

BOOK OF ABSTRACTS 2023

14TH – 16TH JUNE POZNAŃ – POLAND



NANOBIOMEDICAL CENTRE ADAM MICKIEWICZ UNIVERSITY IN POZNAŃ



BOOK OF ABSTRACTS 2023

14TH – 16TH JUNE 2023 POZNAŃ, POLAND



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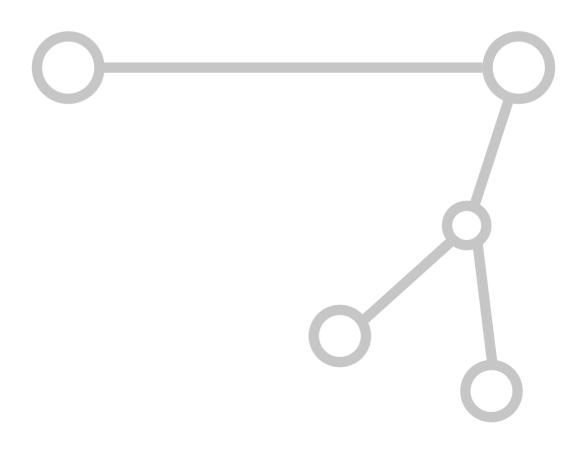
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PLENARY LECTURES



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Novel Materials Chemistry for Energy and Environmental Applications

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The current trend in various energy applications, ranging from batteries to electrolizers, lays in the control of structural, physicochemical and morphological properties of materials and their interfaces. During this presentation, recent scalable strategies for nanostructured materials synthesis, targeting energy and environmental applications will be discussed. Especially, we will focus on one-pot strategies for the fabrication of hybrid and complex nanomaterials focusing on the importance of the organic-inorganic and inorganicinorganic interfaces. Among the examples presented, we will discuss the synthesis of complex nanostructures and the stabilization of metastable phases for applications in energy storage and conversion. We will see that nowadays the available strategies allow a control in terms of composition, crystalline structure, morphology and nanostructuration that would have been unimaginable just few years ago. Finally, the open challenges the field is currently facing and possible further developments which are needed to meet the always growing demand for high performing materials will be also discussed.



Magnetic approaches in NanoBioMedicine: biodegradation follow-up, tissue engineering, and cancer therapy

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Magnetic nanoparticles remain first-in-class agents for tailor-made theranostic functions. In cancer therapy, they have raised the prospect of thermal treatments that have few if any adverse effects [1-3]. In regenerative medicine, the magnetism of iron oxide - based nanoparticles provide cells with sufficient magnetization to manipulate them, with unlimited applications in tissue engineering. We developed magnetic-based methods to manipulate cells, towards the goal to provide magnetic artificial tissue replacements, that can be stimulated on demand [4, 5]. For instance, it could induce mechanically stem cells differentiation [6, 7]. Similarly, it allows to magnetically compress cancer spheroids alongside their genesis or drug testing and even nanoparticles-mediated therapy, then in an all-in-one actor/probe action of the magnetic nanoparticles [8, 9]. Yet, any medical use of nanoparticles raises the more general issue of intracellular nanoparticle long-term fate [10, 11]. Cell spheroids models and magnetic tools were developed to monitor long-term nanomaterials intracellular integrity [12]. It evidenced a massive intracellular degradation, which could be prevented by a polymeric coating [13] or an inert gold shell [14]. Remarkably, human cells could also biosynthesize their own magnetic nanoparticles [15-17], with longer persistence, and limited toxicity. Nevertheless, if degradation of magnetic nanoparticles culminates in Fe(II) release, it can also be translated into an additional asset for cancer therapy, with synergistic thermal and ferroptotic cancer cell death [18].

Acknowledgments

These works were supported by European Union (grants ERC-CoG-2014 MaTissE 648779, ERC-CoG-2019 NanoBioMade 865629 and ERC-2022-POC1 BioMag 101069301).

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Nanomedicine-based delivery solutions for the next generation of biotherapeutics

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Biotherapeutics, i.e. biological molecules such as proteins, peptides, lipids or nucleic acids that are used for therapeutic intervention, have become a valuable asset to medicine. At present, one fifth of the newly marketed drugs consist of biotherapeutics and this number is still increasing. Nevertheless, the formulation and delivery of such biotherapeutic drugs poses substantial challenges due to their large size and susceptibility to degradation upon administration. In this presentation, I will highlight several of these challenges and provide several examples how such challenges can be overcome with the use of appropriate nanoparticulate delivery systems. I will show how light can be used as a trigger to release oligonucleotides for local delivery into the eye, how encapsulation of a therapeutic enzyme in liposomes can prevent toxicity and at the same time provide targeted intracellular delivery, and how lipid nanoparticles can be utilized for CRISPR-Cas mediated gene editing.

