

# **ABSTRACTS BOOK**

7th International Conference 11th-12th October 2023 Katowice, Poland













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7th International Conference InterNanoPoland 2023 11th-12th October 2023 Katowice, Poland

11th-12th October 2023, Katowice, Poland

CHAIR Adam Szatkowski PhD, MBA

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### AGENDA | 11th-12th October 2023 Day 1 - 11th October 2023

9:00 - 9:15 | Welcoming words

· Dr inż. Adam Szatkowski, MBA President in NANONET Foundation

· Bogumił Sobula, Vice President, Katowice City,

·Bank Gospodarstwa Krajowego

9:15 – 10:00 | Plenary lecture | Moderator: Dr inż. Michał Macha, NANONET Foundation

• Benign-by-design nanomaterials for a more sustainable future: from catalysis to energy conversion and storage applications | Prof. Rafael Luque

· King Saud University / Universidad ECOTEC

• EU R&I perspectives for advanced materials: coordinated plan of action on advanced materials and the proposal partnership on advanced materials | Dr Jarosław Piekarski, National Contact Point for Research Programmes of the European Union, NCBR

10:00 - 10:15 | Coffee break

10:15 - 11:45 | Thematic panel: Nanotechnology vs Energy Transformation | Łukasiewicz – Institute of Electrical Engineering | Moderator: dr inż. Iwona Koltsov , Director of the Research Center for Hydrogen Technologies, Łukasiewicz – Institute of Electrical Engineering

· Ultra-Precise Deposition for Next-Generation Energy-Efficient Microelectronics | Dr Piotr Kowalczewski, R&D Manager, XTPL S.A.

• Functional superconducting nano materials and technologies toward energy cable applications | Dr Andrzej Morawski Head of Superconductor Materials Laboratory at IHPP Unipress PAS

Nanoemi - producer of pristine graphene for energy applications | Dr inż.Krzytszof Jakubczak, CEO
 & co-founder nanoEMI

• Nanoporous materials for supercapacitors | Dr hab. Michał Borysiewicz, Łukasiewicz Research Network - Institute of Microelectronics and Photonics

Discussion: Nanotechnology vs Energy Transformation

11:45 - 12:00 | Coffee break

12:00 - 13:00 | Discussion Panel: Technology Entrepreneurship: from lab to market | NANONET Foundation | Moderator: Michał Zwyrtek, Zwyrtek & Wspólnicy

· Małgorzata Skorupa Marketing Specialist & Startup Development Manager, co.brick,

- · Dr Paweł Modrzyński Co-owner of Nanores
- · Dr Marcin Baron University of Economics in Katowice,
- · Wojciech Kalinowski DLA Piper

13:00 - 14:00 | Lunch break

14:00 - 15:00 | Discussion Panel: NanoBreakthrough: nanotechnology in a 3W world | Bank Gospodarstwa Krajowego, Idea 3W | Moderator: Łukasz Nieradko, ew+me

· Dr inż. Iwona Koltsov Director of the Research Center for Hydrogen Technologies, Łukasiewicz – Institute of Electrical Engineering,

· Dr inż. Krzytszof Jakubczak, CEO & co-founder nanoEMI

· Dr Denis Koltsov BREC Solutions

 $\cdot$  Dr hab. Michał Borysiewicz, Łukasiewicz Research Network - Institute of Microelectronics and Photonics

 $\cdot$  Dr Andrzej Morawski Head of Superconductor Materials Laboratory at IHPP Unipress PAS

·Dr Piotr Kowalczewski, R&D Manager, XTPL S.A.

15:00 - 15:15 | Coffee break

15:15 – 17:00 | 3W nano START-UP CHALLENGE | NANONET Foundation, Bank Gospodarstwa Krajowego, Idea 3W | Moderator: Dr inż. Michał Macha, NANONET Foundation

Experts: Dr inż. Adam Szatkowski, MBA NANONET Foundation, Magdalena Cholewińska-Falarz NANONET Foundation, Barbara Miś City of Katowice, Łukasz Żółciak City of Katowice, Maciej Malski-Brodzicki BGK, Idea 3W

- · ECG T-shirt with nanotextronic carbon nanotube coating for long-term Holter-type electrocardiography
- $\cdot$  NGCH Low pressure heat generator from hydrogen
- $\cdot$  Nanosci photocatalytic materials to save Earth
- $\cdot$  SpheroNano the world-first platform for polymer powders spheroidization and properties tailoring
- $\cdot$  Hybrid technology for purification of hydrogen to automotive quality
- · HydroHub
- · Rubber roofing
- $\cdot$  HIPERH2
- $\cdot$  SEAWEED FOAM
- $\cdot$  Innovative biomethane plant
- · Diamond traceabilit technology

19:00 | Networking session | Ceremonial gala of awarding prizes to the winners of the competitions: 3W NANO Startup challenge

### AGENDA | 11th-12th October 2023 Day 2 - 12th October 2023

9:00 | Welcoming words

Dr inż. Adam Szatkowski, MBA President in NANONET Foundation

9:00 – 11:20 | Thematic panel: Organic, carbon and hybrid nanoelectronics | Silesian University of Technology | Moderator: Prof. dr hab. inż. Sławomir Boncel, Silesian University of Technology,

· Soluble two-dimensional donor-acceptor covalent organic frameworks and their electrochromism | Prof. Igor F. Perepichka, Centre for Organic and Nanohybrid Electronics / Silesian University of Technology

· Adaptive down- and up-conversion | Prof. Dirk M. Guldi, Friedrich Alexander, Universität Erlangen Nürnberg

· Advanced nanocomposites for engineering and biomedical applications | Dr Sameer S Rahatekar, Cranfield University

• Turning waste to gold | Dr Hai M. Duong, National University of Singapore / University of Cuu Long

Approach to fully solution-processed organic electronics - role of interlayers | Dr hab. inż. Beata
 Łuszczyńska, prof. PŁ, Technical University of Łódź

• Pursuing the quest for better understanding of charge carrier dynamics in modern semiconductors |Dr inż. Artur Herman, Wroclaw University of Science and Technology

11:20 - 12:00 | Coffee break / Poster session: Research and technologies for the development of the nanotechnology industry

12:00 – 13:00 | Presentation of high-tech and innovative companies | NANONET Foundation | Moderator: Dr inż. Michał Macha

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• HOGER Gloveboxes for convenient work with sensitive materials | Dr inż. Krzysztof Skupień Coowner and CEO of HogerBox Ltd. and 3D-nano.

• Unlocking the potential of nanotechnologies with synchrotron radiation | Dr Piotr Ciochoń, National Synchrotron Radiation Centre SOLARIS Venture Building with Nanores | Piotr Kunicki, Director of Startup Design at Nanores 13:45 – 14:45 | Thematic panel: Correlation microscopy of matter | University of Silesia in Katowice |Moderator: Dr inż. Marcin Libera

Centre of Microscopy Research of Matter SPIN-Lab / University of Silesia in Katowice

• Microscopy in research of new material | Dr inż. Marcin Libera, Centre of Microscopy Research of Matter SPIN-Lab / University of Silesia in Katowice

· Microscopy of nanomaterials | Dr Oleksandr Bondarchuk, International Iberian Nanotechnology Laboratory

· 3D printing and microscopy | Dr inż. Tomasz Gaweł, Centre of Microscopy Research of Matter SPIN-Lab / Univers ity of Silesia in Katowice

• Tescan - a reliable partner in microscopy technologies for scientists and innovative industry | Martin Suchanek, Tescan Area Sales Manager, Czech Republic

14:45 - 15:45 Certification of solid biofuels using microscopic examinations | University of Silesia in Katowice | Dr inż. Marcin Libera, Centre of Microscopy Research of Matter SPIN-Lab / University of Silesia in Katowice

· Centre for Biomass Energy Research and Education | Dr hab. Iwona Jelonek, University of Silesia in Katowice

· Certyfication of solid biomaterials program | Wojciech Szulik

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15:45 End conference

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### BENIGN-BY-DESIGN NANOMATERIALS FOR A MORE SUSTAINABLE FUTURE: FROM CATALYSIS TO ENERGY CONVERSION AND STORAGE APPLICATIONS

Rafael Luque King Saud University/Universidad ECOTEC <u>rafael.luque@ksu.edu.sa</u> <u>rluque@ecotec.edu.ec</u>

The design of benign and environmentally sound methodologies has been the driving force of scientists in recent years towards more sustainable methodologies.

Attractive and innovative protocols that nowadays are even part of industrial ventures including biomass-derived porous carbonaceous materials, designer nanomaterials for catalytic applications and catalytic strategies for biomass/waste conversion into useful materials, chemicals and fuels have been recently developed in our group in recent years. These topics have extensively covered the preparation and design of (nano)materials, biocatalysts and photocatalysts and their utilisation in heterogeneously (bio)(photo)(electro)catalysed processes, flow chemistry as well as in biomass/waste valorisation practices.

In this lecture, we aim to provide an overview of recent efforts from our group in the benignby-design concept applied to nanomaterials preparation, with excelling applications in catalysis and energy conversion and storage.

### EU R&I PERSPECTIVES FOR ADVANCED MATERIALS: COORDINATED PLAN OF ACTION ON ADVANCED MATERIALS AND THE PROPOSAL PARTNERSHIP ON ADVANCED MATERIALS

### J. Piekarski National Contact Point for HE, NCBR, Warsaw. Poland E-mail: Jaroslaw.piekarski@ncbr.gov.pl

The Coordinated Plan of Action on Advanced Materials is mentioned in the Critical Raw Materials Act and will aim to create an inclusive European society through cooperation between downstream and upstream producers as well as citizens. The objectives include developing an inclusive materials ecosystem, maintaining technological leadership, and sharing benefits. The plan intends to align strategies, initiatives, and investments at the European level to address challenges in advanced materials.

The Horizon Europe partnership on Advanced Materials is proposed to support the future the Coordinated Plan, and will focus on research, development and uptake (integration into innovative products and technologies) of a new generation of 'safe and sustainable by design' innovative materials fit for the circular economy.

### ULTRA-PRECISE DEPOSITION FOR NEXT-GENERATION ENERGY-EFFICIENT MICROELECTRONICS

Piotr Kowalczewski XTPL S.A., Stabłowicka 147, 54-066 Wrocław, Poland piotr.kowalczewski@xtpl.com

Additive manufacturing could play a significant role in the design and manufacture of more energy-efficient systems and in the fabrication of next-generation devices that themselves generate and store energy. In this context, XTPL is developing Ultra-Precise Deposition (UPD) technology for high-resolution printing of nanomaterials at a micrometer scale on complex substrates. This technique enables 3D heterogeneous integration, leading to more efficient energy use and reduced material consumption in semiconductor devices and displays. Affordable yet precise printed sensors may be integrated into smart grids and buildings, enhancing energy efficiency and management. Additionally, UPD allows rapid prototyping of energy generation and storage devices, like solar cells or batteries, paving the way to more efficient and reliable systems.

The UPD technology is implemented in the Delta Printing System, which is a state-of-the-art solution designed to offer precision, versatility, and efficiency for R&D and rapid prototyping. One of its key features is the ability to produce fine details with a feature size ranging from 1-10  $\mu$ m. A highlight of the system is the fast and easy exchange mechanism for cartridges and nozzles, significantly reducing downtime and speeding up workflow. Moreover, the system stands out for its versatility, supporting both conductive and non-conductive materials, while also boasting the capability to print on a diverse range of substrates, from heterogeneous materials to complex 3D topographies. Users can expect uniform and clean feature geometries, as there is no overflow or spills that could compromise the design integrity. The system is significantly ink-efficient; not only does it require a mere 0.1 ml of ink to start printing, but it also ensures up to 100% ink utilization, minimizing waste.

#### NANOPOROUS MATERIALS FOR SUPERCAPACITORS

Michał Adam Borysiewicz

Łukasiewicz Research Network - Institute of Microelectronics and Photonics, Warsaw, Poland E-mail: michal.borysiewicz@imif.lukasiewicz.gov.pl

Increasing push towards a decarbonized economy in the EU and other regions has yielded, among others, a significant research and development effort in electromobility as well as household energy production solutions. The limiting factor for widespread applications has been seen to a large degree in the insufficient power density and lifetime as well as high cost of li-ion batteries. To tackle these challenges, significant developments in the area of supercapacitors have been undertaken. These devices offer extremely fast charging and discharging, as well as millions of charge/discharge cycles in their lifetime, several orders of magnitude more than li-ion batteries. These advantages are due to non-reactive charge storage, in an electric double layer, in redox species or by intercalation. The current electrodes for supercapacitors are also quite inexpensive, being made with bio-sourced carbon. To increase the energy density of supercapacitors, which is poor in comparison to batteries, researchers have been studying novel materials with nanoscale porosity including transition metal oxides, graphene, metal organic frameworks, covalent organic frameworks and others.

This short presentation will give the Audience a short review of the challenges and emerging technologies in the supercapacitor R&D field.

### SOLUBLE TWO-DIMENSIONAL DONOR-ACCEPTOR COVALENT ORGANIC FRAMEWORKS AND THEIR ELECTROCHROMISM

Igor F. Perepichka

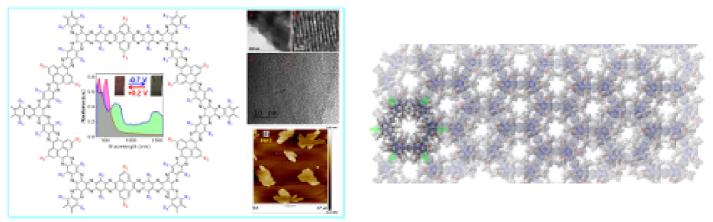
Department of Physical Chemistry and Technology of Polymers, Faculty of Chemistry, and Centre for Organic and Nanohybrid Electronics, Silesian University of Technology, Konarskiego 22b, 44-100 Gliwice, Poland E-mail: <u>igor.perepichka@polsl.pl</u>

Two-dimensional (2D) covalent fused-rings aromatic frameworks, a sub-class of covalent organic frameworks (COFs) can be regarded as holey graphene and hold great potential in many applications. However, the development of such materials has been seriously limited by their poor solubility. An introduction of long-chain side groups can improve their solubility but destroys their ability of ordering through  $\pi$ - $\pi$  stacking in a bulk.

In this work, four soluble 2D aza-fused-ring aromatic frameworks (FAFs), soluble in common organic solvents, were successfully synthesized by creating large pore structures and attaching long side-chain substituents [1]. They possess high molecular weights (Mw = 56 - 87 kDa) and large hydrodynamic diameters (190 - 250 nm). We demonstrated that although FAFs are well-soluble in common organic solvents, they nevertheless show excellent ordering in the solid state with a layer spacing of ca. 0.36 - 0.37 nm, typical for  $\pi$ - $\pi$  stacking.

Due to the presence of electron-deficient pyrazine rings in the main skeleton and electron-rich alkoxyphenyl or alkylthienyl side-chain groups, these FAFs are electroactive in both n- and p-doping processes. They possess low-lying LUMO energy levels of -(3.87 - 4.00) eV and narrow band gaps (Eg = 1.64 - 1.87 eV), classifying them as n-type semiconductors.

Taking advantage of their good solubility, spray-coated films of FAFs have been prepared and their cathodic electrochromic behavior in the UV-Vis-NIR region was investigated for the first time. The FAF framework with 4-(2-ethylhexyloxy)phenyl solubilizing groups, demonstrated superior performance with short switching times between the neutral and n-doped states (few seconds), good contrast ( $\Delta$ T up to 44%) high coloration efficiency (up to 171 cm2 C–1 at 515 nm), and good operational stability (>200 redox cycles). We envisage that such type of 2D fused-ring frameworks possessing good solubility and strong  $\pi$ - $\pi$  interactions between the layers should be promising materials for a wide range of electronic and optoelectronic applications.



