivity towards N\textsubscript{2} reached almost 100%.

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IR spectroscopy studies on functional catalysts based on ceria oxide

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INTRODUCTION
Catalytic combustion has been extensively investigated in recent years. The increasing awareness about the environmental and health concerns arising from the pollution caused by various industries and automobile exhausts has prompted the issuance of stringent regulations on the emission of several pollutants (e.g. NOx, SOx and greenhouse gases). Catalytic combustion of methane has drawn great attention as a well-known greenhouse gas and the most stable and abundant alkane.

It has been found that supported palladium catalysts are the most active for methane combustion, and were extensively studied focusing on the alumina and its modified supported ones [1]. However, the main problem in practice is the deactivation of the Pd-based catalysts. Therefore the efforts of the researchers are focused on the development of new types of catalysts and their optimization. Many studies have referred good properties of ceria as a heterogeneous catalyst support or active component with its redox properties. It was found that it provides improvement of active phase stabilization as well as high methane oxidation activity [2-3]. Moreover, previous in situ FTIR studies of the stable surface intermediate products of methane oxidation on Pd-based catalysts have not realised correct band assignment [4]. Finally, it is not elucidated the mechanism of methane oxidation, whether it proceeds via adsorption step by forming methoxy groups or without.

EXPERIMENTAL, RESULTS AND DISCUSSION, CONCLUSIONS
In presented study, metal oxide catalysts (Fe, Co, Pd) on cerium oxide as a support were tested for activity in the combustion reaction of methane. The evaluation of active centres was done by in situ FTIR method coupled with the application of various probe molecules. The obtained IR vibrations of the surface intermediates have been assigned to different products: formates and carbonates on different active centres. The presence of methoxy groups on the surface of the working catalyst during the experiments performed in situ with FTIR detection proved the Langmuir-Hinschelwood and partially Mars-van Krevelen mechanism for methane catalytic combustion.

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REFERENCES
Magnetic nanoparticles coated with metallic nanoparticles as potential catalysts in organic chemistry

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INTRODUCTION

Nanosized materials belong to the group of materials characterized by specific properties. Those result from their specific size and well-developed surface area. Therefore they can be applied in many areas including medicine, pharmacy and catalysis. Special attention is currently directed into magnetic nanoparticles. These are characterized by a tendency to form agglomerates therefore their synthesis requires application of some types of stabilizing agents or materials forming a layer on their surface that prevents agglomeration.

EXPERIMENTAL PART

Magnetic nanoparticles were prepared by means of Massart synthesis. This process involves co-precipitation of iron ions in an alkaline environment. Next step involves a formation of nanogold layer on the surface of nanoparticles. For this purpose tetrachloroauric acid (as a source of gold) and hydroxylamine hydrochloride (as a reducer) were used. In Fig. 1. scheme of the reaction is presented.

Fig. 1. Scheme of obtaining of magnetic nanoparticles coated with nanogold.

Prepared nanoparticles were subsequently used for the preparation of ethenzamide (component of many drugs). To check catalytic properties of prepared nanomaterials two reactions were conducted in parallel: with magnetic catalyst and without its use.

CONCLUSIONS

As a result of conducted reactions nanosized magnetic nanoparticles coated with nanogold were prepared. Synthesis of ethenzamide conducted with their use proceeded faster compared to this one without their application. Therefore it can be concluded that magnetic nanoparticles coated with metallic nanoparticles can be applied as innovative catalysts in organic chemistry.

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REFERENCES

Electrochemical characterization of novel metal/polycation bioelectrodes based on lactic acid bacteria

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Nowadays, renewable and sustainable energy sources are becoming increasingly important. One of the setups, which can produce green energy are bioelectrochemical systems (BESs). Generally, they consist of bioanode or biocathode which can be colonized by microorganisms [1]. What is more, electrode material and microorganism species have a significant influence on current efficiency. Commonly utilized electrodes are made of carbon (e.g., cloth, brushes and paper). However, they have high background currents [2]. Moreover, microorganisms used in BESs, e.g., from Escherichia, Geobacter, Shewanella genera, are usually virulent or acquired from wastewaters [3]. Therefore, there is a need to find new biomaterials which will be more suitable to use in BESs as well as more human-friendly organisms.

In here, we present novel bioelectrodes consist of copper foil covered by thin gold film and cationic derivatives of natural polymers and Lactobacillus rhamnosus biofilm. Samples morphology was characterized by using scanning electron microscopy (SEM), infrared spectroscopy (IR) and atomic force microscopy (AFM). In order to study electrochemical activity of setups, electrochemical measurements, like voltammetry or chronoamperometry, were performed. Preliminary studies revealed that bacteria formed well-developed lace-like network on investigated substrates. What is more, cyclic voltammetry (CV) studies confirmed that bioelectrodes exhibit electrochemical activity.

REFERENCES
Photodegradation of dye on anodic TiO$_2$

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INTRODUCTION
Titanium dioxide is widely used as a photocatalyst because of its properties such as high stability, non-toxicity, low cost of production, value and position of the band gap [1]. The highly ordered TiO$_2$ nanopore or nanotube arrays may be obtained by a multi-step anodization in an organic electrolyte containing fluoride ions [2]. The conditions of anodic oxidation, e.g., the applied potential, time of the process, temperature and others, can be easily controlled, which leads to obtain the defined titanium dioxide morphology. The size of pores and the thickness of oxide layer are very important parameters of nanoporous TiO$_2$, in particular when titania is used as the photocatalyst [1].