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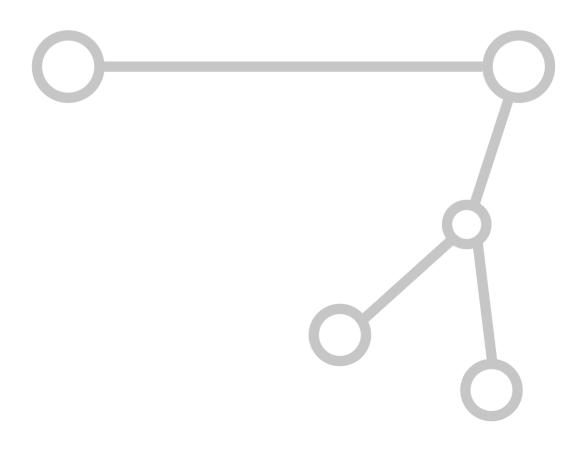
Organic transistors for bio- and neuroelectronics: from nanoscale effects to in vivo recordings

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I will overview the evolution of organic transistors operated in electrolyte environments in vitro and in vivo as specific ultrasensitive biosensors up to neural transducers of evoked signals from the brain cortex. Beyond some examples of sensing biomolecules of increasing complexity. I will highlight some fundamental aspects, and interesting effects occurring at the nanoscale, to explain the extreme sensitivity of these devices and discuss some microscopic mechanism that may explain their unprecedented sensitivity and specificity stemming from weak intermolecular interactions. A final highlight on organic neuromorphic devices as sensors will be given.

SPONSOR LECTURES



Dual Analyte Quadrupole SP-ICP-MS for Quantifying and Characterizing of Nanoparticles

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Single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) is a promising method for analyzing nanoparticles. It enables the acquisition of quantitative data regarding the number, size, size distribution, and concentration of both nanoparticles and the examined element in its ionic form within a solution.

Studying changes in nanoparticles within the environment necessitates determining various physicochemical parameters, such as size, metal concentration in both ionic and nanoparticle forms, dissolution, and agglomeration efficiency. Traditionally, each of these parameters would require separate measurement techniques, often involving extensive sample preparation. Hence, the appeal of SP-ICP-MS lies in its potential to rapidly characterize nanoparticles in different tested systems, offering a more efficient and streamlined approach.

To address the need for simultaneous quantification of two isotopes within individual nanoparticles, a dual analyte quadrupole single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) technique was developed. This innovative approach allows for the measurement of chemical composition and reaction kinetics of single bimetallic nanoparticles in real-time at a rate exceeding 300 nanoparticles per minute [1]. This elemental analysis method has the potential to revolutionize the understanding of nanoparticle composition evolution and transformation within environmental and biological contexts.

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Measuring kinetics of molecules to living cells using Real-Time Interaction Cytometry

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The binding of antibodies to cell surface antigens is a pivotal step in the recruitment of the cellular immune response. The characterization of association and dissociation rates, affinity, and avidity is essential for the development of efficient and safe therapeutic antibodies. Binding kinetic measurements in physiological conditions are expected to have superior predictive value in the treatment of cancer, infection and autoimmunity. However, despite substantial efforts, methods to measure binding kinetics directly on target cells are still not available, which leaves a "biophysical gap" in the research and development of biological drugs.

Here, we present Real-Time Interaction Cytometry (RT-IC), a novel technology that allows characterization of therapeutic antibodies with their targets within their native environment to obtain physiologically relevant kinetic data with high in vivo predictability. RT-IC employs chips functionalized with polymer cages that physically retain single cells in the microfluidic channel. Suspension or adherent cells can be loaded into the cages by an automated workflow using only a few microfluidic somple. Antibodies labelled with standard dyes are subsequently injected into the microfluidic chip under continuous flow allowing the measurement of association and dissociation kinetics of antibodies to/from cell surface antigens in real-time.

In this work we demonstrate the reproducible measurement of association and dissociation rates and compare the binding behavior of anti-CD3 antibodies to living versus fixed Jurkat cells. The interaction data shows different dissociation rates with a biphasic dissociation behavior for fixed cells but a monophasic behavior for living cells. We presume that this effect is caused by the preserved membrane fluidity in living cells in contrast to fixed cells. In live cells, the maintained receptor mobility within the membrane likely promotes bivalent interactions (avidity) by allowing the clustering of receptor molecules. These results demonstrate the importance of measuring binding kinetics directly on cell surfaces to predict the efficacy of therapeutic antibodies.

SECTION A ADVANCED NANOMATERIALS



INVITED SPEAKER

Luminescence-based Optical sensors

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Optical sensors operate by detecting changes in the intensity, phase, polarization, wavelength or spectral distribution of the light beams as they interact with the surrounding medium. This type of sensor usually provides high efficiency due to their exclusive features accounting from their light-based detection mechanism. In addition, these detectors have a great advantage over other detector systems because they do not require physical contact with the system to be measured.