#### References:

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#### ADAPTIVE DOWN- AND UP-CONVERSION

Dirk M. Guldi

Department of Chemistry and Pharmacy & Interdisciplinary Center of Molecular Materials, Engineering of Advanced Materials, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstrasse 3, 91058 Erlangen, Germany

The detailed-balance limit places an upper bound on solar conversion efficiency for a single pn junction solar cell at slightly more than 30%. To surpass this limit, multi-exciton generation is being explored in inorganic semiconductors, while singlet fission (SF) is being investigated in arrays of conjugated organic molecules. In an optimal SF process, the lowest singlet excited state of one molecule (S1) that is positioned next to a second molecule in its ground state (S0) is down-converted into two triplet excited states (T1) each residing on one of the two adjacent molecules. The two triplet states initially form a correlated pair state 1(T1T1), which then evolves into two separated triplet states (T1+T1). As such, the energetic requirement for SF is  $E(S1) \ge 2 \ E(T1)$ .

We have set our focus in recent years on intramolecular SF in molecular materials and their studies in solution rather than on intermolecular SF investigations in crystalline films.

Implicit in intramolecular SF is a resonant, direct excitation of the SF material. In pentacene dimers linked by a myriad of molecular spacers, SF takes place with quantum yields of up to 200%. In addition, all key intermediates in the SF process, including the formation and decay of a quintet state that precedes formation of the pentacene triplet excitons, have been identified. This approach is, however, limited to the part of the solar spectrum, where, for example, the pentacene dimers feature a significant absorption cross-section. To employ the remaining part of the solar spectrum necessitates non-resonant, indirect excitation of the SF materials via either up- or down-conversion. For example, the up-conversion approach is realized with singlet excited states in pentacene dimers, which are accessed by two-photon absorptions (TPA). TPA is then followed in the second step of the sequence by an intramolecular SF – similar to what is seen upon resonant, direct excitation. Quite different is the down-conversion approach, which is based on an intramolecular Förster resonance energy transfer (FRET) and thereby the (photo)activation of the SF material. FRET requires the use of a complementary absorbing chromophore and enables funneling its excited state energy unidirectionally to the SF performing pentacene dimer. Again, SF completes the reaction sequence.

### ADVANCED NANOCOMPOSITES FOR ENGINEERING AND BIOMEDICAL APPLICATIONS

Sameer S Rahatekar and Krzysztof K Koziol Composites and Advanced Materials Centre, School of Aerospace Transport & Manufacturing, Cranfield University, College Road, Bedfordshire, United Kingdom E-mail (corresponding author): S.S.Rahatekar@cranfield.ac.uk

Nanocomposites offer excellent combination of high surface area and multi-functional properties for potential application in wide industrial sectors. This presentation is divided into two parts. The first part is focused on use of carbon nanotubes and graphene nanocomposites for Aerospace and advanced engineering application [1]. we will explore the graphene/carbon nanotube composites for EMI shielding, electrostatic dissipation, electrically conducting textiles and potentially for lightning strike protection. We will report the graphene/carbon nanotubes composites manufacturing process; we will also report electrical and mechanical properties of these composites and its utility in the above-mentioned industrials sectors.

The second half of this presentation will focus on nanofibers manufacturing from natural polymer-based materials for potential applications in biomedical engineering and food packaging applications. We will present our current work in electrospinning alginate nanofibres composite fibres with anti-microbial properties. Alginate is a natural polymer derived from seaweed which is widely used for medical bandages and for food packaging. We developed advanced alginate-based nanocomposite fibres [2] which antimicrobial properties [3] and very high surface area. The alginate nanofibres with high surface area and antimicrobial properties can potentially offer excellent candidate for the new generation of multi-functional anti-microbial bandages and for food packaging sector.

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#### TURNING WASTE TO GOLD

### Hai M. Duong (1,2) Goh Xue Yang (1), Luon Tan Nguyen (1), Ong Ren Hong (1), Bai Tianliang (1)

## Department of Mechanical Engineering, National University of Singapore, Singapore University of Cuu Long (UCL), Vietnam

E-mail (corresponding author): mpedhm@nus.edu.sg

In 2022, humans produced 400 million tons of plastic waste globally including 24.4 trillion pieces of microplastics in the oceans, 92 million tonnes of textiles and old clothes ended up in landfills and 1.2 billion tonnes of food and agriculture waste were mostly left to be rotten or burned. This wastefulness could release harmful chemicals and greenhouse gases, which harm our planet and human health tremendously. To overcome these environmental problems and to benefit farmers, households, communities and businesses, as well as Earth itself, we have created successfully several eco-products and cost-effective technologies to recycle almost all common wastes to high-value aerogel materials with a dozen of useful purposes. We have recycled the wastes of plastic bags and drinks bottles, agricultural waste products (pineapple, areca, coconut etc), food waste, old clothes, old tyres, fly ash, metals etc. Our eco-products produced from these wastes can be used for CO2 absorption, fruit preservation, wastewater treatment, oil spill cleaning, human fat removal, and heat and sound insulation of buildings or clothing or material for treating wounds.

Our solutions can bring many advantages to existing technologies and waste management and lead to the cheaper production with energy efficiency and far fewer harmful emissions. Compared to standard aerogel methods, our aerogel technologies using chemical bonding, mechanical bonding and thermal bonding methods can produce continuously the aerogels with the rate of 1.0 m2/min. They are also very cost-effective (due to 70% of energy saving), faster (18 times) and environmentally friendly (no toxic usage and much less CO2 emission with 0.1 kg CO2 emission/aerogel m2). The affordable products having a wider range of uses can be reused, recycled and disposed safely. A waste-based aerogel production has positive impacts on consumption, production, environmental restoration, innovation and climate change.

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#### PURSUING THE QUEST FOR BETTER UNDERSTANDING OF CHARGE CARRIER DYNAMICS IN MODERN SEMICONDUCTORS

A.P. Herman, S.J. Zelewski, K. Misztal, R. Kudrawiec Department of Semiconductor Materials Engineering, Wroclaw University of Science and Technology, Wroclaw, Poland E-mail (corresponding author): artur.herman@pwr.edu.pl

Emerging semiconductors such as van der Waals crystals (in particular transition metal dichalcogenides, TMDs) and hybrid organic-inorganic perovskites (HOIPs) have garnered substantial attention as they hold a great promise for applications in key domains for civilization in the era of global warming such as (opto)electronics (solar cells, light emitters) or solar-driven chemistry (photocatalysis). Nonetheless, for many potential technologies it is essential to fully understand charge carrier dynamics taking into account the exceptional nature of these materials. Despite significant progress in the field in recent years, the carrier dynamics, particularly at microsecond scale, has remained incompletely understood.

In the first part I am going to introduce the time resolved microwave (photo)conductivity (TRMC) technique and present our results obtained for the most prominent representatives of TMDs family (i.e. MoS2, MoSe2, WS2, WSe2).1 For the first time, TRMC measurements have revealed that laser pulse produces exceptionally long-lived free-charge carriers in both monolayer and bulk TMDs. The lifetime of majority carriers is close to microseconds and can even reach several microseconds due to different contribution of surface and defect states, as well as surface band bending (bulk). Moreover, analysis of TRMC signal allowed us to speculate about the exciton dissociation time. Our findings conform all previous results on ultra-fast carrier dynamics in TMDs obtained using other time-resolved methods (time-resolved photoluminescence, terahertz spectroscopy or pump-probe techniques).2,3

In the second part, tentatively labelled "two birds with a one stone" I will provide a concise overview of our recent breakthroughs in the development of TRMC setup. We are convinced that improvements we made positions it as an unparalleled experimental tool on a global scale, especially when considering the shorter timescales and deeper understanding of recombination processes. Here, the emphasis will be placed on charge carrier dynamics in selected low-dimensional HOIPs.

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#### EDYNAMIC IMAGE ANALYSIS AT THE TOUCH OF A BUTTON

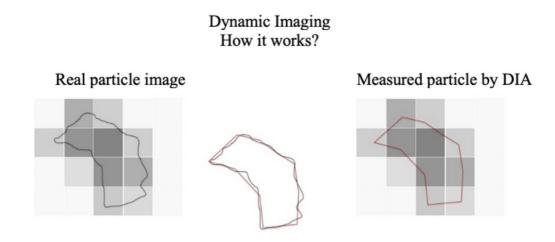
H. Bogusz-Koziarska, R. Flamholc, Anton Paar Poland, Warsaw, Poland E-mail: helena.bogusz@anton-paar.com

Litesizer DIA 500 the Anton Paar Dynamic Image Analyzer is a modular dynamic image analysis instrument, where the main unit is coupled to one of 3 possible dispersion units. Besides a dispersion unit dedicated to liquid samples (Liquid Flow) and another for dry powders using compressed air (Dry Jet), the instrument can analyze powders and free-flowing materials using the Free Fall dispersion.



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Important: detected details can be much finer than the resolution

### HIGH SAFETY HOGER GLOVEBOXES ADJUSTED TO PERFORM OPERATIONS IN ROBOTIC MANNER

K. Skupień,

HogerBox Ltd., Kraków, Poland E-mail (corresponding author): kskupien@hogerbox.com

Gloveboxes - instruments securing operators working with harmful materials but also isolating sensitive compounds from oxygen and moisture, must be designed and produced according to strict requirements ensuring their high safety and reliability. Such approach focused on high quality, as well as increased work ergonomics is implemented by HogerBox Ltd. - polish manufacturer producing individually designed gloveboxes and isolators dedicated for application in scientific laboratories, R&D departments and specialized production lines from pharmaceutical, medical, automotive and other materials related sectors [1].

High safety of the operator working with harmful materials including microorganisms, but also protection of the sensitive compounds, is ensured by new features of considered HOGER isolators and gloveboxes. Among them, extremely high leak tightness of both (class I according to ISO 10648-2 standard), integration of advanced sensors (pressure, temperature, oxygen, moisture, VOC, etc.) and control of environmental parameters must be mentioned. In particular, when operator protection mode is considered, precise regulation of working pressure and air velocity (individually for airlock and isolator itself), as well as ensuring of high filtration efficiency (exceeding 99,995%) and control of ventilation system duty point guarantee full operator protection both in normal and failure operation conditions. In turn, when product protection mode is considered, integration of highly efficient adsorption beds and supervision of the automation system ensures controlled working atmosphere with extremely low concentration of oxygen and moisture if needed.

Designing of HOGER gloveboxes is proceeded taking into account not only safety of operation but also convenience of work with the system. Consequently, considered devices exhibits increased ergonomic obtained by integration of worktop height regulation system, adjustment of gloveports size and position, as well as replacement of standard stainless steel door covers with transparent glass [1], but also by implementation of advanced control systems adopting voice and gesture recognition enabling executing of selected operations (such as change of working pressure, opening of the door or turning the light on) with arms still placed inside gloveports. Additionally, successful integration of HOGER gloveboxes with cobots (i.e. cooperating robots) allows for automatic performing of repetitive operations while granting safety of its simultaneous work with men.

References: [1] <u>www.hogerbox.com</u>

Acknowledgement: HogerBox Ltd. implement a project co-financed by European Funds: "Hybrid isolator combining the features of a laminar chamber and a glovebox with a high safety class and with the possibility of performing operations in a robotic manner"; project number: POIR.01.01.01-00-1240/20-00.







Unia Europejska Europejski Fundusz Rozwoju Regionalnego



### UNLOCKING THE POTENTIAL OF NANOTECHNOLOGIES WITH SYNCHROTRON RADIATION

### Dr Piotr Ciochoń National Synchrotron Radiation Centre SOLARIS

Due to extraordinary properties of synchrotron radiation and the availability of numerous complimentary and often unique characterization techniques, synchrotron – based light sources play a very important role in both basic and applied research in the field of nanoscience and nanotechnology. SOLARIS Centre is the first, and so far the only such source in Central and Eastern Europe, with great potential in boosting the research and development capabilities of both academic research centers and innovative industrial players. This talk will focus on the characterization techniques available at SOLARIS Centre, different available access modes, and the discussion of case studies, highlighting the potential of synchrotron radiation – based techniques in solving crucial problems in the field of nanoscience and nanotechnology. A special emphasis will be placed on discussing effective cooperation of scientists with industrial partners, especially innovative SMEs and start – ups, and boosting their usage of large research infrastructures. In this context, the efforts of the Sylina project will be presented, which aims at increasing cooperation capabilities of the SOLARIS Centre and its international partners with industry.

Sylinda project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 952148.





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### APPARATUS FOR IN SITU DETERMINATION OF THE PROPERTIES OF NANOMATERIALS

R. Pelka (1\*), E. Ekiert (1), A. Brzoza-Kos (2), A. Wyszkowski (3)

1. Faculty of Chemical Technology and Engineering, West Pomeranian University of

Technology in Szczecin, Pulaskiego 10, 70-322 Szczecin, Poland

2. AGH University of Science and Technology, Faculty of Energy and Fuels, al. A.

Mickiewicza 30, 30-059, Krakow, Poland

3. SYSPA Systemy Pomiarowe-Automatyka, Pozdawilska Street 2/1, 71-772 Szczecin, Poland E-mail (\* corresponding author): rpelka@zut.edu.pl

To determine the physical and chemical properties of nanomaterials, an innovative scientific equipment was designed and built to measure simultaneously (under in situ conditions) changes of mass of solid samples, electrical conductivity, magnetic permeability, temperature and gas phase composition at a given temperature and under atmospheric pressure. The currently presented version of the device is equipped with modernized systems, including: buoyancy force compensation, transfer of digital measurement data, more precise temperature and gas flow control. Chemical processes studied may be carried out in the temperature range 300-700oC. The gas phase composition may be changed according to the given program (e.g. during nitriding, carburising, oxidising and reduction reaction). The analytical system is equipped with a tubular differential quartz reactor and enables to conduct measurements both in kinetic and quasi-equilibrium states.

The measurement data gained thanks to the experiments performed in such an apparatus lead to the development in such fields of science, engineering and technology as:

- heterogeneous catalysis – study of new phenomena or reinterpretation of already known ones in reactions with the use of catalytically active substances with a nanocrystalline structure,

- synthesis of nanomaterials – precise determination of the conditions for the fabrication of nanomaterials, functional materials, thin films etc. with designed physical and chemical properties,

- materials engineering – understanding of the phase change mechanisms,

- sensor fabrication – between the active material of the sensor and the gas phase an equilibrium is established; a change in the magnetic properties of the sensor material during its reaction with the gas phase may be used in the construction of innovative sensors,

- characterization of nanomaterials – nanoparticles size distribution studies.