EXPERIMENTAL, RESULTS, AND CONCLUSIONS
Highly ordered TiO$_2$ nanopore arrays were formed by a three-step anodization of titanium foil in an ethylene glycol based electrolyte containing NH$_4$F (0.38 wt.%) and H$_2$O (1.79 wt.%) at 20 ºC at the applied constant potential (30–70 V). Then the samples were annealed at 400 ºC in order to obtain a photoactive anatase phase. Properties of used material were examined by a field emission scanning electron microscopy (FE-SEM) and an X-ray diffraction (XRD).

The photocatalytic properties of anodic titania were studied by performing of the photodegradation of the model dye (methyl red). The photoreactor equipped with a 128 W lamp with a maximum wavelength of 350 nm was used. The concentration of the dye was determined by UV-Vis spectrophotometry, and a rate constant of dye photodecomposition was calculated. The highest photocatalytic activity during photodegradation of methyl red was observed for TiO$_2$ obtained at 40 V (93% after 4.5 h)

REFERENCES
Synthesis of shape-controlled PtRhNi nanoparticles

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Platinum-based shape controlled nanoparticles are considered as one of the most promising catalysts in many reactions [1]. Due to their high-indexed facets and high ratio of corner and edge atoms to surface atoms, shape controlled nanoparticles exhibit better catalytic performance than spherical nanoparticles. However, the synthesis of nanoparticles with more complex shapes can be very challenging. There are many factors, which affect the growth process during the nanoparticle synthesis, such as temperature, heating rate, concentration of metal precursors, presence of capping agents and other. One of the most important factor in shape controlled synthesis of nanoparticles, is the selection of a suitable capping agent, which lowers the surface energy of specific nanoparticle facets and in consequences allows to synthesize shapes different than spherical. For example, PVP stabilizes the {100} facets of Ag and Pd, resulting in obtaining cubic shaped nanoparticles [2], while oleylamine stabilizes the {110} facets of Pt and Ni, forming nanoparticles with rhombic dodecahedral shape [3].

Figure 2. Schematic 3D model of a PtRhNi nanoparticle with three basic projections with the corresponding HAADF STEM images. Note that the models are not in scale.

In the present study the syntheses of phase-segregated PtRhNi rhombic dodecahedral nanoparticles (Fig. 1) were performed. The core of the nanoparticles consists mainly Ni, while the edges are formed by a PtRhNi alloy. The morphology of the obtained nanoparticles and their size distribution was imaged using transmission electron microscopy (TEM) in the HAADF STEM mode. Energy-dispersive X-ray spectroscopy (EDS) was used to examine the distribution of chemical elements in the sample. The crystallinity of the obtained nanoparticles was confirmed by X-ray diffraction (XRD). By probing samples of the intermediates during synthesis and performing TEM analysis it was possible to trace the reaction course. Additionally, Density Functional Theory (DFT) calculations were performed to determine the total energy of the PtRhNi surfaces. The obtained results allow resolving the route of growth of PtRhNi polyhedral nanoparticles and explain the formation of phase segregation.

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REFERENCES
Synthesis and Characterization of PEDOT-Based Surface-grafted Brushes

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INTRODUCTION

Polymer brushes are very promising structures, which can be used in many applications such as: controlled drug delivery systems, platforms for controlled cells growth or chemo and biosensors. Furthermore, the new class of conjugated polymer brushes are expected to be used in next generation polymer solar cells, organic light emitting diodes (OLEDs) or transistors. They have a great ability to transport charge carriers directionally along single polymer chain to the conductive substrate.

EXPERIMENTAL

The aim of the work was to obtain the ladder-like conjugated EDOT-based polymer brushes on ITO substrate. The synthesis of the new monomer was presented. Then the polymer brushes were synthesized by photoiniferter-mediated polymerization. Time and condition of polymerization were optimized. Next the substrates were subjected to the oxidative polymerization with FeCl₃ as an oxidizing agent. Polymerization was carried out under anaerobic conditions and finished in glove box. The obtained materials were characterized using atomic force microscopy (AFM), grazing angle FTIR spectroscopy and UV-Vis spectroscopy. Moreover, images of this material were done by confocal microscopy.

CONCLUSIONS

We synthesized a new PEDOT-based monomer, which serve as building blocks for synthesis polymer brushes. Oxidative polymerization of the neighbouring EDOT groups in the brushes enabled formation of conjugated polymer chains.

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Lactic acid bacteria based bioelectrodes – an influence of glucose content on their electrochemical performance

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INTRODUCTION
Bioelectrochemical systems (BESs) are setups that consists of electrochemically active microorganisms, such as bacteria or yeast [1]. The main idea of the performance of BES is based on the electron transfer phenomenon. In particular, electrons from the microbes respiratory chain are transferred to the electrode surface, and then to the external circuit. The source of the electrons may be either redox processes of the compounds from the electrolyte or metabolic processes within the microorganism. As a result, current generation occurs. Unfortunately, the current efficiency of such bioelectrochemical systems are not sufficient enough [2]. That is why, an extensive studies on the improvement of the current efficiency, and an influence of different parameters (e.g., electrode material, bacteria species, electrolyte content, temperature) on the performance of such systems are being conducted. That is why, the main aim of this studies was to improve the current efficiency of the novel bioelectrodes based on the metal/polycation/lactic acid bacteria (LAB) by changing the way of culturing and the composition of the electrolyte.