Different optical sensors based on luminescence coming from optically active ions were analyzed in this work. On the one hand, the well-known systems based on the Luminescence Intensity Ratio (LIR)-based systems are presented and, on the other, Whispering Gallery Modes (WGM)-based systems on transparent microspheres.

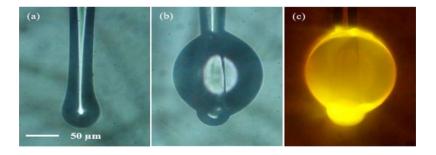


Figure. (a) Optical image of a modified optical fiber, (b) optical image of the liquid resonator made in the tip of a modified optical fiber and (c) optical image of the liquid resonator under excitation at 532 nm.

Acknowledgments

This research was supported by Ministerio de Ciencia e Innovación (MICIIN) under the National Program of Sciences and Technological Materials (PID2019-106383GB-C44, PID2019-107335RA-I00), by Agencia Canaria de Investigación, Innovación y Sociedad de la Información (ProID2020010067 and ProID2021010102) and by EU-FEDER funds.



When Dyes Meets 2D Materials – Spectroscopic and Photocatalytic Properties

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Photocatalysis is a an appealing strategy to exploit solar energy for fuel production and pollutant utilization. Innovative 2D materials with unique layered (2D-LM) structures are expected to enhance photocatalytic activity due to excellent mobility of charge carriers and extremely high specific surface area.

In our work by functionalizing dye molecules (porphyrins, xanthenes) to 2D-LM (GO, RGO, Ti₃C₂T_x, Nb₂C) we constructed novel nanomaterials that were tested in photocatalytic hydrogen production, rhodamine B photodegradation and singlet oxygen generation [1-3]. By applying steady-state and time-resolved absorption and emission spectroscopy the interaction of the excited state dyes with 2D-LM was examined in detail. In our work we explored also the correlation between the photocatalytic activity and graphene oxide morphology (size and thickness) [1]. Subsequently by integrating two types of functional materials: graphene oxide and Co-MOF we designed a stable system with enhanced charge-separation properties which ultimately boost their photocatalytic activity. The activity of our Co-BDC in the presence of graphene oxide was found to be remarkable (33,300 µmol g⁻¹ h⁻¹ per gram of MOF) in comparison to other MOF systems [2]. We also carried out photocatalytic hydrogen evolution experiment of the EY/Ti₃C₂T_x/CoSO₄ system under incident light wavelength. Hydrogen evolution rate of 40.9 mmol h⁻¹ g⁻¹ and AQE = 35.7% at 505 nm has been obtained which is even higher than for the analogue system in which CoSO₄ was replaced by the H₂PtCl₄ and higher than for the system where GO was used as a support.

Our results demonstrate that dye functionalization with 2D-LM provides a promising way to design efficient photocatalysts for H_2 generation from water under the irradiation of solar light.

Acknowledgments: This work was supported by the by AMU "Excellence Initiative - Research University" (grant number: 038/04/NS/0012)

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Nanostructured semiconducting oxides – electrochemical synthesis and photoelectrochemical activity

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Over the last decades, photoelectrochemical (PEC) water splitting has received great scientific attention as one of the most promising approaches for energy conversion. It is also widely known that a significant improvement in PEC performance can be achieved by using nanostructured semiconductors instead of their bulk counterparts. Therefore, considerable attention is still focused on finding efficient and cost-effective methods that can be used for the fabrication of nanostructured semiconductors. Among them, electrochemical methods were found to be extremely promising mainly due to their simplicity, cost-effectiveness, and possibility of scaling up. Moreover, the possibility to control (to some extent) the morphology and composition of the synthesized semiconductor by adjusting conditions applied during the procedure is also an important advantage.

The aim of this presentation is to give a brief overview of our most recent results in the electrochemical (both cathodic and anodic) synthesis of nanostructured semiconductors (e.g., SnO₂ [1–3], ZnO [4], Cu₂O [5], and others [6]). A special emphasis will be put on the photoelectrochemical activity of electrochemically-synthesized semiconductors, as well as methods of their further modification. Correlations between the conditions applied during electrochemical synthesis, morphology, composition, and structure of the materials and their photoelectrochemical activity will be discussed in detail.

Acknowledgments

This work was partially supported by the National Science Centre, Poland (project no. 2018/30/E/ST5/00531) and by the Polish Ministry of Education and Science from budget funds for science in the years 2018–2022 as research project no. 0196/DIA/2018/47 under the "Diamond Grant" program. The authors acknowledge Karolina Gawlak, Krystyna Mika, Aleksandra Knapik, Magdalena Jażdżewska, Sylwia Kemona, and Mateusz Wojtas for their significant contribution to this work.