Acknowledgment

1

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### CHARACTERIZATION OF PEROVSKITE SOLAR CELLS WITH MESOPOROUS TIO2/ZNO ELECTRON TRANSPORT LAYER

A. Drygała (1), Z. Starowicz (2), K. Gawlińska-Nęcek (2), M. Karolus (3), M. Lipiński (2), P. Jarka (1), W. Matysiak (4), E. Tillová (5), P. Palček (5), T. Tański (1)
1. Department of Engineering Materials and Biomaterials, Silesian University of Technology, Konarskiego 18a Street, 44-100 Gliwice, Poland
2. Institute of Metallurgy and Materials Science, Polish Academy of Sciences, Reymonta 25 Street, 30-059 Cracow, Poland
3. Institute of Materials Engineering, University of Silesia, 1a 75 Pułku Piechoty Street, 41-500 Chorzow, Poland
4. Scientific and Didactic Laboratory of Nanotechnology and Material Technologies, Silesian University of Technology, Towarowa 7 Street, 44-100 Gliwice, Poland
5. Department of Materials Engineering, Faculty of Mechanical Engineering, University of Žilina, Univerzitná 1 Street, 010 26 Zilina, Slovakia E-mail (corresponding author): aleksandra.drygala@polsl.pl

Solar energy is the cleanest and most abundant renewable energy source available in the world. Perovskite solar cells (PSCs) have attracted tremendous attention thanks to rising powerconversion efficiency. Electron transport layer (ETL) of perovskite solar cells plays an important role in collecting and transporting photogenerated electrons from perovskite to transparent conductive oxide layer, strongly affecting device performance.. In the present study, the effect of adding ZnO nanostructures with different percentage weight contents to the mesoporous TiO2 on photovoltaic performance of PSC was investigated. The prepared mesoporous ETLs were characterized by scanning electron microscopy, atomic force microscopy, X-ray diffraction, and UV-Vis spectroscopy. The effects of using ZnO nanostructures on the electrical properties of PSCs were also investigated. X-ray diffraction analysis does not reveal a change in the structure of layers with the addition of ZnO nanopowder. The incorporation of ZnO nanostructures into the mesoporous TiO2 layer does not significantly affect light transmission. The highest efficiency was obtained for perovskite solar cells with the addition of 2 wt.% ZnO. These results indicate that the ZnO/TiO2 composite has demonstrated to be a promising candidate as a mesoporous electron transport layer for high-performance mesoscopic perovskite solar cells.

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## COMPARISON OF PROPERTIES OF ROCKET PROPELLANTS WITH ENERGETIC VS. NON-ENERGETIC BINDER

K. Łysień (1), A. Stolarczyk (1), T. Jarosz (1), S. Waśkiewicz (1), A. Mielańczyk (1)
1. Department of Physical Chemistry and Technology of Polymers, Silesian University of Technology, Gliwice, Poland E-mail (corresponding author): kinga.lysien@polsl.pl

Solid rocket propellants are systems consisting of a binder, oxidizer and additives. Currently used solid rocket propellants often contain ammonium perchlorate as an oxidizer and polybutadiene terminated with hydroxyl groups as a binder. A significant disadvantage of such a system, is the release of toxic gaseous substances, following the combustion of propellants in rocket engines. For this reason, new systems with similar high parameters relevant to rocket propellants and with less environmental harm are currently being sought.

The aim of the project was to study the effect of the binder used (polybutadiene terminated with hydroxyl groups - non-energetic binder and poly(azide glycidyl) - energetic binder) on properties of rocket propellants. In addition, the prepared rocket propellants samples differed in the oxidant used - it was, respectively, ammonium perchlorate belonging to the "traditional" oxidants and phase-stabilized ammonium nitrate- its "green" alternative.

As part of the research task, the effect of the substances used on the ignition temperature of the tested rocket propellants was measured. The sensitivity to mechanical stimuli of the prepared formulations, as well as linear combustion velocity was determined. Using differential scanning calorimetry (DSC), the heat of combustion of rocket propellants was investigated and the thermal decomposition characteristics of the binders used were determined. The activation energy values were also determined from the DSC measurements, which were calculated using the Kissinger method.

### COMPOSITE MATERIALS BASED ON CARBON NANOTUBES IN MONITORING OF THE CARDIOVASCULAR PARAMETERS

Jędrysiak R.G.(1,2,3), Boncel S.(1,2,3), Kolanowska A. (1,3), Blacha A. (1,2,3), Ruczka Sz.(1,2,3), Imielski M. 1. Silesian University of Technology, 2. Centre for Organic and Nanohybrid Electronics (CONE), 3. NanoCarbon Group – www.nano-c-group.org E-mail: rafal.jedrysiak@polsl.pl

The problem of cardiovascular diseases in the society of the western world is growing rapidly. Textronics - a sophisticated combination of completely everyday things - clothes and advanced technical solutions based on nanotechnology could solve the problem[1]. Wearable electronics could monitor e.g. heart rate or ECG what is important during physical exercise on different levels of advancement from amatory to professional sport or in medical applications for early detection of heart strokes, atrial fibrillation and other heart-related complications. Healthy life and sport activity can reduce mortality - constant heart rate monitoring during exercise could improve training results. Moreover, if a myocardial infarction occurs, remote ECG monitoring can enable constant monitoring of the patient and significantly facilitate recovery through virtually supervised rehabilitation. The use of textronics as a system for collecting biosignals and the use of appropriate algorithms for their processing can significantly reduce health care costs.

All of mentioned above goals could be achieved by observing heart's work on different levels from a simple heart rate to a complex multi-channel ECG. The recorded signals can be sent wirelessly (Wi-Fi/GSM/others) and initially analyzed by AI algorithms and in case of detecting potentially life-threatening episodes by highly qualified medical personnel who will take the necessary life-saving actions. In our opinion the most comfortable for user core of remote HR/ECG systems are flexible electrical circuits conveniently implantable into textiles.

The flexible, flat electrical circuits could be easily printed by electro conductive pastes based on various polymeric (eg. polyacrylic or polyurethane) dispersions as a matrix and carbon nanotubes with required properties[2,3]. Both the conductive paths and the surface of the electrodes are made of the same conductive paste which makes the printing process much easier. The insulations layers are made of a polymer base which is a matrix in the conductive element - this ensures high compatibility of all elements.

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### DRUG DELIVERY THROUGH ENCAPSULATION OF SELF-ASSEMBLED LINEAR COPOLYMER CONJUGATES

Shadi Keihankhadiv (1), Dorota Neugebauer (1) 1.Department of Physical Chemistry and Technology of Polymers, Faculty of Chemistry, Silesian University of Technology, 44-100, Gliwice, Poland E-mail (corresponding author): shadi.keihankhadiv@polsl.pl

Polymer-based nanocarriers have gained significant attention in medical applications, particularly drug delivery systems (DDS). These polymers offer versatility in designing nanoparticles with various morphologies and architectures. Polymeric micelles, in particular, have emerged as promising DDS due to their ability to encapsulate both hydrophilic and hydrophobic drugs, ensuring efficient loading, protection, and controlled release. The advanced technologies enable accurate precise targeting of the place in the body where medication should be administered, thereby improving the efficacy of the drug while reducing potential side effects [1].

This study has developed the utilization of amphiphilic linear choline-based copolymers as an ionic drug conjugate and as a matrix for drug encapsulation, with the goal of creating micellar drug-loaded systems. First, these copolymers have been synthesized by employing the polymerizable pharmaceutically functionalized monomeric ionic liquid, specifically [2-(methacryloyloxy)ethyl]trimethylammonium p-aminosalicylate (ChMAPAS) [2]. In the next step, these copolymers were employed to encapsulate p-aminosalicylate acid (PASA) or paminosalicylate sodium (PASNa), a drug with demonstrated efficacy against Mycobacterium tuberculosis. The self-assembly capacity of the copolymers was assessed using goniometry, which determined the critical micelle concentration (CMC) within the range of 0.03-0.18 mg/mL. The drug encapsulation significantly increased the drug content in the PAS-based copolymers from 24-47% to 47-86% PASNa vs. 86-137% PASA. Furthermore, this study evaluated the micellar performance of DDSs through in vitro drug release experiments under physiological conditions (PBS, pH 7.4 at 37°C). For PASA, a complete release was achieved within just thirty minutes, with a release efficiency of 100%. In contrast, for encapsulated PASNa, an initial burst release was observed within the first hour, followed by a gradual and sustained release over a period of up to twelve hours with a release efficiency of 80-100%.

In conclusion, polymer conjugate based micellar systems have demonstrated a great ability to encapsulate of drug increasing its content. This highlights the potential of PAS-loaded polymer micelles for drug delivery at a satisfactory level, offering promising prospects for enhancing their therapeutic effectiveness.

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### ELECTROCHEMISTRY AND SPECTROELECTROCHEMISTRY OF DONOR-ACCEPTOR-DONOR POLYMERS OF BIS(ALKYLBITHIOPHENE) AND BIS(CHALCOGENODIAZOLE)S OF ASYMMETRIC COMPOSITION

Andualem Merga Tullu, Wojciech Domagala Silesian University of Technology, Department of Physical Chemistry and Technology of Polymers, 9 M. Strzody street, 44-100 Gliwice, Poland E-mail (Andualem Merga Tullu): Andualem.Merga.Tullu@polsl.pl

Currently, organic semiconductors are attractive materials for the next generation of organic electronic devices since they can be used as a conductive and semiconductive layer in the fabrication of supercapacitors, organic field effect transistors (OFETs), organic light emitting diodes (OLEDs), polymer solar cells (PSCs), electrochromic devices, charge storage devices and others. The electronic and physicochemical properties of organic semiconductors are strictly related to their electronic structure, particularly the energy levels of their frontier orbitals (HOMO and LUMO). Careful modulation of the highest occupied and lowest unoccupied molecular orbitals is key to engineering low-bandgap materials, demonstrating bespoke electronic and optical properties. A common approach to lowering the optical and electron-deficient acceptors in a  $\pi$ -conjugated chain. Thiophene and its derivatives have already demonstrated great potential as donor units due to desirable properties such as stability, ease of synthesis and manipulation, whereas five-membered, six-electron aromatic chalcogenodiazole (1,3,4-thiadiazoles, 1,3,4-oxadiazole and 1,3,4-selenadiazole) systems are good electron accepting motifs to engineer donor-acceptor-donor type organic semiconductors.

Π-conjugated D-A1-A2-D type monomers were synthesised using alkyl(bithiophene) as the electron donor unit and two different chalcogenodiazoles making up the electron acceptor unit. Monomers were chemically synthesised, while the corresponding polymers were obtained through electropolymerisation. Electrochemical and spectroelectrochemical properties of the obtained compounds were investigated. The result revealed that all the compounds undergo reversible reduction and irreversible oxidation processes, whose onset redox potentials are a function of the central acceptor units. The irreversible oxidation of the monomers leads to formation of a polymer film, and the resulting polymer is capable of hosting polaron- and polaron-pair charge carriers. Summarising, easily polymerizable ambipolar low-band gap organic semiconductor molecules comprising alkylbithiophene and chalcogenodiazole motifs were synthesised and characterised. Fine tuning of physicochemical properties of both monomers and corresponding polymers is possible depending on the combination of two different electron-withdrawing chalcogenodiazoles paired together in an asymmetric acceptor unit.

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#### ELECTRODE-ELECTROLYTE INTERFACE AT NANOSCALE: SURFACE SCIENCE APPROACH

A. Bondarchuk

International Iberian Nanotechnology LaboratoryBraga, Portugal E-mail (corresponding author): alex.bondarchuk@inl.int

Currently, commercially available supercapacitors (SC) - make use of activated carbon (specific surface area ~1000 m2g-1 and specific surface capacitance ~0.01mF cm-2) as the electrode material and water based electrolytes (potential window limited to 1.23 V) - have almost reached their capacitance limits. The main charge storage mechanisms in SC are: charge accumulation in electrical double layer (EDL) and Faradaic (redox) reactions at the electrolyte-electrode interface. In this talk we report on an alternative charge storage mechanism – space charge accumulation in a subsurface layer of ~100 nm – experimentally observed in pure VN thin films and responsible for impressively high surface capacitance up to ~3 mF cm-2 in aqueous electrolytes. Combining electrochemical testing with X-ray photoelectron spectroscopy (XPS) has revealed that redox reactions play no or little role in the electrochemical response of pure VN, in contrast to the common wisdom stemming from the electrochemical response of oxygen-containing films.

Room temperature ionic liquids (RTIL) (electrochemical window up to 6 V, thermos- stable up to ~300oC) have been introduced as an alternative to aqueous and organic (electrochemical window 2.5-2.8 V, flammable) electrolytes [1]. Recently it has been reported, that in the concentrated electrolyte solutions (1-10M), including room temperature ionic liquids, the Debye length is ~100 times (!) larger then that predicted by classical the Debye-Hückel theory, thus revealing remarkable long range interactions in concentrated solutions regardless of their chemical composition [2]. In this work we address the puzzling problem of the long range interaction (~10nm) in concentrated electrolytes by taking "surface science" approach combining in-situ electrochemical XPS, AFM, SEM and thin film deposition techniques (thermal evaporation in vacuum). The experimental setup allowed to measure potential distribution in the interface between HOPG and imidazolium based RTILs ([Emim][FSI], [Emim][TFSI], [C8mim][TFSI]). Mapping of the electrochemical shifts of the XPS lines was deployed to measure potential gradient across the electrode-electrolyte interface. We observed potential driven reversible morphological transformations of the RTIL, which was tentatively explained as the liquid-solid transition under the conditions when the screening length was comparable with the thickness of the electrolyte layer - conditions characteristic of nanoconfinement of liquids in porous and in solvation shells.

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#### FABRICATION OF QUANTUM DOT PHOTONIC STRUCTURES BY XENON PLASMA FOCUSED ION BEAM

Maciej Jaworski (1,2), Aleksandra Chudzyńska (2,3), Paweł Mrowiński (1), Grzegorz Sęk (1)

1. OSN Laboratory, Department of Experimental Physics, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

2. Nanores, Bierutowska 57-59, 51-317 Wrocław, Poland

3. Department of Optical Spectroscopy W. Trzebiatowski Institute of Low Temperature and Structural Research of the Polish Academy of Sciences, Okólna 2 Wroclaw 50-422, Poland

We demonstrate a 3D processing of GaAs-based photonic microstructures with quantum dots (QDs) using xenon-plasma focused ion beam (Xe-PFIB) technology. The sample contains InGaAs/GaAs QDs covered with InGaAs strain reducing layer to red shift the emission towards the telecom O-band. By using a series of structures with different cap layer thickness in range of 50 nm to above 600 nm we fabricated cylindrical mesas to find optimal conditions with respect to the emission from optically active QDs to examine the limitations of the used processing methodology. In the first approach we used Xe-PFIB for both reducing the cap layer thickness as well as the in-plane shaping of the microstructures. Whereas in the second approach we used wet chemical etching for cap layer removal and subsequent Xe-PFIB for the in-plane milling. The latter appeared more efficient and allowed us to get bright photoluminescence from single QDs. We also calculated the emission extraction efficiency for various microstructure geometries to find the optimized geometrical parameters. Eventually, in order to minimize the ion-induced material degradation even further, we processed a sample with 200 nm cap of an additional protecting layer of platinum, efficiency of which found confirmation in the microphotoluminescence spectra. These results indicate on suitability of processing efficient QD-based single-photon Xe-PFIB sources for for quantum communication.

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#### FUTURE PHOTOSENSITIZING MATERIALS - SYNTHESIS AND CHARACTERIZATION OF PERYLENE DERIVATIVES

K. Socha (1), K. Nastula (1), R. Motyka (2), A. Blacha-Grzechnik (1,3),

1. Department of Chemistry, Silesian University of Technology, Gliwice, Poland

2. Center for Polymer and Carbon Materials, Polish Academy of Sciences, Zabrze, Poland

3. Silesian University of Technology, Center for Organic and Nanohybrid Electronics, Gliwice,

Poland

E-mail: karolina.socha@polsl.pl

The observed increase in drug resistance among bacteria constitutes a threat and is the basis for searching for new solutions to eliminate pathogenic microorganisms that we can find on the surfaces surrounding us. One possible solution to this problem is the use of singlet oxygen (1O2), which is characterized by antibacterial, antiviral and antifungal properties.1

The mechanism of action of singlet oxygen is based on its high chemical reactivity. An excited 1O2 molecule seeks to reduce its energy state, which is achieved in the oxidation of various substances. It reacts readily with lipids, proteins and nucleic acids, changing their structure.2 Singlet oxygen can be created by photogeneration, in which a suitable photoactive molecule, called a photosensitizer, is excited by light and transfers excess energy to triplet oxygen to form reactive oxygen species (ROS).3

In the present work, new triplet photosensitizers based on perylene derivatives were obtained. Perylene dianhydride, as a compound with radiation energy acceptor properties, was modified to obtain compounds with better solubility and by attaching donor groups - phenothiazines, which are highly bioactive and have wide applications. Phenothiazines are electron donors and transfer charge with multiple acceptors, yielding compounds that are promising triplet photosensitizers. An attempt was made to attach surface-anchoring groups, like (3-aminopropyl)triethoxysilane APTES, to such a compound for futher immobilization of PDI-derivatives on a surface. As a result, it is possible to obtain an antimicrobial surface with non-selective and multipotential activity having wide applications in the medical sector, among others.