EXPERIMENTAL, RESULTS AND DISCUSSION
Bioelectrodes were based on the copper substrate covered with a thin gold layer. Firstly, copper electrodes were electrochemically and chemically polished in the phosphoric and sulfuric acids, respectively. Then, electrodes were sputter coated with a thin gold layer, which was then thickened by using chronopotentiometry method. A commercially available gold solution was used for thickening (Auruna®5000). Process was conducted in a three-electrode configuration with platinum mesh and wire as counter and reference electrodes, respectively. As prepared electrodes were covered with a nanometric layer of cationic dextran derivative that was proven to enable adhesion of LAB. Furthermore, two different seeding methods were used for culturing, namely gravitational and preferential. Culturing was conducted for 48 h, independently on the culturing method. For electrochemical tests, only preferential method of culturing was used. Cyclic voltammetry measurements were conducted in the electrolytes based on culture medium with 20 g/L glucose and electrolyte without glucose. CV experiments were conducted in the potential range -0.6 – 0.5 V vs. Ag/AgCl with the scanning rate of 10 mV/s. Voltammograms revealed that visible oxidation and reduction peaks are connected to the glucose oxidation with the use of lactic acid bacteria.

REFERENCES
Influence of magnetic field on 3D prints metallization

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The 3D printing is one of the newest methods of precise elements production. One of advantages of this technique is possibility of production elements with any geometry, very often impossible to obtain in traditional techniques, very good tolerance of dimensions, low costs and good scalability. Often in this technology plastics are used, but depending on the purpose, the prints can be improved by additional properties through applying metallic coatings.

As a result, there is a possibility to obtain elements with combination of properties of plastics and metal. To obtain such special properties the prints should be coated by metallic layers. This operation gives the plastic elements new functionalization like electric and thermal conductivity or magnetism. As a results of this, elements with mix of plastic and metallic properties are obtained. It allows to increase the number of application of these elements. Depending on the material, the plastics covered by metallic coatings can find application in many field of technology like medicine, automotive, metallurgy or energy industry.

In this work was presented process of metallization of 3D prints from light-hardened resins. The metallization is a few steps process demanding precise parameters. The prints are coated by copper or nickel coatings or bimetal coatings containing of these metals.

In results of this work the optimum parameters of metallization processes are obtained. Variation of many parameters like duration time of every steps of process, composition of electrolytes were analyzed. Additionally, the influence of magnetic field on the coatings was investigated. The magnetic field can significantly change the morphology of obtained surfaces.

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Non-covalent TMAP-GO hybrid as a potential nanomaterial for energy conversion

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INTRODUCTION

Functionalization of the carbon nanostructures is a rapidly developing research field. The main aim is to design and obtain a hybrid nanostructure characterized by remarkable properties of the carbon substrate combined with the strong light absorption of the absorbed molecules, such as porphyrins which have molar coefficients of $10^5$ M$^{-1}$ cm$^{-1}$. In this study, the noncovalent complexation of GO sheets with the cationic porphyrin TMAP (5,10,15,20-tetra(4-trimethylammoniophenyl)porphyrin tetra(p-toluenesulfonate)) have been investigated. Free porphyrin and its hybrid with GO were characterized using steady-state and time-resolved absorption and emission methods.

The absorption spectra of the porphyrin-GO hybrid show distinct red shifts of the Soret and Q-bands compared to free porphyrins, which is attributed to the flattening of the porphyrin molecules adsorbed on the GO sheet. Changes in the UV-vis absorption spectra are indicative of the formation of the porphyrin-GO nanohybrid already in the ground state. Interaction between the excited-state of porphyrins and GO in solution was probed by measuring the fluorescence spectra of porphyrin at different GO concentrations. Although the fluorescence of the porphyrin was quenched in the presence of GO no shortening of the singlet excited state lifetime of the porphyrins was detected. It can be concluded that fluorescence quenching is due to static quenching. Interestingly no fluorescence has been detected for the nanohybrid.

Femtosecond transient absorption measurements carried out with TMAP adsorbed on GO revealed very fast decay of the singlet excited state. It could be attributed to the fast electron transfer (ET) process from the excited state of the porphyrins to the GO.

ACKNOWLEDGEMENTS

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REFERENCES

Magnetic and magnetotransport properties of Co/Pt-IrMn nanopatterned multilayers

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Nanopatterned Co/Pt multilayered thin films (MLs) possessing perpendicular magnetic anisotropy (PMA) offer great opportunity for various applications such as magnetic sensors, logic devices, media for high-density recording. Exchange bias (EB) effect induced in the films normal direction by adding antiferromagnetic (AFM) IrMn layer is expected to increase magnetic hardness of MLs and their PMA because of exchange coupling at FM-AFM interface. Additionally, EB-effect available up to room temperature expands application of the materials in magnetoelectronics for designing tunnel junctions and spin-valve structures.