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Multiscale Modelling of Carbon Dots

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Nowadays, methods of theoretical chemistry are commonly used not only to support experimental data, as they provide us very fine atomistic and femtosecond resolution simultaneously. Carbon dots (CDs) are defined as quasi-spherical objects with a diameter below 10 nm possessing a multilayer graphite core and oxygen and/or nitrogen functional groups on the CD shell [1]. Determining the relationship between structure and photoluminescence (PL) remains a major challenge in the field of CDs. It is now widely recognized that different structural domains can evolve during CD preparation, but we are still far from being able to capture the specific features that determine the overall PL of CDs. Therefore, over last few years we employed different theoretical approaches, mainly methods of molecular dynamics MD simulations, and calculations based on (time-dependent) density functional (TD)-DFT theory, with the goal to address various questions in the field of CDs. First we provided atomistic detail on dynamics and structural organization of quasi-spherical CDs [2] and MD simulations also demonstrated the tendency of molecular fluorophore IPCA to non-covalently bound onto or incorporate into CDs [3]. TD-DFT calculations then addressed optical properties of IPCA in gas, water and in environment of CDs [4,5]. Eventually, (TD-)DFT computation were helpful in the study of the communication between the different PL centres within CDs depending on the mutual arrangement of these centers (Figure 1) [6].

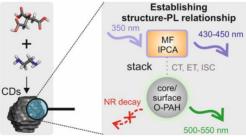


FIGURE 1. Example of the processes occurring in the representative model of CD structural domains after the irradiation with a 350-nm energy source presumably targeting the absorption maximum of IPCA (displayed as incoming arrows). Notation: LE - local excitation, CT - charge transfer, ET - energy transfer, ISC - intersystem crossing, NR - non-radiative de-excitation, HB - hydrogen bond, MF - molecular fluorophore, PAH - polyaromatic hydrocarbon.

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INVITED SPEAKER

Nanostructured unsupported and carbon-supported titanium (hydro)dioxides for photocatalytic organic synthesis: mechanistic insights by experimental and computational studies

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The investigation for "greener" and economically feasible approaches such as photocatalysis for the selective transformation of organic-waste-derived compounds like aromatic alcohols by avoiding the drastic reaction conditions/reagents have concentrated the focus of attention of the last years [1,2,3]. The design and fabrication of novel photocatalysts for organic synthesis are very challenging. In this research work [1,3], the synthesis of TiO₂-based and carbon-supported TiO₂ were performed by the ultrasound-assisted via precipitation, and sol-gel-based hydrosolvothermal methods, respectively.

The additive-free photoactivity showed that TiO_2 and TiO_2 -containing carbophotocatalytsts revealed the highest yield of the target product than commercial TiO_2 and $g-C_3N_4$. The physicochemical features of the most promising materials were determined by N_2 sorption, HR-TEM, XPS, XRD, EDX, among other techniques. Novel nanostructured titanium based as it is, and also immobilized on chitosan-lignin-based carbon supports, are very promising materials for the additives-free selective partial oxidation of benzyl alcohol BnOH (a biomass model compound) to benzaldehyde (PhCHO) at ambient conditions under low-power ultraviolet (365 nm) or royal-blue (465 nm) light irradiation.

DFT calculations in combination with the detailed physicochemical features as well as various scavengers' tests, revealed that the photo-oxidation of BnOH can be achieved via different mechanisms and with different reactive oxygen species to be involved, depending on the catalyst's physicochemical feature and the nature of light. The diluted molecular oxygen and the photo-induced holes play a crucial role in the selective oxidation of BnOH, while the formation of free hydroxyl radicals has a negative impact since they are responsible for non-selective reactions. BnOH is adsorbed differently on the surface, bridging oxygen vacancies compared to the hydroxyl groups, affecting the antenna/photosensitization effect.

Acknowledgments

This research is partially supported by the National Science Centre (NCN) in Poland within research projects OPUS 20 No. 2020/39/B/ST5/00076, and OPUS-13 no. 2017/25/B/ST8/01592.

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Lighting-up nanocarbons through hybridization: Optoelectronic properties and perspectives

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In recent years, a plethora of material systems have been designed and prepared to increase the performance of light harvesting and light-emitting technologies, and to develop new and attractive applications. Limitations of state-of-the-art devices based on organics (both conjugated polymers or small molecules/oligomers) derive largely from material stability issues after prolonged operation. This challenge could be tackled by leveraging the enhanced stability of carbon nanostructures (CNSs, including carbon nanotubes and the large family of graphenebased materials) in carefully designed nano-hybrid or nanocomposite architectures to be integrated within photo-active layers, paving the way to the exploitation of these materials in contexts in which their potential has not been yet fully revealed [1]. In this talk, I will discuss the theoretical background behind CNSs hybridization with other materials such as graphene with donor-acceptor molecules [2], for the establishment of novel optoelectronic properties and provide an overview of new optoelectronic and transfer properties of twisted graphene nanoribbons with controlled peripheral size [3-5] that allow to forecast interesting future perspectives for use in real devices.