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#### HOW TO TAME NANOMATERIALS IN DISPERSION? THE LUBRINAN PROJECT

J. Woch (1), I. Scudło (1), K. Korasiak (1), B. Dejnega (1), A. Drop (1), H. Mitka (1), M. Osika (2), D. Koltsov (3) 1. Łukasiewicz Research Network – Institute of Heavy Organic Synthesis "Blachownia", Kędzierzyn-Koźle, Poland 2. Orlen Oil Sp. Z o.o., Gdańsk, Poland 3. BREC Solutions, Warsaw, Poland E-mail: julia.woch@icso.lukasiewicz.gov.pl

The LUBRINAN project focuses on the development of a number of lubricants, in which conventional additives are being replaced or supplemented with nanocomponents. The introduction of nanomaterials aims at improving the anti-wear and anti-seizure properties of lubricants at elevated temperature, higher pressure and long operating time of mechanical devices [1]. Whether it is aqueous or non-aqueous dispersion, the application of nanomaterials in practice is challenging and limited because of difficulties with formation of stable liquid dispersions. It is not usually acceptable for the dispersion such as an industrial lubricant to form sediment or sludge. When dispersed in liquid media, CNTs and other carbon-based nanomaterials are prone to aggregation, which results in sedimentation or flocculation.

When nanometals such as silver or copper are used in more complex liquid compositions, they tend to interfere and react with other ingredients, effecting the product's stability and performance.

The poster presents different solutions used in the LUBRINAN project to obtain more stable dispersions, in relation to the formation of deposits and sludge, as well as maintaining the dispersions quality. For the preservation of aqueous dispersion, we used modified nanoparticles (made by core-shell technique) to not interfere with other ingredients. For delaying the aggregation of carbon materials we use a combination of methods, assuming chemical modification of nanomaterials and various homogenization techniques.

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#### INFLUENCE OF Gd 3+ CO-DOPING ON OPTICAL PROPERTIES OF Eu3+ IONS IN SOL-GEL MATERIALS

J. Śmiarowska (1), N. Pawlik (1), T. Goryczka (2), W.A. Pisarski (1) 1. University of Silesia, Institute of Chemistry, Szkolna 9 Street, 40-007 Katowice, Poland 2. University of Silesia, Institute of Materials Science, 75. Pułku Piechoty 1A Street, 41-500 Chorzów, Poland

E-mail (corresponding author): asiasmiarowska@gmail.com

In recent years, rare-earth-doped materials have gained considerable attention of researchers. Among rare-earths, Eu3+ ions are the most widely used dopant due to strong emission in the reddish-orange light spectral range as well as the possibility to be used as spectroscopic probes [1]. Additionally, one of the strategies to improve the luminescence efficiency is an indirect excitation of Eu3+ ions via energy transfer, using other rare earth ions, like Gd3+, as a sensitizer. Energy transfer between Gd3+ and Eu3+ ions is possible because of the relatively small energy gap between their certain energy levels. Hence, co-doping optical materials with Gd3+ ions could significantly enhance the luminescence of Eu3+ [2,3].

In this work, the series of sol-gel materials co-doped with Gd3+ and Eu3+ ions were synthesized. The fabricated xerogels with the variable La3+:Gd3+ molar ratio in composition were further processed into glass-ceramics containing LaF3:Gd3+, Eu3+ nanocrystals. Crystallization of fluoride nanophase was verified by using X-ray diffraction (XRD). The spectroscopic properties were studied through analysis of PLE ( $\lambda$ em=612 nm) and PL spectra recorded via direct ( $\lambda$ exc=393 nm) and indirect ( $\lambda$ exc=275 nm) excitation pathways. Furthermore, decay curves were recorded for the 6P7/2 state of Gd3+ ions. Based on determined lifetime measurements, Gd3+  $\rightarrow$  Eu3+ energy transfer efficiencies were estimated. Moreover, the R/O- ratio values (defined as intensity ratio of 5D0  $\rightarrow$  7F2/5D0  $\rightarrow$  7F1 transitions) were calculated to examine the changes in local environment symmetry around Eu3+ during controlled heat- treatment. The influence of heat-treatment and increasing amounts of Gd3+ ions in the samples on the luminescent performance of Eu3+ ions has been studied.

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#### INVESTIGATION OF SYNTHETIC METHODS OF SOME 1H-PYRAZOLO[3,4-B]QUINOLINES FOR NANOSENSORS

A. Danel (1), O. Havrysh (1), K. Markiel (1), E. Porębska (1), E. Tokarska (1) 1. Krakow University of Technology, Department of Materials Engineering and Physics, Krakow, Poland E-mail: andrzej.danel@admin.pk.edu.pl

Pyrazoloquinolines are azaheterocyclic systems exhibiting intense blue and green fluorescence. This phenomenon has been used to fabricate organic electroluminescent cells OLED in the form of dopants in polymer matrice and as vacuum evaporated layers Moreover these class of compounds was applied as fluorescent sensors for various cations[1]. The synthetic methods used so far include the Friedländer condensation, reactions of aromatic amines with 4-formyl-5-chloropyrazoles and three-component synthesis using aromatic amines, substituted aromatic aldehydes and appropriate pyrazolones. All these methods have their limitations and disadvantages when it comes to the final product. Details are described in the review publication on 1H-pyrazolo[3,4-b]quinolines[2]. Recently, we came across an interesting publication that describes the reaction for obtaining 4-aryl-4,9-dihydro-1H-pyrazolo[3,4b]quinolines in a multi-component reaction from aniline, aromatic aldehydes, pyrazolones and L-proline as a catalyst[3]. The reaction took place under relatively mild conditions and the yields of the obtained products were around 80-90%. We decided to check the suitability of this procedure for our applications and unfortunately it turned out that we were unable to repeat the described results. To be sure, we obtained the compounds described in the publication using a different method and used them as standards for the previously mentioned reaction. It turned out that the compounds described by the authors are not formed even in trace amounts. For this reason, fluorescent chelating units will be synthesized using other methods and then attached to silica nanoparticles SNP.

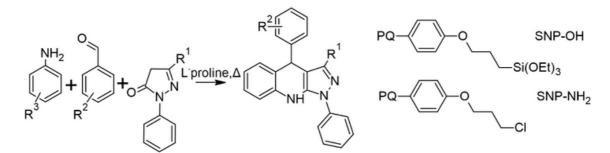


Fig.1. The scheme of investigated three component reaction leading to 4-aryl-4,9-dihydro-1H-pyrazolo[3,4-b]quinolines and general structures of modified PQ fluorescent sensors for SNP modification.

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#### IONIC NANOCARRIERS FOR THE DELIVERY OF PHARMACEUTICAL ANIONS IN ANTITUBERCULOSIS THERAPIES

Aleksy Mazur (1), Dorota Neugebauer (1)

 Department of Physical Chemistry and Technology of Polymers, Faculty of Chemistry, Silesian University of Technology, 44-100 Gliwice, Poland. E-mail (corresponding author): aleksy.mazur@polsl.pl

Due to the intricate nature of certain illnesses and the potential harmful effects of medications, there is a growing focus on enhancing drug-delivery methods. Polymeric nanoparticles are emerging as crucial tools to boost drug efficiency or control its delivery. The versatility of polymers suggests they are well-suited to meet the unique demands of drug-delivery system [1].

The main goal of this research was to develop a novel approach for delivery of antituberculosis drug using a polymerizable ionic liquid (IL) derived from choline, specifically

[2-(methacryloyloxy)ethyl]trimethylammonium chloride (TMAMA). This compound was biofunctionalized through an ion exchange with para-aminosalicylate (PAS), a currently available antibiotic for tuberculosis treatment. The resulting biocompatible IL monomer (TMAMA/PAS) was copolymerized with methyl methacrylate (MMA) via "grafting from" technique to produce ionic graft conjugates. The multifunctional macroinitiators were used to regulate a grafting degree of the side chains which varied from 18 % to 48 %. Number of monomeric units in conjugates were assessed based on monomer conversions. The polymeric side chains, varied in length from 12 to 89. Copolymers contained adjusted ionic fraction with up to 49 % PAS anions, serving as drug nanocarriers. During in vitro tests, drug release was initiated by ion exchange in a PBS medium, resulting in a release range of 71-100 % (2.8-9.8  $\mu$ g/mL).

Controlled polymerization of TMAMA/PAS allowed to obtain a series of well-defined conjugates with significant drug content and effective PAS release. These nanocarriers are seen as promising drug delivery systems for tuberculosis treatment.

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#### ILUMINESCENT DYES IN CORE/SHELL STRUCTURES AS POTENTIAL MATERIALS FOR LUMINESCENT SOLAR CONCENTRATORS

K. Wojtasik (1), B. Pacyna (1), W. Kłos (1), M. Wełna (1), M. Zięba (2), K. Matus (3), E. Gondek (1), P. Karasiński (2)

1. Department of Physics, Faculty of Materials Engineering and Physics, Cracow University of Technology, Kraków, Poland

2. Department of Optoelectronics, Faculty of Electrical Engineering, Silesian University of Technology, Gliwice, Poland

3. Materials Research Laboratory, Faculty of Mechanical Engineering, Silesian University of Technology, Gliwice, Poland

E-mail (corresponding author): katarzyna.wojtasik@pk.edu.pl

Photovoltaics is currently one of the most dynamically developed renewable energy sources (RES) [1]. Despite this, the efficiency of the use of photovoltaic panels remains far from optimal. In order to improve their efficiency and reduce production costs, solar radiation concentrators are additionally introduced. Solar radiation concentrators can be reflective, lens or luminescent. Luminescent concentrators (LSC - Luminescent Solar Concentrator) unlike the others, they also operate efficiently in cloudy conditions, which is their big advantage [2]. The development of an ideal structure with the best properties is the subject of research by many centers around the world. Materials for LSC matrices with optimal properties are being sought (high refractive index, high level of phosphor solubility, possibility of optical coupling with photovoltaic cells, high stability in various atmospheric conditions). On the other hand, new phosphors with characteristic properties are being sought (large Stokes shift, photostability, high luminescence quantum yield, broad absorption spectrum, good solubility in the matrix). The problem of the solubility of the phosphor in the matrix is an important issue due to, among other things, the tendency of particles to agglomerate at high concentrations in the matrix. One way to improve this property of phosphors is to trap dye particles in a silica shell (core/shell structure) [3].

The aim of the presented work was to compare the photophysical properties of a selected luminescent dye among 1H-pyrazolo[3,4-b]quinoxaline derivatives (PQX) and this dye trapped in silica (PQX/SiO2). The influence of these dyes on the optical properties of chemically doped silica layers was also investigated. The core/shell structures were created using the modified Stöber method, while the layers with dyes were created using the sol-gel method and the spin-coating technique.

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#### MULTILAYER SYSTEMS WITH NANOMETRIC LAYERS THICKNESS OBTAINED BY ELECTROLYTIC DEPOSITION

M. Spilka, R. Babilas, W. Łoński Silesian University of Technology, Gliwice, Poland E-mail (corresponding author): monika.spilka@polsl.pl

The demand for engineering materials with properties that enable work in difficult conditions forced the development of new materials, including multi- and thin- layer systems. The concept of these materials is based on an alternating sequence of thin non-magnetic and magnetic layers just a few nanometers thick. In recent years, multilayer systems have gained importance due to their gigantic magnetoresistance (GMR) properties. Multilayer systems are usually produced using physical vapour deposition techniques, but the electrolytic deposition method, although a traditional process, still provides the opportunity to develop new materials with unique properties by controlling the deposition parameters [1-3].

The work involved the production of multilayer systems consisting of ferromagnetic layers (Co, Ni), separated by layers of nonferromagnetic metal (Cu), with a variable number and thickness of layers deposited on a different substrate. The Co/Cu and Ni/Cu multilayer systems obtained by electrolytic deposition were subjected to investigations of microanalysis of the chemical composition using an energy dispersive X-ray fluorescence spectrometer (XRF). The thickness of the layers was determined by calculation method and on the basis of observations of sample cross-sections using a scanning electron microscope (SEM). The surface topography of multilayer systems was examined using an atomic force microscope (AFM), determining roughness parameters. The corrosion resistance of the samples was measured using the potentiodynamic method by recording the change in open circuit potential (EOCP) during 3600 s. Corrosion current density (jcorr), polarisation resistance (Rp) and corrosion potential (Ecorr) were determined by extrapolation of Tafel curves. The change in the surface of the systems after electrochemical tests was also observed. Moreover, the magnetic properties of multilayer systems were performed by a vibrating magnetometer.

It was found that the electrolytic deposition method can produce multilayer systems with nanometric layer thicknesses, which are characterised by a compact and homogeneous structure. The number of deposited layers and their thickness have a direct impact on the corrosion resistance of multilayer systems and magnetic properties. The open-circuit potential for all samples became negative with immersion time, so the tested systems are not completely resistant to corrosion. The results of magnetic properties tests showed that these multilayer systems can be classified as magnetically soft materials.

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#### NANOINDENTATION BEHAVIOR OF Mg65Zn30Ca4Pr1 ALLOY PRODUCED BY POWDER METALLURGY

J. Popis (1), S. Lesz (1), B. Hrapkowicz (1), M. Basiaga (2)

1. Silesian University of Technology, Faculty of Mechanical Engineering, Department of Engineering Materials and Biomaterials, Gliwice, Poland

2. Silesian University of Technology, Faculty of Biomedical Engineering, Zabrze, Poland Email (corresponding author): sabina.lesz@polsl.pl

The paper presents a study of the nanoindentation of Mg65Zn30Ca4Pr1 alloy powder produced by mechanical alloying after 20 and 70 h milling. Test results for sinters produced using the Spark Plasma Sintering method were also presented. The tests were carried out on the Micro Indentation Tester (MHT) from CSM Technical Features. The values of Indentation Hardness HIT, Vickers Hardness HIT, and Elastic modulus EIT are presented. The work presents the scanning electron microscopy results of the tested materials.

The sintered elements used improved the hardness and elastic modulus. After 20 h of milling, HIT and EIT were 2.2 GPa, 43.3, 4.2 GPa, and 86.8 for powder and sinter, respectively. Following after 70 h of milling, HIT and EIT were 1.7 GPa, 29.8, and 6.1 GPa, 109.3 for powder and sinter, respectively. The milling time also affects the tested parameters. The highest values of the tested parameters were obtained for sintered samples after 70 hours of milling.

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#### NEURAL NETWORKS AS A TOOL SUPPORTING THE IDENTIFICATION OF POLLUTANTS IN GROUNDWATER

P. Radek (1), M. Sładek (1), J. Tlołka (1), B. Zieliński (1), P. Kołodziejczyk (1), G.J. Nowak (2,3), M.M. Szindler (4), M. Szindler (5)
1.Students of the Silesian University of Technology, Faculty of Electrical Engineering, Gliwice, Poland
2. Silesian University of Technology, Faculty of Biomedical Engineering, Department of Biomaterials and Medical Devices Engineering, Zabrze, Poland
3. Łukasiewicz Research Network – Krakow Institute of Technology, Centre of Biomedical Engineering, Zabrze, Poland
4. Silesian University of Technology, Faculty of Mechanical Engineering, Department of Engineering Materials and Biomaterials, Gliwice, Poland
5. Silesian University of Technology, Faculty of Mechanical Engineering, Scientific and Didactic Laboratory of Nanotechnology and Material Technologies, Gliwice, Poland

E-mail (corresponding author): magdalena.szindler@polsl.pl

The article presents the possibility of using neural networks as a tool supporting the identification of metallic contaminants in groundwater. The article explains why water testing is and explains how neural networks can help important in water quality testing. The goal of the study was to obtain a network that efficiently determines the level of magnesium in groundwater. In order to train the network to recognize the appropriate concentration for metal ions, reference samples from magnesium salt (MgCl2  $\cdot$  6 H2O) with different concentrations were prepared. Prepared samples were examined using a spectrophotometer. The results obtained were used to create a database for learning neural networks. The network model was developed in the PyCharm 2022.3.3 environment. Having model thresholds and a learned network, it was decided to test samples taken from groundwater. The spectra of each water was shown in Figure 1.