In the present study, Co/Pt-IrMn MLs are deposited on porous TiO\textsubscript{2} templates with flattened surface and homogeneously distributed pores (40-60 nm in diameter). Significant EB-shift of magnetization loops $\mu(H)$ up to 740 Oe accompanied by perfect curves squareness is achieved for continuous films in their normal direction. Simultaneously, nonsymmetric field dependences of magnetoresistance $MR(H)$ are characteristic for these films, hysteresis and shift of $MR(H)$ curves being comparable with corresponding parameters of $\mu(H)$ loops. Exchange coupling between FM and AFM layers is diversified by pinning effects in the similar porous films that increases effectively coercive field $H_C$, saving high PMA and EB with full shift of $\mu(H)$ loop to the negative field region. The EB-field and $H_C$ are tailored successfully by varying surface morphology of templates and stacking order of MLs.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{Perpendicular hysteresis loops of $\mu(H)$ (a) and $MR(H)$ (b) dependences of Co/Pt-IrMn and IrMn-Co/Pt MLs measured at room temperature.}
\end{figure}
Optimization of preliminary preparation process of amorphous metal surface

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INTRODUCTION

Metallic glass is an amorphous metal with long-range disorder in its structure. It is an alloy made of three or more components, and some of them are magnetic metals. As it possess high electrical conductivity and good magnetic properties (e.g. low-magnetization loss), it found an application as high-efficiency transformer core. Such core exhibit up to 99% efficiency, nevertheless work on it is still evolving. However, before the main research would be implemented, a raw material has to be carefully prepared and characterized.

EXPERIMENTAL, RESULTS AND DISCUSSION, CONCLUSIONS

This work contains results of complementary surface preparation and characterization of amorphous metal surface, namely Metglas 2605. Two aspects were examinated, namely cleaning, oxidizing and activation process. First of them was controlled with Surface free energy measurements by means of Drop Shape Analyzer. In the second step, enhanced amount of useful oxides were obtained by annealing. It was verified with scanning electron microscopy, x-ray photoelectron spectroscopy and Raman spectroscopy. At the last stage, surface activation by plasma treatment was performed and controlled similarly as at the beginning with surface free energy measurements.

Presented examinations allow to verify usefulness of each step of pretreatment process and selecting an appropriate parameters for it. As a result, well prepared surface of Metglas was obtained prior to further experiments on coupling to functional layers.

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Determination of depth-dependent stress profile in the near surface region of mechanically treated samples

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INTRODUCTION
A new way for analysis of the energy dispersion (ED) synchrotron data is proposed and tested. The main focus is put on the investigation of residual stress gradients in the near surface region of materials.

EXPERIMENTAL, RESULTS AND DISCUSSION, CONCLUSIONS
The multireflexion methods were used to measure stress variation in near surface layers of mechanically treated samples. Firstly, the multireflexion grazing incidence diffraction method (MGIXD) was applied on a classical diffractometer (Cu/Kα radiation) [1]. Next, the white synchrotron beam was used during energy dispersive measurements (EDDI, BESSYII, Berlin, Germany) [2].

The new method of analysis (called MMXD) allowed to determine depth-dependent stress profile. For the mechanically treated surfaces a good convergence was obtained between the stresses measured using synchrotron radiation (MMXD and standard ED) and those determined with Cu/Kα radiation on laboratory diffractometer (MGIXD).

The indisputable advantage of the MGIXD and MMXD methods is the possibility of determination of both $a_0$ and $c/a_0$ lattice parameters in the well-defined surface region of the sample. Certainly, synchrotron radiation allowed measurements for larger depths in comparison with laboratory X-rays.

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REFERENCES
Preparation and characterization of carbon-sensitized Ho-TiO$_2$ nanoparticles

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Semiconductor-based heterogeneous photocatalysis is a promising technology for water purification without using consumables and generating harmful by-products [1]. Lanthanide ions have become current interests because of possible anti-Stokes fluorescence effect and the improvement of photocatalytic activity of titanium dioxide, absorbing only ultraviolet light, working under visible-light irradiation [2]. However, the relatively low luminescence efficiency of Ln-based nanoparticles is one of the main factors limiting their further applications. Carbon, which is present on the surface of the TiO$_2$ photocatalyst can be responsible for luminescence quenching processes, which responsible for lower photocatalytic activity of TiO$_2$. Here we present our recent studies on the luminescence properties and photocatalytic activity of C/Ho-TiO$_2$ samples under visible-light irradiation.

The C/Ho-TiO$_2$ photocatalysts were prepared by hydrothermal method. The obtained samples were characterized by diffuse reflectance spectroscopy (DRS), photoluminescence spectroscopy (PL), scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET) method, and X-ray powder diffraction analysis (XRD). The photocatalytic activity of the powder samples was assessed by the degradation of phenol in the liquid phase under visible light irradiation. To provide insight into the reactive inviduals participating in the degradation mechanism, a test with scavengers was also performed.

Experimental results showed that the titania surface modification with carbon caused a decrease of the luminescence properties of holmium. It was observed that photoactivity decreased with further increasing carbon in Ho/TiO$_2$. Photocatalytic activity tests in the presence of C/Ho-TiO$_2$ and scavengers confirmed that mainly superoxide radicals, as well as hydroxyl radicals and holes, were responsible for the visible-light-induced degradation of the model pollutant in aqueous solution. Modification of titania with holmium and carbon greatly affected the light absorption property of the photocatalysts. The enhanced activity is probably attributed to the presence of new states in the band gap, the introduction of Ho and C extended the absorption spectrum of TiO$_2$ into the visible region and decreased the titania band gap, which was assigned to the charge transfer between the Ho ion 4f level and C ion 1s level and the titania conduction or valence band.