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Microellipsometry of ordered planar lattices of plasmonic nanoparticles

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Ordered lattices of plasmonic nanoparticles, especially on substrates with their own resonances are, probably, the most tunable plasmonic structures, the optical properties of which depend on material and geometrical parameters of the nanoparticles, type and period of the lattice, the substrate, and the interaction with substrate resonances [1,2]. Additionally, the orientation of the lattice according to the direction of the exciting light affects the interparticle interactions and, correspondingly, the optical properties of the system. The latter is proved by the consideration of the symmetry and calculation of lattice sums.

Ellipsometry is well known to be a suitable method for the investigation of plasmonic structures providing not only amplitude but also the phase information [3,4]. Moreover, microellipsometry with a spatial resolution of a few micrometers is appropriate for the investigations of ordered lattices of plasmonic nanoparticles, which are usually restricted in size because of the preparation by electron-beam lithography. It allows not only the influence of the substrate, ordering of nanoparticles, geometrical parameters, or the lattice orientation on the optical properties to be demonstrated, but also the dispersion of different electromagnetic modes of the system to be restored and the interaction and splitting of these modes to be exhibited.

All these details of the optical properties of ordered lattices of plasmonic nanoparticles on different substrates revealed by microellipsometry are discussed in this presentation.

Acknowledgments

We acknowledge DFG grants no. ZA 146/43-1 and no. FL 670/8-1. EB appreciates the travel support of the COST Action MP1302 "Nanospectroscoy" and the funding through the MSCA4Ukraine project, which is funded by the European Union.

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Arbitrary chiral patterns from achiral molecules by microscopic photothermal patterning

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Fabrication of hierarchical structures with spatially-controllable chirality remains a challenge due to difficulty of controlling a handedness of the material without resorting to the intrinsicaly chiral materials, i.e., materials composed chiral mlecules, chiral dopants or to chirality-inducing biases such as circularly polarized light. In this study, we present an autonomous microscale photothermal chirality patterning device that operates on an algorithm that reads, identifies, and controls the recrystallization of nanostructured organic thin films by promoting homochiral growth of supramolecular organic helices formed of achiral molecues. This molecular achirality of individual molecules and the synchronization of local chirality allow for unrestricted chiral writing in the film, with both handednesses of helices available. The patterning process is guided by the collective chiroptical response of assembled molecules, providing a foundation for optically secured information. This methodology achieves dissymmetry factor values for circular dichroism one order of magnitude higher than previously reported, as confirmed by state-of-the-art, synchrotron-based Mueller matrix polarimetry. Furthermore, we demonstrate the application of our technique to nanocomposites containing gold nanoparticles, enabling tuning of the circular dichroism in the plasmonic region. Our strategy uncovers the potential of photothermal processing through laser-directed melting, expanding the selection of nanostructured materials with precisely designed chiroptical functionalities for photonic applications.

Acknowledgments

This work has been generously supported by the National Science Center, Poland through the Sonata Bis grant no. 2020/38/E/ST5/00328.

INVITED SPEAKER

Functional Metal Oxide Surfaces: Photocatalytic, Self-Cleaning, Sensing, and Micro-/Nanostructuring Applications

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Titanium oxide (TiO₂) is one of the most used photocatalytic materials for various applications such as environmental remediation, (solar)water splitting, and self-cleaning due to its high activity, low cost, high chemical, and physical stability. However, the photocatalytic activity of TiO_2 is limited by the wide energy of the bandgap, low quantum efficiency, and rapid recombination of photogenerated charge carriers (electrons and holes). During the last decades, numerous approaches, such as tailoring the morphology (nanoparticles, thin film, etc.), combining with metal, noble metal, and metal oxide micro/nanostructures, have been demonstrated to enhance the photocatalytic activity of TiO₂. However, it is still a major challenge to find the best photocatalytic combination for specific applications. Recent studies have revealed that particle size plays a considerable role in the photocatalytic activity of TiO₂. Reducing the particle size (increasing active surface area) indicates a higher photocatalytic activity. Nevertheless, the use of photocatalytic nanoparticles in continuous flow systems (such as water remediation, water splitting, etc.) has some practical limitations such as reusing and splitting them up from the reaction media. Hence, the use of robust and stable thin film photocatalysts becomes more suitable rather than nanoparticle systems for practical applications. Nevertheless, thin films are restricted by low surface area in contrast to nanoparticles and they show extremely limited photocatalytic activity. Here we present some case studies on enhancing the photocatalytic performance of TiO₂ thin film by modification with metal [1-3] and oxide [4,5] nanostructures for practical applications such as water purification, self-cleaning, selective oil absorption [6], and organic molecule sensing [7].