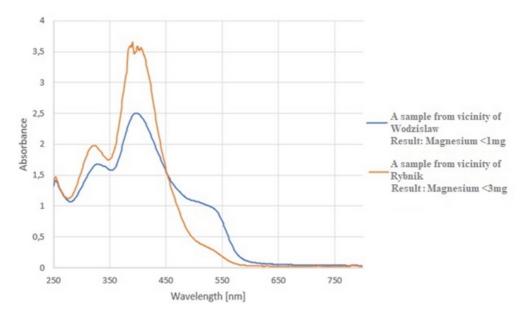


Figure 1. Wavelength dependence of absorbance for groundwater samples recognition of magnesium content using neural networks.

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#### NOVEL SNO2/SE ONE-DIMENSIONAL NANOSTRUCTURES

W. Smok (1), P. Jarka (1), T. Tański (1)

1.Department of Engineering Materials and Biomaterials, Faculty of Mechanical Engineering, Silesian University of Technology, Gliwice, Poland E-mail (corresponding author): weronika.smok@polsl.pl

Semiconductor one-dimensional (1D) nanostructures based on SnO2 are currently extremely popular due to optical transparency in the visible range, chemical stability, good electron mobility, and tunable band gap [1]. In order to improve the physicochemical properties of SnO2, nanowires can be decorated with nanoparticles of other materials. The latest reports indicate that it is worth paying attention to the addition of selenium to this oxide [2]. The aim of the work was to manufacture 1D SnO2/Se nanostructures using the electrospinning method with subsequent calcination. Analysis of the structure and morphology of the prepared material using SEM and TEM showed that it was in the form of porous nanowires with an average diameter of 140 nm, made of interconnected nanoparticles. Based on EDX mapping of a single nanowire, a uniform distribution of Se nanoparticles was observed throughout the entire volume of the structure. Additionally, FTIR analysis confirmed the chemical composition of the obtained material. The optical properties of the produced nanostructures were examined using a UV-Vis spectrophotometer. It was observed that the maximum absorption of electromagnetic radiation of nanowires lies in the near ultraviolet range. Moreover, the obtained composite semiconductor nanowires were compared with undoped SnO2 nanowires and it was shown that the addition of Se nanoparticles shifted the absorption edge towards visible waves, which significantly increases the application potential of this material in photocatalysis and photovoltaics.

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#### PERCHLORATES AND INORGANIC PEROXIDES AS GREEN ADDITIVES FOR ANFO

#### M. Fabin, T. Jarosz Silesian University of Technology, Department of Physical Chemistry and Technology of Polymers, Gliwice Magdalena.fabin@polsl.pl

Nitrate(V)-based explosives such as ANFO are inexpensive and easy to produce, but highly susceptible to a detonation failure, the remaining explosive in the shot-hole poses a significant risk to occupational safety and can become an environmental contaminant. This paper presents the results of a study on the addition of various chemical compounds from the chlorate(VII) group (Mg(ClO4)2, Ba(ClO4)2)and inorganic peroxides (NaBO3·nH2O, Na2CO3·1.5H2O2) to reduce the susceptibility of ANFO to detonation interruption and to improve detonation parameters.

In addition to the standard methods of friction or impact sensitivity testing, measurements were made using, among others, an ignition temperature (AET) apparatus. The tests showed an improvement in the thermal and energetic properties of the tested mixtures. An additional aspect is a slight increase in the sensitivity of ANFO denatured with selected compounds to simple stimuli, and a reduction in the decomposition temperature of ANFO with additives compared to unmodified ANFO.

Key words: perchlorates, inorganic peroxides, ANFO

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# PHOTOMECHANICAL EFFECT IN AMORPHOUS AZO POLYIMIDES

J. Konieczkowska, K. Nocoń-Szmajda, M. Siwy, E. Schab-Balcerzak Centre of Polymer and Carbon Materials, Polish Academy of Sciences, Zabrze, Poland E-mail (corresponding author): jkonieczkowska@cmpw-pan.pl

Amorphous azo polymers are a wide group of materials intensively studied in the field of photonics and optoelectronics applications [1]. Exposure of the azo polymer layer/cantilever to a polarized light beam leads to multiple and reversible cycles of trans-cis-trans isomerization. This allows the generation of optical anisotropy in the material, allowing for the study of dichroism, birefringence or the recording of diffraction gratings [1,2]. In recent years, azo polymers have been used as advanced photosensitive materials in photomechanical studies [3], which opens new possibilities for their applications.

The photomechanical effect is usually observed for amorphous main-chain azo polyimides, where azobenzene groups are incorporated into the main-chain of the polymer backbone [3]. Our recent studies showed the presence of photomechanical effects on "side-chain" azo polyimides, where azo moieties are located as elements in the side chain of the polymer structure. The maximum bending of the cantilevers was in the range of  $30 - 40^{\circ}$ , depending on the flexibility of the polymer structure and content of azo dye (Fig. 1). No relaxation of the cantilevers to their original positions was found after 6 months after turning off the excitation light.

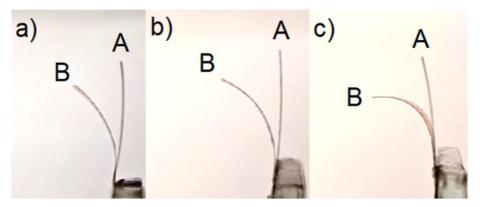


Fig. 1. Bending of the cantilevers for three azo polyimides different in chemical structure, where position "A" is the initial state, position "B" is after 1h of 405 nm light irradiation,

E || x. The laser beam propagation direction is from left to right.

This research was funded by the National Science Centre, Poland, grant number UMO-2019/35/D/ST5/00533.

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#### PHTHALIMIDE DERIVATIVES AS ELEMENTS OF HYBRID OPTOELECTRONIC DEVICES

Sonia Kotowicz (1), Ewa Schab-Balcerzak (1,2), Sebastian Maćkowski (3), Krzysztof Z. Łączkowski (4)
1.Institute of Chemistry, University of Silesia, 9 Szkolna Str., 40-006 Katowice, Poland
2. Centre of Polymer and Carbon Materials, Polish Academy of Sciences, 34 M. Curie-Sklodowska Str., 41-819 Zabrze, Poland
3. Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, 5 Grudziadzka Str., 87-100 Torun, Poland
4. Department of Chemical Technology of Pharmaceuticals, Faculty of Pharmacy, Nicolaus Copernicus University, 2 dr. A. Jurasza Str., 85-089 Bydgoszcz, Poland E-mail (corresponding author): sonia.kotowicz@us.edu.pl

Obtaining and characterizing the physicochemical properties of compounds dedicated to organic electronics is still a current research topic for many groups of scientists. The study of thermal and electrochemical properties and a wide-ranging study of optical properties allow for determining their physicochemical properties, which are vital when designing the structure of devices [1]. Obtaining information about the chemical structure and physicochemical properties of organic compounds enables their classification for applications in optoelectronic devices, such as light emitting diodes (OLEDs), dye cells (DSSCs) or perovskite cells (PSCs). An important aspect is also initial application research (pilot studies), during which we can simulate the conditions in the surrounding environment in real-time.

The presented research results are intended to indicate the structural elements of given groups of compounds in terms of their application possibilities in OLEDs as a blue emitters. The compounds were subjected to comprehensive physicochemical measurements: thermal, optical and electrochemical. They were melting at a temperature from 179 to 271 °C. DSC studies have shown that the five from seven compounds are a molecular glasses. The electrochemical investigations (in cyclic voltammetry and differential pulse voltammetry) have shown the low ionization potentials levels (-5.81 eV - -6.14 eV) and the energy band-gap below 3eV. Photoluminescence studies in solution, films, powder and blends with PVK:PBD showed their ability to emit light in the range from blue to green spectral region. On their basis, compounds with appropriate properties were used to verify their ability to electroluminescence in OLED devices, where they played the role of component in PVK:PBD matrix [2,3]. The obtained OLEDs (ITO/PEDOT:PSS/ compound:PVK:PBD/Al) were emit light from blue spectral region and get started to emit under external voltage about 10V.

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# PHYSICOCHEMICAL MODIFICATIONS OF CARBON NANOTUBES AND GRAPHENE

- I. Scudło (1), J. Woch (1), B. Dejnega (1), K. Korasiak (1), A. Drop (1), S. Boncel (2)
   1. ŁUKASIEWICZ Research Network Institute of Heavy Organic Synthesis
   BLACHOWNIA, Kędzierzyn-Koźle, Poland
  - 2. Silesian University of Technology, Faculty of Chemistry, Gliwice, Poland E-mail (corresponding author): ilona.scudlo@icso.lukasiewicz.gov.pl

The poster presents the research on chemical modification of carbon nanomaterials aiming totheir use as components of industrial lubricants.

Commercially available lubricants composed of base oil and conventional additives do not always provide the required performance, some issues related to insufficient friction reduction and rapid wear of machine components are being observed.

Carbon nanotubes and graphene show the potential to improve the lubricating properties of the media in which they are homogeneously dispersed [1, 2, 3]. These materials have ability to form a protective film at the point of contact between metal surfaces. The other mechanism of decreasing the friction is Rolling – enabling smooth sliding between two surfaces. It is also possible to smooth out irregularities on the contact surfaces of the working metals (Smothing asperities) and improve load transfer at the contact point, which is called Bearing.

The presented research are focused on chemical modification of carbon nanotubes and graphene aiming to their use as lubricant additives. Forming of their stable dispersions in hydrocarbons, which are the most used basis for industrial lubricants, presents certain difficulties. The proposed solution is the physico-chemical modification of nanomaterials with a strictly controlled morphology, which causes reduction of their tendency to agglomerate.

The functionalizing chemical units having potential to improve lubricating properties are presented together with functionalization pathways for carbon nanomaterials to obtain nanoparticles forming stable dispersions in hydrocarbons. The following functionalization reactions were performed in several steps via reactions with selected groups of aliphatic, aliphatic-aromatic and amphiphilic compounds:

I - obtaining a derivative with an amine bond: Nano-NH-linker

II - obtaining a derivative with an amide bond: Nano-CONH-linker

III - obtaining a derivative with an ester bond: Nano-COO-linker.

The dispersions containing functionalized nanomaterials were prepared and their lubricating properties were evaluated by determining the bonding load according to PN-EN ISO 20623:2018-02.

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#### 23 POLYCARBAZOLE AS RECEPTOR MATERIAL FOR ROOM TEMPERATURE HYDROGEN GAS SENSING

K Głosz (1), A Stolarczyk (1), T Jarosz (1), M Procek (2)
1. Department of Physical Chemistry and Technology of Polymers, Silesian University of Technology, Gliwice, Poland
2. Department of Optoelectronics, Silesian University of Technology, Gliwice, Poland E-mail (corresponding author): Karolina.Glosz@polsl.pl

The major issue with using hydrogen, is that H2 is highly flammable and able to explode in mixtures with air, at wide range of concentrations. The relevance of the flammability of H2 is increased due to its ease of leaking (due to its small molecular weight and tendency of auto-ignition of such leaks (due to its miniscule ignition energy). The high flammability of H2 and its ability to explode restrict many applications, because international and national regulations for dealing with possible explosive atmospheres require the monitoring of H2 concentrations in air at any relevant sites, in the case of an accidental H2 release.

Due to the fact that polycarbazole is a well-known conjugated polymer that has found application in organic photovoltaics, corrosion protection and gas sensing, we used polycarbazole as receptor material in our hydrogen gas sensors. In our study, we attempted to deposit polycarbazole on interdigitated Pt transducers from a solution, using electrochemical polymerisation.

In our work, at first we synthesized polycarbazole via cyclic voltammetry on interdigitated Pt electrodes. After that, we examined the obtained polymers layers in terms of their chemical structure (IR spectroscopy) and changes in their conductivity upon exposure to hydrogen gas, in order to investigate their potential as materials for chemoresistive hydrogen sensors.

The results of our investigations show that polycarbazole-based sensors are sensitive to hydrogen gas in the range of 1-4% (and even in further research sub ppm concentrations of hydrogen) at room temperature. Simultaneously, they have been fabricated using an inexpensive, cost-efficient and repeatable method, making for a promising sensing material.

This work was financed by the National Center for Research and Development in Poland under the M-ERA.NET 3 program in the framework of project: "Room temperature hydrogen sensors based on polycarbazole and its derivatives" (M-ERA.NET3/2021/93/HYDROSENS/2022).

#### PORPHYRINS AS VERSATILE PHOTOACTIVE MATERIALS – DUAL-APPLICATION OF OPTOELECTRONIC SYSTEMS

A. Nyga (1,2), M. Ferreira (1), I. Gusev (2), P. Pander (1,2,3), A. Blacha-Grzechnik (1,2)
1. Centre for Organic and Nanohybrid Electronics, Silesian University of Technology, Gliwice, Poland

 Faculty of Chemistry, Silesian University of Technology Gliwice, Poland
 Department of Physics, Durham University, South Road, Durham DH1 3LE, U.K. E-mail (corresponding author): <u>aleksandra.nyga@polsl.pl</u>

In the rush for better and more efficient optoelectronic systems such as organic photovoltaics, or organic light-emitting diodes, non-obvious applications of used organic compounds are often missing [1]. Due to that, the potential of promising materials is not fully recognized and, as a result, the development of fields at the border of photochemistry and photobiology is slowed down. For this reason, the main goal of the presented project is to determine the influence of structural changes on the photophysical and photochemical properties of investigated molecules, and consequently, on the application of the studied compounds. As one of the most versatile photoactive molecules, porphyrin derivatives become the project's focus. Porphyrins are well-known photoactive compounds applicable in various areas. i. They can be used in optoelectronic applications such as OLEDs or OPVs, biomedical applications, but also as photosensitizers (PS) for singlet oxygen (1O2) photogeneration e.g. in fine chemical synthesis [2]–[3]. Due to the characteristic structure of porphyrins and their modification susceptibility, these compounds are ideally suited to the project's goal as core compounds.

During the research, porphyrin derivatives, lacking a central atom and molecules based on a ruthenium core have been characterized for their emissive and photosensitizing abilities using absorption and emission spectroscopy. They were then used in the process of photogeneration of singlet oxygen as photosensitizing materials. Extensive studies of the changes in physicochemical and photophysical properties that occur with a change in structure will allow for a deeper understanding of this relationship and the identification of potential applications of the studied systems in various areas of photochemistry such as materials capable of singlet oxygen generation, photocatalysts or active layers in organic optoelectronics.