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REFERENCES
Luminescence properties and photocatalytic activity of Eu/Tb-organic frameworks-modified titanium dioxide photocatalysts

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At present, rare earth (RE) metals have attracted much attention due to their unique ability to converting long-wavelength radiation into shorter wavelength through multiphoton processes. This attribute is particularly needed for development of visible-light inducted photocatalysts (such as titanium dioxide). Nevertheless, the luminescence of RE ions is very susceptible to the local crystal field environment [1–3]. In view of this, we proposed to obtain RE-containing metal-organic frameworks (REOF) to overcome the abovementioned drawback. The aim of this work was to understand the effect of carboxylate-based ligands and the amount and type of RE ions on luminescence and optical properties, and their relation with photocatalytic properties of titanium dioxide in visible light.

A series of EuOF-TiO2, TbOF-TiO2 and EuTbOF-TiO2 photocatalysts were obtained via a two-step method. Namely, RE-OFs structure were synthesized in the first step by hydrothermal method using Eu/Tb as metals and pyridine-2,6-dicarboxylic acid/p-phenylenediacetic acid as a ligand, followed by REOF-TiO2 nanocomposites prepared in the second step via surface impregnation technique. The photocatalysts were characterized by diffuse reflectance spectroscopy (DRS), photoluminescence spectroscopy (PL), scanning electron microscopy (SEM). The photocatalytic properties were investigated by employing the photodegradation of phenol in the aqueous phase as a model pollutant.

All Eu/TbOF-TiO2 samples exhibit much enhanced photocatalytic activity in degradation of phenol under visible (λ> 420 nm) light irradiation, than pristine TiO2. The presence of Eu/Tb-organic frameworks in the samples influenced the changes in UV-Vis absorption spectra, probably because of the presence of new states in the band gap, which produces a new photonic absorption process and shows photoluminescence properties.

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REFERENCES

Organic Light-Emitting Diode (OLED) Materials - electrochemical and spectroscopic tests

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Nowadays OLEDs are commonly used as surface light sources in phone displays, televisions or other portable devices. The advantages of displays made in OLED technology include the possibility of obtaining a very good image contrast, low production costs and more environmentally friendly production process compared to LCD displays. What's more, displays of this type are characterized by high flexibility, small thickness, low weight and a much shorter response time (on the order of 0.01 ms) compared to LCD monitors. Organic or organo-inorganic electroluminophores play an important role in the OLED diodes. An important parameter characterizing this type of compounds is HOMO-LUMO energy gap. The value of the energy gap can be determined by means of both spectroscopic and electrochemical measurements. The value of this parameter determines the suitability of luminophores for use in OLEDs. A serious problem is the fact that the OLED structures are subject to aging processes, which contributes to a systematic decrease in the luminance of the emitted light. Therefore, there is still a need to look for new compounds for the role of electroluminophores in OLEDs systems. Another important aspect of the OLED technology is the production of protective coatings. These coatings must be characterized by high light transmittance over a wide range of the spectrum. Such coatings can be produced by photopolymerization. An important factor is the selection of appropriate initiating systems for this type of processes.

Due to the high demand for a new type of surface light sources, a search for new electroluminophores for the OLEDs was undertaken. The analyzed luminophores were tested using spectroscopic and electrochemical techniques (such as UV-Vis spectroscopy and cyclic voltammetry). What is more, the search for new co-initiators for use in bi-component systems initiating the photopolymerization of polymeric coating materials was undertaken. For this purpose, for the proposed initiating systems, the Gibbs Free Energy of electron transfer between the co-initiator and the initiator was determined. On this basis, the initiating systems best suited for the production of protective coatings in OLEDs were selected.

REFERENCES
Catalytic activity of cobalt-palladium catalysts in methane combustion process

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INTRODUCTION
One of the fossil fuels regarded in automotive industry is methane. Its use in vehicle engines is, however, inevitably connected with its release to the atmosphere. Despite its low extent the problem cannot be neglected as methane is considered to be the primary greenhouse gas responsible for a recorded increase in the average temperature on Earth. Depending on different literature sources greenhouse effect of methane is from 21 times to even 1000 times greater than that of carbon dioxide which explains why its removal from exhaust is very important [1]. The most effective method for this is catalytic combustion. The published sources indicate that used so far in the catalytic methane combustion catalysts based on noble metals have very high catalytic activity and seem to be irreplaceable. The catalysts based on palladium oxide are the most commonly used and have been described extensively in the literature [2]. However, due to their high price and depleting the source of rare earth metals, alternative, cheaper catalysts are being sought. It was reported in literature that high catalytic activity have the mixed metal oxides systems. Among others mixed catalysts: manganese, copper and the cerium-cobalt have been studied extensively [3]. The mixed palladium catalysts have also been studied.

EXPERIMENTAL, RESULTS AND DISCUSSION, CONCLUSIONS
In this study, a series of Co-Pd metal oxide supported catalysts were prepared by impregnation. To determine the catalyst composition X-ray Fluorescence spectroscopy was used as one of commonly available spectroscopic methods. The catalysts activity during the methane combustion was determined by using plug flow reactor Catlab (Hidden Analytical). The effluent gas composition (N₂, CO, CO₂, O₂, H₂O) was analyzed with a quadrupole mass spectrometer (QMS). According to the research carried out, cobalt catalyst with small amount of palladium showed a higher activity than its counterpart consisting of pure palladium oxide.