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Reduced graphene oxide-based electrodes for energy storage devices

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One of the most important topics of the scientific research today is energy storage. Supercapacitors (SCs) have relatively simple structures and inherent electrochemical properties and can be the most promising candidates in comparison to batteries and fuel cells. High-performance SCs need to show high energy and power density, fast charge-discharge and long cycle life. Investigation of materials for electrodes with high capacitance and high electrical conductivity ensures fast charge-discharge.

Graphene that has large specific surface area and high electrical conductivity is a promising material for the energy storage. In the current work, composite electrodes based on reduced graphene oxide (rGO) aerogel prepared by freeze-drying and annealed at different temperatures were used for the fabrication of composite electrodes and further analysis of single electrodes and symmetric SCs. Moreover, due to the development of flexible energy storage devices with high performance for next-generation wearable and flexible electronics, the textile substrate (carbon cloth) was used in the current work.

Calculated specific capacitance of obtained electrodes strongly depended on processing details such as annealing temperature, wettability of materials and others. The highest specific capacitance value was obtained for the electrode on the carbon cloth with rGO aerogel annealed at 180 °C that was much higher than that for electrodes with rGO aerogel annealed at 700 °C. Prepared rGO-aerogel-based electrodes were found to be chemically stable after long cycling test (after 10 000 charge/discharge cycles). Further study of structure-properties relationship is planned.

Acknowledgments

This work was supported by national funds, through FCT (Fundação para a Ciência e a Tecnologia) in the scope of the framework contract foreseen in numbers 4, 5, and 6 of article 23 of the Decree Law 57/2016, of 29 August, UIDB/00481/2020 and UIDP/00481/2020; and CENTRO-01-0145-FEDER-022083-Centro Portugal Regional Operational Programme (Centro2020), under the PORTUGAL 2020 Partnership Agreement, through the European Regional Development Fund and developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, financed by national funds through the FCT/MEC (PIDDAC) as well as within FCT independent researcher grant 2021.02284.CEECIND.



Ferromagnetic Nanoparticles: Synthesis, Properties, Application

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Nanoparticles based on the magnetic oxide systems can find practical application both in medicine (MRI, hyperthermia, drug delivery etc.) and technology (wireless communication system etc.) due to their unique properties. However, it is often necessary to obtain the weakly agglomerated superparamagnetic nanoparticles as well as the film-materials to solve certain practical challenges. Noteworthy that synthesis of weakly agglomerated magnetic nanoparticles reveals to be the complicated scientific and technological issue.

The aim of this work included synthesis of weakly agglomerated nanoparticles of ferromagnetic materials based on magnetic oxide systems of different structural types, study of their properties as well as the clarification of the possibilities for their practical use.

The conditions for fabrication of weakly-agglomerated nanoparticles as well as the polycrystalline films with the anisotropy shape of the particles were clarified for the magnetic materials with the spinel, perovskite and barium hexaferrite structures.

Ferromagnetic nanoparticles were synthesized using different methods: the precipitation in non-aqueous solutions and reverse microemulsions, sol-gel synthesis. It allowed finding out the conditions for fabrication of the weakly agglomerated crystalline nanoparticles.

The dependence between the crystalline structure of magnetic material and conditions of synthesis of weakly agglomerated nanoparticles particles was demonstrated. Magnetic properties of synthesized nanosystems in the wide temperature range were examined. Composite resonance microwave elements "high-Q dielectric/magnetic film", which frequency can be controlled by an external magnetic field, were developed based on the fabricated magnetic films. The possibility to obtain left-handed materials was shown. Based on the synthesized nanoparticles magnetic fluids demonstrated the effective and controllable heating in an alternating magnetic field. Consequently, their ability to be used as the inducers of the magnetic hyperthermia of malignant tumours was shown *in vitro* and *in vivo*.

Acknowledgments

This work was performed within Program from The Institute of Electrical and Electronics Engineers (IEEE) Magnetics Society "Magnetism for Ukraine 2022" (project No 9918) and partially supported by grant G5683 within the NATO Science for Peace and Security Programme.



Mesoporous silica as a carrier for a metal uptake

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Heavy metals in soils and groundwater potentially threaten living organisms, but their long-term environmental impact has yet to be fully understood. These effects result from the dynamic development of industrialization, constantly providing waste containing metals. As a result, for several decades, new solutions and materials have been sought to solve such problems, improving the quality of the environment, comfort, and quality of life on Earth.

One of the most promising modern solutions to limit environmental pollution is bioperforated, mesoporous silica with a large surface area, channels with a diameter of 5 nm, and length of the order of micrometers. High silica elasticity in chemical modification gives a chance to functionalize pore walls using practically any functional group (outer- or inner walls) with the determination of precise control of their concentration in the volume. For this purpose, n-active (n = 1-3) units have been considered depending on the type of metal captured that can be uptake. A functionalization was proposed by propyl-carbonate (metalbinding I, e.g., silver) and propyl-phosphate (metal-binding II, e.g., copper).