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SPARK PLASMA SINTERING AS A METHOD FOR MANUFACTURING IN NANOTECHNOLOGY

I. Kredowska (1), W. Pilarczyk (1)

1. Department of Engineering Materials and Biomaterials, Silesian University of Technology,

Konarskiego 18a St., Gliwice 44-100, Poland

E-mail (corresponding author): inez.kredowska@polsl.pl

Spark Plasma Sintering is known mostly by being an alternative for conventional methods by visibly reducing sintering time and using lower temperature of the process. [1] With this method it is also possible to manufacture materials which can be classified as nanomaterials. [2] SPS allows to achieve better mechanical properties of samples in the case of hardness or wear resistance. [3]

Chosen materials for manufacturing in this case were two commonly used grades of sintered carbide — S30 and S40S. Samples were sintered using HP 5 machine made by FC, at two different temperatures — 1250oC and 1275oC, but for the same time and the same pressure. It allowed to obtain samples with the same dimensions. For the research parts samples were prepared for testing by inclusion in STRUERS CitoPress-20, and were polished on STRUERS Tegramin-30, then evaluated for wear resistant by using Al2O3 ball as a counter sample, wear factor, microhardness in Vickers scale, weight in air and in water, and density by MPIF 42 method.

Research showed that SPS sintering method indeed allows to obtain samples with better process parameters and with better mechanical properties. Changes can occur even for a slight difference in process parameters like temperature. Hardness for samples was improved even for 200HV. Wear resistance is better. For S30 samples, the wear factor can be omitted because of its high resistance. Samples made from S40S grade showed comparable results in hardness and wear resistance improvement, also in reducing wear factor and weight of the samples.

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#### SPIN-COATED NANO-SURFACES WITH STAR-SHAPED POLY(IONIC LIQUID)

T. Fronczyk (1), A. Mielańczyk (1), O. Klymenko (2), D. Neugebauer (1)

- 1. Department of Physical Chemistry and Technology of Polymers, Faculty of Chemistry, Silesian University of Technology, M. Strzody 9 Street, 44-100 Gliwice, Poland
- 2. Department of Histology and Cell Pathology, School of Medicine with the Division of Dentistry in Zabrze, Medical University of Silesia, 41-808, Zabrze, Poland

E-mail (corresponding author): tomasz.fronczyk@polsl.pl

The expanding field of nanotechnology has caused an excess of applications, ranging from biomedical to environmental engineering. Within this scope, our current research aims to contribute to the understanding of star-polymer coatings with nanoscale thickness, specifically those fabricated from poly(2-(methacryloyloxy)ethyl trimethylammonium chloride) (PMETA) by spin coating. PMETA is an ionic polymer that exhibits antifungal and antibacterial properties, making it suitable for various surface modification purposes.[1]

The study is designed to elucidate the influence of three critical variables: rotational speed of spin coater, polymer arm length, and polymer concentration, on the morphological and surface properties of the resultant coatings.

The star-polymers employed in this investigation exhibited variable arm lengths to elucidate their influence on coating characteristics. Spin coating was executed on glass plates at rotational speeds 1500 and 5000 rpm and different PMETA concentrations of 0.5 mg/mL and 5 mg/mL. Subsequent characterization was performed using Atomic Force Microscopy (AFM) for topographical analysis, and a goniometer was employed to measure the contact angle, thereby assessing the wettability characteristics of the coatings.

Initial data reveal that higher rotational speeds (spin coating technique) result in thinner coatings, a finding that aligns with existing fluid dynamics data.[2] The study provides a comprehensive understanding of the role of studied variables in the fabrication of PMETA-based nano-height polymer coatings. The research serves as a foundational step towards the development of customizable nano-height coatings with tailored properties, thereby contributing to the broader scientific understanding of nanomaterial fabrication techniques.

This research was funded by the Polish Budget Funds for Scientific Research in 2023 as core funding for R&D activities at the Silesian University of Technology-funding for young scientists, grant number BKM-545/RCH4/2023 (04/040/BKM23/0259).

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## STABILITY EVALUATION OF DISPERSIONS CONTAINING MICRO AND NANOPARTICLES

 J. Woch (1), N. Brzeźniak (1), K. Korasiak (1), A. Drop (1), K. Zielińska (1), B. Wąsik (1) and J. Iłowska (1)
 1. Łukasiewicz Research Network – Institute of Heavy Organic Synthesis "Blachownia", Kędzierzyn-Koźle, Poland E-mail: julia.woch@icso.lukasiewicz.gov.pl

The poster presents the methods of evaluation of stability of dispersions containing micro and nanoparticles used within the projects conducted by Lukasiewicz - ICSO "Blachownia", including the "MgO" project. One of the project's tasks assumes composition and determination of the suitability of an aqueous wax dispersion to reduce the flammability of wood-based boards.

The methodology assumes the use of light scattering techniques for quantification and describing changes in the studied liquid occurring over time. The dispersions containing colloidal particles and/or solid material suspended in continuous phase are a subject of these studies. The stability, expressed as differences in the quantified value of backscattered light is being observed within 90-days period and analysed by the software. After this time, the calculated value of stability index is compared to value scale, that we developed.

Studied dispersions are based on aqueous and wax phase, synthetic or natural-based, and are characterized with maximum droplet size about 370 nm, similar as the emulsions described here [1]. The size of the dispersion droplets is measured by dynamic light scattering or laser diffraction methodology. Some of the dispersions are enriched with solid particles of different sizes, soluble, or not soluble in aqueous phase. The stability of the particular formulation is the key issue, taking into consideration placement of the product on the market.

The other methodology that we are describing for fast detecting sedimentation in the dispersion containing solid nanoparticles, is static light scattering.

PROJECT CO-FINANCED FROM THE STATE BUDGET

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#### STRUCTURAL AND MICROSTRUCTURAL EVOLUTION OF CoFe2O4@SiO2 CORE-SHELL NANOCOMPOSITES BY ANNEALING

A. Czempik (1), A. Bajorek (1), F. Grasset (2), S. Auguste (3), A. Rousseau (3), N. Randrianantoandro (3)

- A. Chełkowski Institute of Physics, University of Silesia in Katowice, Chorzów, Poland
   Institut des Sciences Chimiques de Rennes, Université de Rennes, Rennes, France
  - 3. Institut des Molécules et Matériaux du Mans, Le Mans Université, Le Mans, France E-mail (Adam Czempik): adamczempik@gmail.com

Our study focuses on the structural, microstructural and magnetic characterization of coreshell-type composite particles CoFe2O4@SiO2 obtained by coprecipitation method followed by microemulsion process. They come in the form of several nanoparticles of spinel ferrite CoFe2O4, a few nanometers in diameter, coated in a porous silica ball, 40 to 80 nm in diameter.

Technologically, CoFe2O4@SiO2 composites are potential candidates in the field of data storage or medicine, where they are used as nanobiosensors for cancer diagnosis, a contrast agent in medical imaging (MRI) or potential drug candidates against cancer and microbial infections [1]. A stable structure with well-defined magnetic properties is therefore of great importance.

On a fundamental level, we seek to understand the influence of thermal stimulation and the environment on the composite structure and the stability of the ferrite-spinel core. Our contribution concerns a study of CoFe2O4@SiO2, where we present the results of the evolution of their structure and microstructure as a function of the annealing temperature. We also study their behaviour in magnetic field. The results were obtained by X-ray diffraction, transmission electron microscopy, Mössbauer spectrometry of 57Fe, magnetic measurements and X-ray photoelectron spectroscopy.

The CoFe2O4@SiO2 exhibits better crystallinity and more uniform magnetic properties, resulting in greater component stability. Some interesting effects like a decrease of lattice parameter by lower annealing temperatures or unusual jump on magnetic hysteresis loops were also detected. Such effects may be caused by the structural changes of the tested nanometric compound by annealing treatment. The component is still being investigated for the impact of the annealing process on the electronic structure as well as possible interactions between the MFO cores and silica shells.

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#### SUPERHYDROPHOBIC NANOCARBON-BASED MATERIALS

M. Małecka (1), S. Boncel (1)

 Department of Organic Chemistry, Bioorganic Chemistry and Biotechnology, Faculty of Chemistry, Silesian University of Technology, Gliwice, Poland E-mail (corresponding author): magdalena.malecka@polsl.pl

Over the past decades since the discovery of fullerenes in 1985, carbon nanotubes in 1991, and graphene in 2004, research interest focused on carbon nanomaterials and their properties. [1] One of these features is superhydrophobicity demonstrated by coatings, surfaces and composites made using carbon nanomaterials like: fullerenes, graphene, graphene oxide, carbon nanotubes (single-walled, double-walled and multi-walled) and carbon nanohorns as well as their functionalized forms.

Materials called superhydrophobic exhibit contact angle of water droplet on solid surface larger than 150° and a sliding angle smaller than 10°. Superhydrophobicity is a result of combining roughness and low surface energy material. [2]

Superhydrophobic properties of nanocarbon materials give opportunity to potential use them as sensors, anti-corrosion, anti-icing, anti-biofungical and biomedical materials as well as in technology of oil separation.

In my brief poster review, I would like to focus on sp2-hybridized carbon nanomaterials such as graphene, carbon nanotubes, nanohorns, nanofibres, and fullerenes - both as pristine and functionalized materials. I would like to show the current state-of-the-art considering the number of articles discussing selected types of carbon nanomaterials and their potential applications. Next, I would like to discuss the properties of the most interesting superhydrophobic materials characterized by the larger contact angle.

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#### THE APPLICATION OF A GEL ELECTROLYTE CONTAINING AZOBENZENE DERIVATIVES IN DYE-SENSITIZED SOLAR CELLS (DSSCS)

P. Gnida (1), J. Konieczkowska (1), M.F. Amin (1), A. Jankowski (1), E. Schab-Balcerzak (1,2)

1. Centre of Polymer and Carbon Materials, Polish Academy of Sciences, 34 M. Curie-Sklodowska Str., 41-819 Zabrze, Poland

2. Institute of Chemistry, University of Silesia, Szkolna 9, 40-006 Katowice, Poland E-mail (corresponding author): pgnida@cmpw-pan.pl

Given the ever-increasing demand for electricity, as well as increasing levels of environmental pollution, much attention and work should be devoted to developing renewable energy sources to replace fossil fuels. In addition to being an environmentally unfriendly way to generate electricity, the use of fossil fuels is also becoming increasingly expensive due to extraction from increasingly hard-to-reach locations. Currently, one of the most intensively developed branches of renewable energy sources is photovoltaics. Solar cells, especially organic solar cells classified as third generation, are the object of research by many groups of scientists around the world. Among them can be distinguished dye-sensitized solar cells (DSSCs) [1]. However, due to the operating conditions of this type of devices, a significant disadvantage is the use of liquid electrolyte.

The work sought to replace the liquid electrolyte containing the I-/I3- redox pair with a gel electrolyte, thus obtaining quasi-solid state dye-sensitized solar. The use of a polymer electrolyte makes it possible to reduce the adverse effects of atmospheric conditions such as temperature change, which results in increasing or decreasing solvent volume in the device, and consequently may cause a decrease in solar cell performance [2]. However, it should be borne in mind that charge mobility in the polymer electrolyte is hindered compared to its liquid counterpart, hence the idea of using azobenzene derivatives to aid charge transport due to the possibility of trans-cis isomerisation [3]. This effect was sought to be exploited in the present work. Preliminary studies were mainly carried out using the commercial ruthenium dye N719. In the experiments carried out, better results were achieved with the azobenzene derivative mainly through an increase in Voc and Jsc. This resulted in an increase in efficiency from 1.77% (reference cell) to 2.06% (10% AZO).

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#### THE EFFECT OF DIFFERENT NANOADDITIVES ON THE LUBRICATING PROPERTIES OF LUBE OILS

A. Drop (1), K. Korasiak (1), I. Scudło (1), J.Woch (1), B. Dejnega (1), M. Osika (2), D. Pykosz (2)

1. Łukasiewicz Research Network - Institute of Heavy Organic Synthesis "Blachownia",

Kędzierzyn-Koźle, Poland

2 Orlen Oil Sp. Z o.o., Gdańsk, Poland

E-mail (corresponding author): adam.drop@icso.lukasiewicz.gov.pl

Lubricant additives are organic or inorganic substances in liquid or powder form that, when added to oils, greases or other lubricating materials, improve their lubricating and protective properties. Nanotechnology has become a promising area of research in the development of lubricants, enabling the improvement of their properties in a precise and concentrated manner. Nano-additives, such as carbon nanotubes and nanosilica, offer unique possibilities in modifying the properties of lubricants.[1] They are able to improve wear resistance, reduce friction and increase durability in various types of machines and mechanical devices. The current problem with their use in oil bases is the lack of stability of the dispersions prepared in this way.[2] This is related to their properties characterized by the formation of agglomerates in a very short time after being introduced into the oil base. A solution that can significantly improve this problem is their chemical and/or physical modification of individual nanoadditives, which not only increases the stability of the resulting oil suspensions, but also the possibility of giving them the desired tribological features for specific industries.

The results of the conducted research suggest that a properly selected combination of modified carbon nanotubes and modified nanosilica can significantly improve the anti-wear properties and friction resistance of lubricants. Ultimately, by developing more advanced and effective lubricants, we contribute to improving the efficiency of mechanical devices and reducing energy consumption, which has a significant impact on the economy and the environment.

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#### THE INFLUENCE OF METAL CATION AND SUBSTITUENT ON THE ELECTROCHEMICAL AND SPECTROELECTROCHEMICAL PROPERTIES OF PORPHYRIN DERIVATIVES

M. Zawadzka (1,2), P. Wagner (3), M. Łapkowski (1,2,4), S. Pluczyk-Małek (1,2)
1. Faculty of Chemistry, Silesian University of Technology (SUT), Gliwice, Poland
2. Centre for Organic and Nanohybrid Electronics, SUT, Gliwice, Poland
3. Intelligent Polymer Research Institute, University of Wollongong, Wollongong, Australia
4. Centre of Polymer and Carbon Materials of the Polish Academy of Sciences, Zabrze, Poland magdalena.zawadzka@polsl.pl

Multifunctional electro- and photoactive organic materials have gained great popularity in recent years due to their properties enabling their use in organic electronics, optoelectronics and photovoltaics. Their characteristic features include, among others, the ability to quickly and reversibly respond to an external stimulus (electrical potential), high electrochemical stability and absorption of electromagnetic radiation in a wide range of wavelengths. Electroactive materials are used in organic light-emitting diodes (OLEDs) and displays [1]. In turn, photoactive compounds, such as porphyrins, are popular materials in photodynamic therapy (PDT). They may contain cations of various metals located centrally in the porphyrin ring and may be additionally functionalized with groups of various chemical nature [2].

The influence of the presence of zinc and copper cations in the porphyrin ring and the type of organic substituent:  $\alpha$ -terthienyl and 3,4-ethylene-1,4-dioxythiophene on the electrochemical and spectroelectrochemical properties was investigated. Electrochemical characterization was performed by cyclic voltammetry, and analysis of spectroelectrochemical properties using UV-Vis-NIR spectroelectrochemistry. The measurements made it possible to assess the electrochemical stability and reversibility of redox processes, as well as to determine the impact of the applied potential on the optical properties of the tested compounds.

The conducted analyzes confirmed the electroactivity of all tested derivatives. The materials underwent quasi-reversible electrochemical oxidation and quasi-reversible electrochemical reduction. Additionally, in the case of the derivative containing the zinc cation and EDOT, it was observed that a thin, orange layer of film (polymer) was deposited on the working electrode.