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REFERENCES
Vermiculites modified with d-electrons metals and their catalytic properties in denox processes

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INTRODUCTION

Natural aluminosilicate - vermiculite was given to the intercalation process according to the modified procedure of Kudła [1]. The resulting material was further modified (by the incipient wetness) with selected d-electron metals: Mn, Ni, Fe, Cu (5% wt) and Ce as the active material (0.5% wt).

EXPERIMENTAL, RESULTS AND DISCUSSION, CONCLUSIONS

Treatment with azodicarboamide of vermiculites increased its surface area and pore volume (2 for pure vermitulite and 86 m²/g for modified and from 0.016 to 0.100 cm³/g). Modification with Cu, Ni, Fe and Cu slightly decreased SBET (74, 64, 68 and 59 m²/g respectively). The addition of cerium slightly affects the surface area.

In XRD, characteristic reflection for introduced metals were observed in diffractionograms, in FTIR, the modification with azodicarboamide decrease of the band attributed to OH vibrations.

Vermiculite modified with manganese and ceria, the highest value of NO conversion reached 96% at 300°C, while at 350°C 89%. However, high N₂O concentration values were recorded in the post-reaction mixture (about 240 ppm). This is due to the fact that the Mn²⁺ manganese cations are highly oxidizing [2]. At high temperatures oxidation of NO to N₂O is occurred, where high concentrations of N₂O were visible, as compared to other catalysts.

At slightly higher temperatures (350 and 400°C), the addition of cerium causes the nickel catalyst which is inactive in the SCR reaction (10 and 18%, in 350 and 400°C) to achieve a conversion rate of 66% and 53%, with a low concentration of N₂O at these temperatures (61 and 63 ppm).

The iron-cerium catalyst also proved to be a good catalyst in the SCR reaction. The obtained values of NO concentration are low at 350 and 400 °C and reached average values in the recorded temperature ranges of 90 and 89 ppm NO.

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REFERENCES

Modified cenospheres as catalysts in Selective Reduction of NO by Ammonia (SCR-NH₃)

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INTRODUCTION
Cenospheres are the by-products present in fly ash from the power plants. They are gas-filled aluminosilicate spheres, which have many universal properties, and can be used in many fields of industry. The most important properties of the cenospheres are: thermal insulation, good frost resistance or fire resistance. Therefore, there is a growing interest in recovery and the modification of microspheres and their usage in many fields of science and industry.

EXPERIMENTAL, RESULTS AND DISCUSSION, CONCLUSIONS
The aim of this work was to study the properties of gray and white cenospheres promoted with manganese, iron, copper and nickel ions using IR spectroscopy, X-ray diffraction, scanning electron microscopy and textural properties. New catalysts were also tested in the selective catalytic reduction NO by ammonia, which are very promising materials in this process.

The highest NO conversion 95% were reached by Mn modified cenospheres, but this catalysts produce 270 ppm N₂O at 300°C. The best catalysts were modified with copper which have about 90% NO conversion at 250°C.

Fig. 1 Catalytic properties of studies samples

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Conductive polymer brushes based on ethynyl-pyridine monomer

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INTRODUCTION
Conjugated polymer chains have many advantages over classical polymer films. Highly ordered, conjugated polymer chains within such structures enable directional transport of charges while their covalent attachment to the inorganic surface stabilizes the system and facilitates charge injection to and from electrodes. These features are very desirable in electronic devices like LED and photovoltaic cell. In these studies we use self-templating polymerization approach as the method of formation of conjugated polymer chain.

EXPERIMENTAL, RESULTS AND DISCUSSION, CONCLUSIONS
Bifunctional monomers containing methacrylate and ethynyl-pyridine groups are used in the synthesis of polymer brushes. In the first step, methacrylate groups are polymerized by surface initiated photoiniferter polymerization (SI-PIMP) or by surface initiated atom transfer radical polymerization (SI-ATRP). The formed polymer brushes containing pendant acetylene groups undergo polymerizations in two ways: via activation by quaternization of pyridine rings or using rhodium-based catalyst. As a result, conjugated ladder-like polymer brushes are obtained exhibiting semi-conducting properties. After doping with oxidative agents significant increase of their conductivity occurs.

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Selective photocatalytic oxidation of benzyl alcohol into benzaldehyde under blue LED irradiation

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INTRODUCTION
Selective oxidation of alcohols to their corresponding carbonyl compounds is of significant importance. Aldehydes and ketones are groups of substances widely used as valuable intermediates in the fragrance, confectionary and pharmaceutical industries [1]. They are often produced via chemical oxidation reactions which require oxidants such as chromate, hypochlorite, peroxo acids and permanganate, or require the use of precious metal complex catalyst at increased temperatures while using dioxygen as oxidant [1]. Therefore, it is necessary and beneficial to develop a green, highly selective and environmentally friendly approach to produce aromatic aldehydes under moderate conditions.

The aim of this research is to efficiently obtain the aromatic aldehydes using the heterogeneous photocatalysis under visible light and to evaluate the light emitting diodes as a cheap source of irradiation.