BET and spectroscopy techniques (AAS, ICP-MS) verified the metal ion uptake potential. The sorption potential was checked on individually prepared pellets. However, as the first, the Young modulus parameters were estimated using four forces levels (AFM: nN, nanoindenter, and microcombitester: μ N, mN, testing machine: N) to determine the mechanical properties. All methods of pore wall functionalities and checking the sorption potential are directed into developing an entirely new class of materials with unique properties for the remediation of contaminated environments.

Acknowledgment

M.D. and L.L. are thankful for the financial support from the National Center of Science (NCN) based on 2020/37/B/ST8/03637.



A novel approach in organosilicon compounds in the fabrication of various SiC structures via CVD

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Silicon carbide (SiC) is widely used as a matrix or fibrous reinforcing component in ceramic composite technologies. A review of the latest literature indicates that thin SiC layers made of 1D SiC nanostructures, e.g., nanofibers, nanotubes, nanowires, etc are becoming increasingly important to functionalize the carbon surface for optical, optoelectronic, and electronic systems, including MEMS, NEMS, and photoluminescent devices. The most commonly used synthesis method of SiC layers is chemical vapor deposition (CVD), where liquid volatile double precursors, i.e., methylchlorosilanes (MTS), or single source are used [1]. Double-source precursors, have an advantage over single precursors due to the lower complexity of the process and easier control over the C/Si stoichiometry of the deposit. However, The disadvantage of using these chemicals is the health and environmental risks results from their pyrophoric and corrosive nature [2].

One of the possible solutions to some of the above problems is the use of polysiloxane solutions. Polysiloxanes have already been widely described in the literature as "precerams" and successfully used in the PIP techniques. However, their potential for use in the CVD process is unknown and has not been verified so far.

The work focuses on determining the necessary CVD parameters that affect the conversion of the gas phase-containing polysiloxane molecules to the intermediate SiOC and SiC, and on determining the dominant forms of carbides crystallizing on a carbon substrate. Polymethylsiloxane was used as the precursor to obtain SiC via CVD. The precursor was supplied to the reaction zone by saturating the N₂ gas. Depending on the synthesis temperature and N₂ flow rate, various nanocrystalline forms were deposited on the graphite foil, including SiO-C powders, micrometric layers containing SiC-core nanofibers, nanochains and nanofibers. These structures crystallized preferentially in the [111] direction by heterogenic nucleation on graphite surface in the VS process. Morphology changes of SiC deposit were caused by local fluctuation of SiO/CO and N₂ concentrations. The activation energy for SiC nanostructure growth was about 96 kJ/mol. CVD processing of polysiloxane precursor for Si-based nanocomposites presents a new cost-effective and eco-friendly approach in the fabrication of various SiC nanostructures.

Acknowledgments

This study has been supported by the National Science Center, Poland, project no. UMO-2019/35/N/ST5/02532.

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Unveiling the phytochemical basis and mechanism of plant extractmediated green synthesis of silver nanoparticles

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Despite the popularity of plant extract-mediated synthesis of nanoparticles (NPs), the phytochemical basis of this process and the exact mechanism are still unclear. Phenolics containing hydroxyl groups are known to reduce metal ions to corresponding NPs; however, the stabilizing ligands of such NPs have rarely been studied. St. John's wort (Hypericum perforatum L.) is an important medicinal plant species that possesses unique classes of compounds (xanthones, phloroglucinols, naphthodianthrones, etc.) among other common secondary metabolites, making this species an ideal candidate for study aimed at understanding the role of phytochemicals in the green synthesis process. In the present study, a systematic study was carried out to reveal the mechanism of synthesis of Ag NPs using H. perforatum extract. The analysis of the supernatant remaining after the synthesis of Ag NPs using the biomass extract and the metabolites eluted by washing the Ag NPs with different solvents by ultra-performance liquid chromatography, coupled with photodiode array and high-resolution mass spectrometry (UPLC-PDA-HRMS), shows that phenolic acids and flavonoids are involved in the reduction of Ag^+ ions, while xanthones and phloroglucinols act as capping agents and naphthodianthrones are involved in both steps (Fig. 1) [1]. Considering this fact, the inclusion of an enol group unites all the projected reducing agents, while the putative capping agents all share the presence of methoxy and/or prenyl groups [2]. Overall, the present study not only contributes significantly to the understanding of green synthesis of NPs from plant extracts, but also opens new avenues for the purification of low polar plant compounds from complex plant extracts and makes the process economical and sustainable.

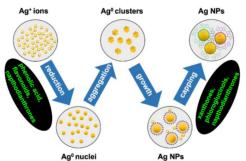


FIGURE 1. Putative model for the H. perforatum extract-mediated green synthesis of Ag NPs.