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#### THE INFLUENCE OF METAL CATION AND SUBSTITUENT ON THE THE SELF-HEALING BIOPOLYMER'S COATING WITH NANOHAP ADDITION ON ZINC ALLOY

K.Cesarz-Andraczke

Department of Engineering Materials and Biomaterials, Faculty of Mechanical Engineering, Silesian University of Technology, Gliwice, Poland E-mail (corresponding author): <u>katarzyna.cesarz-andraczke@polsl.pl</u>

The research conducted in this work focuses on determining the self-healing properties of a new functional material from the group of intelligent materials intended for biomedical applications. The work presents the research results on the observed self-healing phenomenon of a biopolymer's with nanoHAp layer formed on zinc alloy surface considered as a potential resorbable implant material. However, the idea of coating zinc alloys for biomedical applications has already been explored. Both the authors of paper [1] and paper [2] indicate that coatings for zinc alloys intended for implant applications are necessary to increase the biocompatibility of the alloy itself, and in particular to control the amount of zinc ions released into the recipient's body. In this work the proposed bath coating to create self-healing protective layers based on casein from caw milk on the biocompatible zinc alloy, which will ensure controlled release of degradation products and its steady progress. The results of microscopic observations confirm the phenomenon of self-healing of the produced layer after an hour immersion in Ringer's solution at 37°C. Both in the central part and on the edges of the previously created scratch, products resembling the morphology of the components of the casein coating are visible.

The paper analyzes the study's results explain the mechanism of self-healing and the influence of the given technological factors in the Ringer's solution at the 37°C. Taking into account the results, it was found that the self-healing mechanism of the casein-based layers consists of two main stages. The first stage is probably hydrolysis of casein, as a result of which it gets inside the scratch. The next stage is the movement of the nanoHAp powder bound in casein to the scratch area, and thus the formation of "ribs" connecting the edges of the scratch. Both stages probably occur simultaneously, only to a different extent in different scratch areas. It seems that nanoHAp particles play two roles: as a component of the self-healing layer and as a reservoir of casein as a healing agent. On the other hand, casein also has two roles as it serves as a component of the healing film and as a courier of nanoHAp molecules as healing ingredients. These materials therefore play complementary roles, making self-healing the nanoHAp-casein coating.

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#### THE STRUCTURE OF THE ALD LAYER AND ITS INFLUENCE ON THE PROPERTIES OF HYBRID PVD/ALD COATINGS

Marcin Staszuk

Silesian University of Technology, Department of Engineering Materials and Biomaterials, Konarskiego St. 18a, 44-100, Gliwice, Poland E-mail (corresponding author): marcin.staszuk@polsl.pl

PVD (Physical Vapour Deposition) coatings consisting of nitrides or carbides of metals mainly from the transition metal group usually provide high mechanical properties to the coated metal materials. However, their electrochemical properties are generally poor. This is due to microstructural defects present in these coatings, mainly the grain boundaries and craters present on their surface. Therefore, these coatings not only do not provide improved corrosion resistance, but often impair it. Therefore, to achieve high mechanical properties while maintaining high corrosion properties, the effect of the conditions of deposition of titanium oxide layers by the ALD (Atomic Layer Deposition) method on nitride PVD coatings was studied. PVD/ALD hybrid coatings were obtained. The coated substrates were 316L steel and Al-Si-Cu alloy [1].

The ALD process produced layers at 200, 500, and 1000 cycles. A low number of ALD cycles ensures the amorphous structure of TiO2. A completely amorphous structure of the layer is obtained in 200 ALD cycles. On the other hand, at 500 ALD cycles, there are already embryos of the amorphous matrix of the crystalline phase in the NSL (nanocrystalline level structure). The amorphous structure of titanium oxide influences a significant improvement in corrosion resistance by reducing the transport of electrical charges. There are already distinct crystalline grains of anatase in the TiO2 layer obtained at 1000 ALD cycles. This results in an increase in corrosion current and deterioration of the corrosion properties. Transformations in these layers driven by the difference in free energy between the different titanium oxides follow the Ostwald-Lussac law in the direction of the amorphous phase  $\rightarrow$  anatase  $\rightarrow$  rutile [1,2].

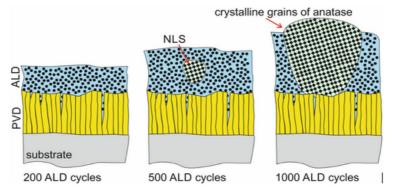


Fig. 1. Scheme of changes in the structure of the ALD layer in hybrid PVD/ALD coatings depending on the number of ALD cycles

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#### THE USE OF A LASER HEAT SOURCE TO IMPROVE THE MECHANICAL PROPERTIES OF 3D PRINTED ELEMENTS

S. Nowak (1), J. Popis (2), M.M. Szindler (2), M. Szindler (3)

1. Students of the Silesian University of Technology, Faculty of Mechanical Engineering, Gliwice, Poland

2. Silesian University of Technology, Faculty of Mechanical Engineering, Department of Engineering Materials and Biomaterials, Gliwice, Poland

3. Silesian University of Technology, Faculty of Mechanical Engineering, Scientific and Didactic Laboratory of Nanotechnology and Material Technologies, Gliwice, Poland

E-mail (corresponding author): sn307434@student.polsl.pl

In recent years, 3D printing has been gaining popularity due to the increasing access to materials with different properties and the accessible production process. One of the biggest disadvantages of the 3D printing process is the different strength relative to the object's axis. The mechanical strength drops significantly at the junction of the printing layers. In this work, we present attempts to eliminate this defect by providing additional thermal energy to liquefy the existing and newly applied layers, thereby improving the mechanical strength of the object's layers. Improving this characteristic will eliminate the strength analysis of the designed object, which will result in reduced costs, working time, and energy in the process of prototyping elements. In times of problems with waste recycling production, we strive to improve the production process to ensure the best use of available resources. This paper uses a laser beam to directly interfere with the printed material, changing the properties of the contact surface of the layers, which results in better adhesion and increased strength (Fig.1).

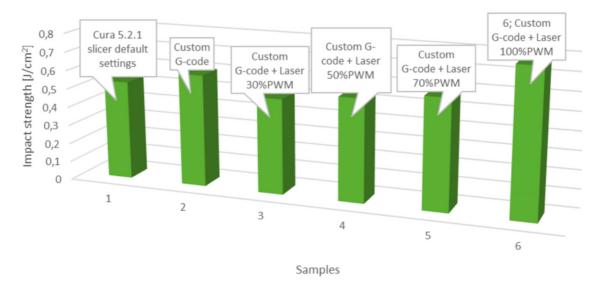


Figure 1. Charpy impact test results

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#### TOWARD SMART NANOCOATINGS: SUBTLE APPLICATION-DRIVEN TUNING OF FUNDAMENTAL ALUMINA THIN FILM PROPERTIES

A. Przybyła (1), P. Powroźnik (1) and M. Krzywiecki (1)

1.Institute of Physics – Centre for Science and Education, Silesian University of Technology, S. Konarskiego Str. 22B, 44-100 Gliwice, Poland

E-mail (corresponding author): aleksandra.przybyla@polsl.pl; maciej.krzywiecki@polsl.pl

Nanotechnology is one of the most high-ranking and rapidly growing branches of technology or industry. Materials covered with thin oxide layers are used in a wide range of applications. Aluminium oxide, as a thin layer, is applied, for example, in microelectronics, optical devices, protective and anticorrosive coatings, (bio)sensors, or molecular separation [1,2]. The presence of defects at the nanoscale can clearly influence the properties of materials. That is why the comprehensive characterisation of alumina's chemical, electron, morphological properties, and structural defects is crucial in designing modern applications [3,4].

In this work, we present how technological modification influences the thin layer's chemical, electron, and structural properties. For our research, we used the sol-gel method followed by spin-coating deposition. The technological process change was involved in the alteration of spin speed. In our research, we combine experimental data with modelled data for the most comprehensive description. The chemical and electron properties we determined through photoelectron spectroscopies in X and UV range and to define surface topography we applied atomic force microscopy. The results show that the thin layer's properties can be tuned to the desired application by controlling properties through the technological process.

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#### TOWARD THE TREATMENT OF A NEURODEGENERATIVE DISORDERS: POLYPYRROLE AS A MATRIX FOR RELEASE NEUROLOGICALLY ACTIVE DRUG SUBSTANCES

Sylwia Golba (1), Sara Krawczyk (2), 1. University of Silesia, Katowice, Poland 2. Doctoral School, University of Silesia, Katowice, Poland E-mail (corresponding author): <u>sylwia.golba@us.edu.pl</u>

Every year the percentage of people suffering from neurodegenerative diseases like Alzheimer's or Parkinson's disease that damage the neural system has increased. Such diseases weaken the body and lead to the destruction and death of nerve cells. There exist only two kinds of medical substances: acetylcholine inhibitors which are responsible for the breakdown of acetylcholine, which helps transmit impulses between neurons and maintain memory. The second kind of medicine is the N-methyl- D- aspartate receptor which blocks the effects of glutamate, a chemical that, when released in excessive amounts, damages neurons. Nowadays only available treatment contains medical substances that only alleviate symptoms like memory or movement problems but with low effectiveness [1]. The fundamental question arises - how to make a treatment more efficient?

To increase the effectiveness of the treatment of Alzheimer's disease and the regeneration of damaged nerves, a new neuroprotective layer with a polypyrrole matrix was proposed. Polypyrrole matrix with incorporated medical substance that is used for the treatment of neurodegenerative diseases was synthesized using electrochemical techniques. Polypyrrole is a polymer known for its conductive properties and biocompatibility. The research aimed to find a stable matrix which after applying potential will release effectively drug substances. Successful incorporation of drug substances was confirmed by Fourier-Transform Infrared Spectroscopy. Chronoamperometry was used to apply a constant potential to the matrix in terms of released medical substances. UV-Vis Spectroscopy was used to calculate the releasing curves of medical substances.

Results show that it is possible to obtain a stable matrix sensitive to potential stimulation that can effectively release drug substances. Such polymer matrix is loaded with the amount of substance that ensures the achievement of therapeutic doses in the treatment of Alzheimer's disease. The cargo can be released in a controlled way with on demand stimulation procedure.

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#### **I**-CONJUGATED COMPOUNDS FOR APPLICATIONS IN INORGANIC-ORGANIC SOLAR CELLS

A. K. Pająk (1,2), S. Kotowicz (1), E. Schab-Balcerzak (1,2)

1. Institute of Chemistry, University of Silesia, 9 Szkolna Str., 40-006 Katowice, Poland

2. Centre of Polymer and Carbon Materials PAN, 34 M. Curie-Skłodowskiej Str., 41-819

Zabrze, Poland

E-mail (corresponding author): agnpajak94@gmail.com

Despite the significant progress that has been made in recent years in the field of organic semiconductors, there is still a search for new, stable, and processable materials which are able to meet the continually increasing demands are being sought. To develop charge transport materials, critical to the further development of organic optoelectronics,

it is necessary to understand the correlation between the chemical structure and their essential properties in terms of application. Many publications on the search for new semiconductors focus on small-molecule compounds with defined semiconductor properties.

An intensive direction of global research concerns the search for a new generation

of processable organic semiconductors with the ability to transport positive charges (HTMs) for applications as layers covering perovskite in PSCs (perovskite solar cells).

HTM's task is the extraction and transport of holes from the perovskite to the electrode

in PSCs. Moreover, HTM prevents the transfer of electrons to the electrode and isolates the perovskite from it.

The presented results include fundamental research, i.e. the relationships between the chemical structure of the applied new low-molecular compounds containing  $\pi$ -conjugated bonds and crucial properties in organic electronics were determined, as well as the construction of FTO/b-TiO2/m-TiO2/perovskite/HTM/Au cells. Selected physicochemical properties of the compounds (electrochemical, thermal, absorption, emission) were tested, allowing to determine their application possibilities.

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#### THE NANOSTRUCTURED ZRO2 OBTAINED BY ANODIZATION IN A MIXED INORGANIC ELECTROLYTE

#### O. Tynkevych, K. Ryczek, J. Grzybowska, L. Zaraska Jagiellonian University, Krakow, Poland E-mail: olena.tynkevych@uj.edu.pl

In a recent decade, anodized ZrO2 has attracted interest due to its great potential for catalysis [1], chemical sensing [2] and biomedical implants technology [3]. The morphology of the anodized ZnO2 nanostructeres strongly depends on the anodization conditions as well as the type of used electrolyte.

The purpose of our study was to systematize data of Zr anodization in (NH4)2SO4/ NH4F electrolyte mixture. A one-step anodization at room temperature was used to prepare nanoporous anodic ZrO2 on the previously chemical polished Zr foil with high purity (99,2 %). The anodization was carried out in electrolyte mixture of 1M (NH4)2SO4 and 0,5% NH4F at different potentials (10-50V).

The effect of the anodizing potential and anodization time (10, 20 and 30 min) on the morphology and structural features of obtained anodized ZrO2 was studied. The linear dependencies between pore diameter and ZrO2 layer thickness depending on the anodizing potential were observed. Depending on the potential applied during anodization the diameter of nanopores within the ZnO2 layer can be adjusted from 20 up to 150 nm. An unusual surface morphology of the ZnO2 oxide films obtained at 30V was found. This tendency is preserved for all series of samples obtained at different durations of anodization. It was also found that stirring of the electrolyte has a noticeable effect on the thickness and morphology of the obtained ZrO2 layers.

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#### ANALYSIS OF THE FEASIBILITY OF THE INCREMENTAL MANUFACTURING PROCESS BY ATOMIC DIFFUSION METHOD UNDER LABORATORY CONDITIONS

D. Caus, D. Piwowarski, M. Polak, Ł. Ruba, J. Tarasiuk, S. Wroński Faculty of Physics and Applied Computer Science, AGH UST, Cracow, Poland tarasiuk@agh.edu.pl

Over the past two decades, digital design tools such as CAD (Computer Aided Design) have gained tremendous popularity, significantly speeding up the process of designing and manufacturing parts, especially with Additive Manufacturing (AM) technology. AM uses various processes to add material incrementally, allowing objects to be created layer by layer. Various advanced methods are used in the production of metal parts; however, these methods often generate macro- and microstructural defects, residual stresses, which limits their strength and applications. In recent years, new techniques have been developed, and a promising one is A.D.A.M. (Atomic Diffusion Additive Manufacturing) developed by Markforged. This 3D method involves extruding a mixture of metal and polymer, after which the part undergoes a sintering process, achieving a density of 99.7%. It is claimed that such parts are as strong as cast or forged, have isotropic mechanical properties, and are more cost-effective and promising in the industrial fields and applications [1][2].

The purpose of our research was to produce samples using the A.D.A.M. method under laboratory conditions: design and 3D printing samples with designed shape and filling (using BASF 316L filament), annealing, sintering and characterization of the produced samples using X-ray microtomography, scanning electron microscopy (SEM) and X-ray diffraction (XRD). Furthermore, the properties of the samples produced by the filament manufacturer were analyzed and compared with the samples produced under laboratory conditions. We found that the produced samples exhibit no residual stress, are isotropic and have the desired crystallographic structure. Due to insufficient sintering time the structure is not perfectly merged, but further research would allow us to optimize the sintering conditions.

The results obtained are a strong foundation for research in the field of atomic diffusion methods under laboratory conditions and a valuable source of knowledge for further material analysis.

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# ORGANO-MODIFIED LDH NANOFILLERS ENDOWING MULTI-FUNCTIONALITY TO BIO-BASED POLY(BUTYLENE SUCCINATE)

A. A. Marek (1)

#### 1. Faculty of Chemistry, Silesian University of Technology, Gliwice, Poland E-mail (corresponding author): adam.a.marek@polsl.pl

Polymers are one of the most important used materials in the world globalizing a whole production estimated at 311 million tons in 2014 and expected to double again in 20 years. About 26% of this total volume is used in packaging domains, for mostly single-use products. The enormous scale of production and use of polymers comes down to a large amount of generated waste. An alternative solution more sustainable may be the replacement of petroleum-based polymers by eco-friendlier and renewable materials like bio-based aliphatic polyesters which are more and more often used in products. One of the most promising member is poly(butylene succinate) (PBS), semi-crystalline polymer obtained by the direct poly-condensation of succinic acid (biobased) and butane-1,4-diol (partially bio-based). By the addition of organic and inorganic nanofillers, the properties of PBS can be significantly improved, thus making PBS possible to replace classical polymers in a wide range of applications.