EXPERIMENTAL
Selective oxidation benzyl alcohol (BA) into benzaldehyde (BAD) were performed over Bi₄O₅Br₂, BiOClBr, BiOCl₁.₃Br₀.₇ and BiOBr. All bismuth oxyhalides were synthesized via solvothermal methods using glycerol and bismuth nitrate as a bismuth source. Halogen source of BiOBr, BiOClBr, BiOCl₁.₃Br₀.₇ was inorganic salt KX (X=Cl, Br) and BiOBr was made using 1-Butyl-3-methylimidazolium bromide. The prepared photocatalysts were characterized by analyzing spectra of UV-vis/DRS, PL and SEM. Photocatalytic oxidation tests was performed for 6 hours. In experiments 30 mg (1 gL⁻¹) of photocatalyst was dispersed into 30 ml of 0.₅ mmolL⁻¹ benzyl alcohol acetonitrile solution under blue light emitting diode LED irradiation (sixteen blue LED for 1W each) as a light source.

RESULTS AND CONCLUSIONS
BiOBr was demonstrated the highest photocatalytic activity in experimental conditions. After irradiation for 6h hours up to a 48% BA was oxidized to BAD while on Bi₄O₅Br₂, BiOClBr and BiOCl₁.₃Br₀.₇ conversion were 40%, 31% and 27%, respectively.

In summary, bismuth oxyhalides were able to oxidized BA into corresponding aldehyde. Moreover, light emitting diodes were an alternative, more eco-friendly light source than xenon lamps. LED and prepared catalysts exhibits potential for practical applications.

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Fabrication of Ag/AgX/Bi$_{20}$TiO$_{32}$ heterostructures with enhanced visible-light driven photocatalytic activity toward cytostatic drug imatinib

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INTRODUCTION

Bismuth titanates is a large family of visible light photocatalysts including Bi$_2$Ti$_2$O$_7$ (2.82 eV), Bi$_4$Ti$_3$O$_{12}$ (2.79 eV), Bi$_{12}$TiO$_{20}$ (2.65 eV), Bi$_{20}$TiO$_{32}$ (2.36 eV) and so forth [1]. Thus, Bi$_{20}$TiO$_{32}$ have the narrowest bang gap it is the most promising materials in visible light photocatalysis. However, Bi$_{20}$TiO$_{32}$ has two major problems including a more positive conduction band edge position and rapid recombination of photo-generated carriers. To overcome these defects, a novel strategy has been applied via construction Z-scheme heterostructure Ag/AgX/ Bi$_{20}$TiO$_{32}$.

Cytostatic drugs are a group of carcinogenic, mutagenic and teratogenic pharmaceuticals used in chemotherapy of cancer, treatment of skin diseases and have been reported to have low biodegradability so their concentration in environment is gradually increased [2]. Due to the high toxicity methods for removing them from the environment should be found as soon as possible.

In this research, Ag/AgX (X=Cl, Br) has been used to couple with a Bi$_{20}$TiO$_{32}$ photocatalysts to enhance utilizing visible light and exhibited more efficient cytostatics drug degradation.

EXPERIMENTAL

Bi$_{20}$TiO$_{32}$ was prepared via hydrothermal methods at 120°C for 24 hours, washed several times ethyl alcohol and deionized water, vacuum-dried and then heated at 300°C for 2h. Ag/AgBr/ Bi$_{20}$TiO$_{32}$ was obtain by photoreduction. AgNO$_3$ was used in concentration of 0.05, 0.1, and 0.2 molL$^{-1}$ as a silver precursor. As a chlorine and bromine source were used CTAC and CTAB, respectively. Photocatalytic reaction were performed with Xenon lamp as a source of light and in SUN Test CPS+ solar simulator. Photocatalyst concentration was 0.5 gL$^{-1}$ and cytostatic drug (imatinib) was 15 mgL$^{-1}$.

RESULTS AND CONCLUSIONS

The Ag/AgX/Bi$_{20}$TiO$_{32}$ composites have been successfully synthesized via hydrothermal and photodeposition reaction. The selected modification of the bismuth titanate caused an increase in the removal rate imatinib on the activity of the unmodified Bi$_{20}$TiO$_{32}$ obtained in the same way under solar and visible light irradiation. Ag/AgCl/Bi$_{20}$TiO$_{32}$ has the higher photocatalytic performance under solar light than Ag/AgBr/Bi$_{20}$TiO$_{32}$ whereas in the visible light it was the opposite. The concentration of AgNO$_3$ has negligible impact on photocatalytic activity.

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Effect of MWCNTs modification on photocatalytic activity of MWCNTs/BiOBr synthesized via ionic liquid toward anticancer drug 5-fluorouracil

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Cytostatics drugs (CSDs) are a group of carcinogenic, mutagenic and teratogenic pharmaceuticals used in chemotherapy of cancer, treatment of skin diseases and treatment of infections. Due to the high toxicity, the continuous using of CSDs potentially exerts adverse effects on the ecosystem and aquatic environment even at trace levels. Anticancer drugs have been reported to have low biodegradability so their concentration is gradually increases [1]. Among them, 5-fluorouracil is the most commonly and widely used worldwide. According to the International Agency for Research on Cancer (IARC), the concentration thresholds for toxicity (carcinogenicity, ng L⁻¹) of 5-fluorouracil is 230 [2].