Polybutylene succinate (PBS) were processed in melt extrusion by dispersion of organomodified layered double hydroxide (LDH). Depending on the organic anion interleaved into LDH fillers (L-tyrosine (TYR), L-tryptophan (TRP), L-ascorbate (ASA) and 3-(4hydroxyphenyl)propionate (HPP)), it was possible to control and tune the properties of the resulting PBS composites. Each LDH filler is found to act differently toward PBS, thus modifying its viscoelastic properties (as expressed by a chain extending effect), its antibacterial activity as well as its rate of hydrolysis and photo-degradation. The highest chain extending effect was observed in the case of LDH with L-tryptophan, the worst – with L-ascorbate anion. However, L-ascorbate anions interleaved into LDH present 100% activity in antibacterial properties. A better compromise may be achieved when PBS is mixed with different LDHs such as those combining HPP and ASA, making possible to target efficiently multi-properties such as biocide activity, small rate of hydrolysis, photo-stability as well as chain extension, thus turning to a multifunctional (bio)nanocomposites with new possible applications. Finally, a possible scale-up is demonstrated on thin films.

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#### NEW BOTTOM-UP APPROACH FOR SYNTHESIS OF CARBON NANOTUBES

A. Kolanowska (1,2,3), S. Boncel (3)

1. University of Silesia, Faculty of Science and Technology, Institute of Chemistry, Katowice,

Poland

2. Silesian University of Technology, Biotechnology Center, Gliwice, Poland

3. Silesian University of Technology, Faculty of Chemistry. Department of Organic Chemistry,

Bioorganic Chemistry and Biotechnology, Gliwice, Poland

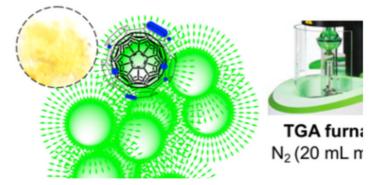
E-mail (corresponding author): anna.kolanowska@polsl.pl

Carbon nanotubes (CNTs), with their electronically tunable nitrogen-doped structural variants (N-CNTs), continue to appeal to both scientists and technologists worldwide. This attraction is driven by their 'all-in-one' superb mechanical, electrical, thermal, chemical and biological properties. N-CNTs are synthesized mainly via arc discharge, laser ablation, and chemical vapor deposition (CVD) from different carbon sources with the employment of catalytic amounts of metallic nanoparticles.

In 2004, the family of carbon nanoallotropes grew to include carbon dots (CDs) – fluorescent nanomaterials with a carbon core and oxygen/nitrogen functionalities on their surface. Those novel and per se unique 0D carbon nanomaterials serve as biocompatible fluorescent probes, drug delivery systems, sensors, light emitters and photocatalysts.

Although the synthesis of CNTs and N-CNTs has been studied for more than three decades, the catalyst-free methods were elaborated only for CNTs (with a single report on N-CNTs). But more importantly, there are no reports on the synthesis of N-CNTs from CDs as a carbon source [1-3].

We present a novel catalyst-free route for the synthesis of N-CNTs from amino acid-derived CDs as sustainable resources. N-CNTs (~4-26 at. % of N) were comprehensively characterized by complementary techniques while the synthetic strategy emerges as an important alternative and, simultaneously, a simply-scalable approach. After synthesis, CNTs were characterized by transmission electron microscopy (TEM), thermogravimetric analysis (TGA), Raman spectroscopy and X-ray Photoelectron Spectroscopy (XPS). This work was supported by the National Science Centre grant PRELUDIUM-18 (UMO-2019/35/N/ST5/02563).



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#### FLUORESCENT INK BASED ON SEMICONDUCTOR QUANTUM DOTS FOR HIGH RESOLUTION PRINTING

Jakub Śliwiński – presenting author QNA Technology S.A., ul. Duńska 9, 54-427 Wroclaw, Poland E-mail (corresponding author): maciej.zieba@qnatechnology.com

Quantum dots (QDs) are fluorescent, semiconductor particles sized less than 20 nm. Due to the unique luminescence properties, quantum dots have already found a lot of various applications including: printed electronics, displays, lighting, security printing, medical imaging, solar cells. The aim of this project is to obtain fluorescent RGB (Red, Green, Blue) inks, containing colloidal QDs that can be used to print optoelectronic elements in high resolution.

Due to specific core-shell structure of quantum dots, the manufacturing process is complicated and contain several steps. Starting from multi-step synthesis of quantum dots through their surface functionalization (in order to match the matrix of the final ink), up to ink formulation itself. Each step requires meeting specific parameters: high level of quantum yield (QY), proper photoluminescence wavelength, viscosity and surface tension, so that the final product in form of ink can be used in selected application.

QNA Technology developed inks based on QNA's quantum dots. Selected ink formulation allows printing on various surfaces (paper, glass, plastic etc.) making it easy to deposit QDs on rigid or flexible substrates. Formulations were tested using Dimatix inkjet printer and the stability of QDs-based inks were confirmed in long-term tests.

Acknowledgment to all member of QNA Technology team working on fluorescent ink development.



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### **HIGH QUALITY HEAVY-METAL FREE QUANTUM DOTS** FOR BLUE LIGHT EMITERS

Hanna Woźnica – presenting author QNA Technology S.A., ul. Duńska 9, 54-427 Wroclaw, Poland E-mail (corresponding author): hanna.woznica@qnatechnology.com

Solution processed semiconductor Quantum Dots (QDs) emerged as a candidate to replace organic dyes as emitters in lighting and display industry due to their remarkable color purity, tunability and durability. However currently implemented devices use only red and green QDs, whereas obtaining high quality cadmium-free blue QDs still remains a challenge. Blue emitting QDs are needed to introduce a new type of AR (augmented reality) and VR (virtual reality) displays that require high brightness and high resolution.

In QNA Technology we develop zinc based blue emitting quantum dots, that not only have zero cadmium content, but also meet specific requirements, such as high quantum yield and narrow emission (FWHM < 35 nm). The emission wavelength (~455 nm) is chosen so that the color space is wide enough for a high quality display while satisfying the human eye safety condition at the same time.

Our PureBlue.dots are customized to use in electroluminescence e.g. QD-EL or light conversion e.g. color conversion filters (CCL) applications.

Acknowledgment to all member of QNA Technology team working on fluorescent ink development.



QNA Technology S.A. implemented a project co-financed by European Funds: "Fluorescent ink based on semiconductor quantum dots for high resolution printing", under the Intelligent Development Operational Program 2014-2020, Priority I "Support for R&D by enterprises", Sub-measure 1.1.1. project number: POIR.01.01.01-00-0210 / 19-01

# NANOMATERIALS AFFECTING HEAT TRANSFER OF A LIQUID DISPERSION – A REVIEW

Rahul Venugopal (1), Julia Woch (1), A. Drop (1)

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1. Siec Badawcza Lukasiewicz - Instytut Ciezkiej Syntezy Organicznej "Blachownia",
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Kedzierzyn-Kozle, Poland

E-mail (corresponding author): rahul.venugopal@icso.lukasiewicz.gov.pl

Various branches of industries, including specialty chemicals, have been researching and improving ways to boost the efficiency of heat transfer. In recent years, dispersions enriched with nanoparticles has emerged to overcome the requirement of better heat transfer because of possible higher thermal conductivity and heat transfer coefficient than conventional fluids [1]. Though various fluids enriched with CuO, Al2O3, TiO2, and SiO2 or hybrid nanoparticles are studied, the thermal conductivity of CNTs (carbon nanotubes) is far more enhanced. Attempts to utilize them as heat transfer modifiers by dispersing them into any kind of base fluids have been thoroughly conducted.

In this work, a review on nanomaterials, including CNT, affecting heat transfer of a liquid dispersion is presented. The rheological and tribological behavior, thermo-physical properties of such dispersion is discussed, based on the latest research papers and patents [2, 3].

However, one of the challenges faced by many researchers in applying their prepared CNT nanofluids is to maintain its homogeneous state and long-term stability.

Keywords: nanofluids, heat transfer, dispersion

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#### STABLE DISPERSION OF CARBON NANOMATERIALS IN ENIGNE OIL

S. Ruczka (1), S. Boncel (1)

#### 1. Faculty of Chemistry / Department of Organic, Bioorganic Chemistry and Biotechnology Center for Organic and Nanohybrid Electronics (CONE), Silesian University of Technology, Gliwice, POLAND

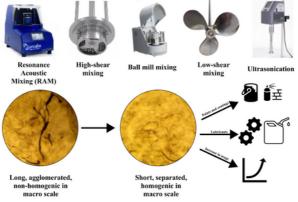
E-mail (corresponding author): szymon.ruczka@polsl.pl

Carbon nanomaterials constitute a large collection of nanoparticles with various pseudodimensions, morphology and physicochemical properties. Many years of research on pure carbon nanoallotropes have led to the publication of a number of works correlating the chemical structure with the desired properties, thus leading to not only potential, but now realistic applications. However, recently conducted market research indicates a low share of nanomaterials in ready-made "nanoproducts" with 1D and 2D pseudo-dimensions, such as nanotubes, nanodiamonds or graphene. The main obstacle to the industrial use of nanomaterials with 1D and 2D pseudo-dimensions is the need to use complex dispersion procedures and significant production costs. Nanoparticles tend to agglomerate due to intermolecular interactions with a strongly developed surface (Van der Walls forces,  $\boxtimes$ - $\boxtimes$ stacking). Researchers are working hard to produce stable nanodispersions containing nanotubes, graphene, fullerenes and their use in finished products.

Fig. 1 – Creating stable diffusion of carbon nanomaterials

In our research we lookout to achive homogenic dispersion of different carbon nanomaterials in engine oil. With different types of mixing we apply various energy inputs to separate individual nanomaterials. To stabilise dispersion we use covalent functionalized nanomaterials, surfactants or addition of ionic liquids. In the figure 1 we can see different methods to achieving stable dispersions.

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#### INTEGRATION OF FIBER OPTIC SENSORS IN GFRP COMPOSITE RODS IN PULTRUSION PROCESS

M.Knutelski Silesian University of Technology, Gliwice, POLAND Reinbar Sp. z o.o.

This study presents a novel approach to manufacturing glass fiber reinforced polymer (GFRP) gauge rods integrated with fiber optic sensors using a pultrusion process. The integration aims to increase the functionality of the gauge rods by enabling real-time structural health monitoring.

The article begins with an overview of the pultrusion process, highlighting its suitability for producing consistent, high-quality GFRP composites. It then discusses the challenges of pultruded fiber optic sensor deposition.

The results show that pultruded GFRP rods with integrated sensors maintain mechanical strength and stiffness, which is essential for measurement applications. The integrated sensors successfully provide real-time data on strain changes, proving their potential for structural integrity monitoring. This research represents a significant advance in the field of composite materials, proposing a cost-effective and efficient method for producing GFRP smart gauge rods with embedded sensors. Applications of these rods in various industries, including construction and aerospace, are discussed, highlighting their potential to revolutionize structural health monitoring practices.

Keywords: Pultrusion, GFRP, Fiber Optic Sensors, Composite Materials, Structural Health Monitoring, Manufacturing Process.

#### IMPACT OF N-ALKYL CHAIN LENGTH IN PHENOTHIAZINES ON PHOTOVOLTAIC PARAMETERS OF DYE SENSITIZED SOLAR CELLS

Muhammad Faisal Amin (1), Paweł Gnida (1), Sylwia Zimosz (2), Aneta Słodek (2), Ewa Schab-Balcerzak (1,2)

 Centre of Polymer and Carbon Materials, Polish Academy of Sciences, 34 M. Curie-Sklodowska, 41-819 Zabrze, Poland

2. Institute of Chemistry, University of Silesia, Szkolna 9, 40-006 Katowice, Poland

Dye sensitized solar cells (DSSCs) employ photosensitizers adsorb on metal oxide surfaces to convert solar light into electricity through photovoltaic effect [1]. The structure of the compounds applied as photosensitizer, which harvests photons and initiates the electrochemical process, plays a significant role in the overall performance of the cell. The best photovoltaic efficiency is reached by DSSCs based on metal-based dyes mainly ruthenium compounds [2]. Currently, metal-free organic dyes have drawn greater attention due to several advantageous over the metal-based dyes, such as easy availability, design versatility, high molar extinction coefficients, and cost effectiveness in their synthesis. The design of the new efficient metal-free dyes requires the basic knowledge concerns relationship between structural elements of compounds and the most important their properties from the point of view DSSC.

In this study, the impact of the alkyl chain on nitrogen atom: N-ethyl, N-butyl, N-octyl and N-dodecyl in phenothiazines with bis-2-cyanoacrylic acid units on DSSCs photovoltaic response was investigated [3]. Moreover, the idea of dye cocktails (with commercial N719) utilization was also developed. The electronic absorption spectra of dyes anchored to TiO2 were registered and the surface morphology of prepared photoanodes was studied using AFM. The fabricated DSSCs with structure FTO/TiO2@dye/electrolyte(EL-HSE)/Pt/FTO were characterized by current voltage measurements.

It was found that higher power conversion efficiency (PCE=4.85%) exhibited device based on the compound with shorter aliphatic chain, i.e., N-ethyl unit also compared to cell sensitized with a commercial dye N719 (PCE=4.45%). The utilization of this dye and N719 mixture increase of PCE by 52% compared to cell with a neat N719.

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#### FOCUSED ION BEAM BASED TECHNOLOGIES FOR GEMSTONES

A. Zięba (1), K. Hreczycho (1,2), P, Kunicki (1)

1. Nanores sp. z o.o. sp.k., Bierutowska 57-59, 51-317, Wrocław, Poland

2. Mathematical Institute, University of Wrocław Joliot-Curie 15, 50-383, Wrocław, Poland

E-mail (corresponding author): aneta.zieba@nanores.pl

Focused ion beam microscopy is known mostly by its applications in microelectronics industry, but its nano scale precision can be also valuable for gemstones processing. We present three solutions: NanoPatterning for changing visual impressions by changing colors of a desired area (or whole facets), NanoIndividualiza- tion for engraving images on a gemstone table and NanoMarking for fabricating invisible to the human eye marks for ensuring their authenticity. Each of those structures have depth of up to 200 nanometers, so gem- stone weight and value is not lowered.

Focused ion beam (FIB) microscope is a device used for imaging and processing material with precision up to tens of nanometers. It is used mostly in manufacturing of semiconductors and transmission electron mi- croscopy sample preparation (lamellas), but its possibilities make it useful in many different industries. On this poster we present FIB technology applied to fabricating micro and nano scale solutions on gemstones.

Value of the most desired gemstones (e.g., rubies and diamonds) comes from their qualities like clarity, car- at weight and cut. Those parameters are visually assessed before the gemstone is introduced to the market, so it is important to mark it beforehand. Common methods like laser marking produce symbols visible to the naked eye, so their counterfeits are easy to fabricate. On the other hand, FIB can fabricate patterns with details smaller that wavelength of the light.

In conclusion we developed three technologies for gemstones' modification and security. NanoPatterning focuses on increasing diamond brilliance by fabricating a diffractive grating on its table. NanoIndividuali- zation focuses on engraving unique images on gemstone tables, so that they can be seen by the naked eye. NanoMarking combines simple patterns with data stored in a database. By containing 25-bit word (which gives us more than 2 billion possible sequences) in  $5x5 \mu m$  area, which coordinates are stored in the data- base, we fabricate mark close to impossible to find.

References:

We pursued the project within instrument Fast Track 1/1.1.1/2015 about "Development of NanoPatterning, NanoMarking and NanoIndividualization services together with innovative technology of ion sources for Focused Ion Beam.", funded by the European Union from European Regional Development Fund under Smart Growth Operational Programme 2014-2020.

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