Bismuth oxyhalides (BiOX, X=Cl, Br, I) are V-VI-VII ternary semiconductors compound with tetragonal matlockite structure, a layer structure characterized by [Bi₂O₂]²⁺ slabs inserted by double slabs of halogen atoms. The engineering such as microstructure modulation, heterologous hybridization and structural design of BIX for efficient photocatalytic applications is crucial and attract the attention of many researchers groups [3]. Among the bismuth oxyhalides, BiOBr shows the appropriate band-gap (2.75 eV) which results in the best photocatalytic oxidation and reduction activity under visible light irradiation. Modification by multi-walled carbon nanotubes this type of semiconductors increases photocatalytic activity and gives an innovative approach, still undergoing research.

Multi – walled carbon nanotubes (MWCNTs) are widely reported to synergistically enhance the photocatalytic activity of semiconductors through high-surface area and high quality active sites, retardation of electron–hole recombination and absorption under visible light by modification of band-gap and/or sensitization. Furthermore, there is also a possibility of their surface modification with the introduction of the functional groups, like hydroxyl, carboxyl or carbonyl. It increases hydrophilicity of CNTs’ surface and creates new possibilities of interactions with water contaminant which can result in faster and more effective removal. In this research, BiOBr was modified by unmodified MWCNTs, MWCNTs with hydroxyl group (MWCNTs-OH) and MWCNTs with carboxyl group (MWCNTs-COOH).

The aim of this work were evaluated effect of modification MWCNTs as a component of MWCNTs/BiOBr nanocomposites on their synthesis and photocatalytic activity toward 5-fluorouracil under solar light irradiation.

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Polymeric microstructures based on interactions between oppositely charged polyelectrolytes

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COMPLEX COACERVATES – BRIEF INTRODUCTION

Complex coacervates are structures formed as a result of self-assembly of a pair of oppositely charged macromolecules (e.g.: polymers, proteins, surfactants). When forming the complex coacervates, two liquid phases can be observed: one – compositing mostly of water and the other – with a higher content of macromolecule [1].

PREPARATION, PROPERTIES AND APPLICATION OF COMPLEX COACERVATES

The complex coacervates were prepared from aqueous solutions of a pair of oppositely charged strong polyelectrolytes. Analysis of the morphology of the obtained structures was performed using dynamic light scattering (DLS) and optical microscopy. These techniques indicate the presence of spherical objects in the micrometer range. The physicochemical properties of the coacervates (stability, effect of changes in ionic strength) were also examined. Isothermal titration calorimetry (ITC) and turbidimetry experiments show that the structures formed from oppositely charged strong polyelectrolytes are unstable in high ionic strength.

To show the possibility of using complex coacervates in pharmacy, biotechnology and industry, we encapsulated quantum dots (QDs) and invertase from baker’s yeasts in the polymeric microstructures. Entrapment of QDs and labeled invertase inside the coacervates was confirmed using confocal laser scanning microscopy (CLSM). ITC was also applied to analyze the thermodynamics of the saccharose inversion reaction. The experiments show that the immobilized invertase exhibits catalytic activity.

Figure 1. CLSM micrographs of coacervates with encapsulated: FITC-labeled invertase (A) and QDs (B).

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WORKSHOPS
AND
DISCUSSION PANEL
Elsevier Workshop

Workshop has been prepared by Dr. Eng. Katarzyna Gaca-Zając and presented by Witold Zieliński.

The Workshop topics were:

- Scopus: how to choose a good journal wisely?
- How to successfully write a research paper?

Dr. Eng. Katarzyna Gaca-Zając

Katarzyna Gaca-Zając, PhD Eng. – a graduate of University of Strathclyde, with almost a decade of experience in research and teaching at an academic level in Europe; a specialist in polymer chemistry and studies of chemical reactions’ kinetics. Currently a Customer Consultant for Central-Eastern Europe in Elsevier. A knowledgeable expert on scientific databases and Elsevier solutions for researchers and information specialists, who is passionate about ethics in scientific publishing, as well as about widely understood bibliometrics.
Experts presentations

Marek Kula from the Atest Sp. z o.o (Agent of Sympatec GmbH) has given lecture entitled:

“DLS instrument – NANOPHOX”

As the representative of ABL&E-JASCO POLSKA Sp. z o.o Dr. Krzysztof Skupień who is the president of 3D Nano Company has given lecture entitled:

“Safe preparation of nanomaterial samples for spectrophotometric measurements”

Dr. Krzysztof Skupień

Krzysztof Skupień holds a Ph.D. in Materials Science from the Cracow University of Technology and a M.Sc. in Materials Science from AGH University of Science and Technology. Since 2002, his core expertise in technology is in nanomaterials used in photovoltaic cells. This includes several international scientific projects abroad, most notably at the Fraunhofer Institute for Solar Energy in Freiburg, Germany, recognized as the leading research facility concerned with solar power in the world. From 2002 to 2007 he had been a R&amp;D Assistant at the Cracow University of Technology. In 2007 he worked as an associate researcher at the Nanotechnology Research Center at the Industrial Technology Research Institute (ITRI) in Taiwan. Dr. Skupień founded 3D-nano in 2009. Currently, he uses his knowledge and skills to build devices that help in working with nanomaterials and dangerous substances. Together with an experienced team of specialists, he created a new brand – Hoger which manufactures gloveboxes ensure the safety of operators during exposure to harmful compounds, isolate sensitive materials from oxygen and moisture, and protect the working environment from undesirable agents. Hoger gloveboxes are already used in such companies as: ABB, Aptiv (formerly Delphi) or the National Centre for Nuclear Research in Świerk.
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