Acknowledgments

This work was supported by the National Science Centre (NCN), OPUS Project Reg. No. 2016/21/B/NZ9/01980, and the NANOPLANT project, which received funding from the European Union's Horizon 2020 research and innovation program under grant agreement no. 856961.

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UV-Vis sintering method for ink based on Ni@Ag core@shell nanoparticles on the flexible substrate

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In the last years, the interest in printed electronics has risen in the application of printing technology for the production of flexible circuits and devices. Conductive inks based on metal nanoparticles (NPs) are important materials in the fabrication of flexible printed electronic devices [1-2]. Optimal characteristics of nanoparticle-based inks are crucial for ink rheology, printing, post-print treatment, and performance of printed electronic devices. One of the most critical parameters is the ability to produce highly conductive patterns using low-cost technology on heat-sensitive substrates. Therefore, a low sintering temperature to avoid the destruction of the substrates is crucial of importance for obtaining printed flexible electronics.

In our research, we focused on the fabrication of printed conductive circuits based on low-cost metallic nanoparticles on flexible plastic substrates. The method of the formation of Ni NPs and their stabilization by the formation of the silver shell to form Ni@Ag core@shell NPs was developed. Such nanoparticles with an average size of 220 nm were utilized for the preparation of conductive inks. The applicability of the UV-Vis irradiation for the sintering of the coatings composed of Ni@Ag NPs was examined. The effects of the wavelength of the UV-Vis irradiation and the time of sintering on the resistivity of the deposited metallic coatings were investigated.

The obtained results suggest, that UV-Vis irradiation is an effective method of sintering of Ni@Ag NPs, suitable for obtaining conductive metallic coatings from NPs based inks. The lowest value of resistivity ~24 $\mu\Omega$ ·cm was obtained after 90 minutes of irradiation. The calculated conductivity of such coatings corresponds to 29-30% of that for a bulk nickel. To the best of our knowledge, this is the first time when coatings composed of Ni@Ag NPs were sintered by UV-Vis irradiation and such low resistivity/high conductivity has been obtained. In contrast to thermal sintering UV-Vis irradiation can be applied for the preparation of electronic tracks on heat-sensitive substrates like papers and plastics.

Acknowledgments

This research was funded by the National Polish Centre, Poland, grant number 2020/39/D/ST5/01937.

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INVITED SPEAKER

Generation and control of high frequency spin waves in nanoscale Dielectric Thin Films of Iron Garnets

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Magnetic garnets are a class of materials that have a large variety of useful properties at room temperature due to the complexity of the garnet structure together with its chemical flexibility. For this reason, they have always been the subject of extensive research for both fundamental science and technological applications. In recent years, magnetic garnets are still widely explored in several modern fields of condensed matter physics such as spintronics, magnonics, femtomagnetisem, picomagnetoacoustics, as well as in the field of photonics.

One of the ultimate goals of spintronics and magnonics is to use collective and coherent spin oscillations, known as spin waves (SWs) or magnons, to carry information in future information processing technologies. A challenging problem for high-speed applications is the generation of SWs that combine high frequency with low damping at weak external magnetic fields. Because of its low magnetic damping, the yttrium iron garnet (YIG) has attracted a lot of attention in the field of magnonics. However, due to the small saturation magnetization of YIG, the frequencies of the SWs did not exceed a few GHz at low fields, which is a limiting factor for ultrafast data transport and processing.

In this talk, I will present our recent work on the generation and control of SWs in nanoscale dielectric thin films of bismuth substituted yttrium iron garnet (Bi-YIG) using femtosecond laser pulses. Bi-YIG materials have, in addition to a low magnetic damping, very large magneto-optical Faraday effects, which make them well adapted for new photo magnonics devices. We show that femtosecond laser pulses can trigger high frequency SW modes. We proved that two distinct branches of the dispersion relation are excited for all the modes. This is reflected in particular at a very weak magnetic field (~ 33 mT) by a spin dynamic with a frequency up to 15 GHz, which is fifteen times higher than the one associated with the ferromagnetic resonance mode. We also demonstrated that the excitation of the SWs is triggered by ultrafast changes of the magnetic anisotropy via laser excitation, we demonstrate an amplification or suppression of the SW resonance modes by precisely tuning the time delay between the two laser pulses (see Figure 1). We explain the results by the constructive or destructive interference of the SWs induced by the first and second laser pulses [1].

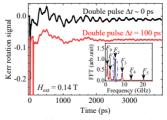


FIGURE 1. SWs induced by a double pulse with separation times $\Delta t \sim 0$ and $\Delta t=100$ ps. For better visualization a vertical offset is introduced. The inset shows the FFT spectrum of the Kerr rotation signal.

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Magnetic fraction of the particulate matter emitted from coal-fired power plants

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On the contrary to previous studies, we have focused on research material coming directly from emission sources (sampling was accomplished in industrial plants from flue gases behind air pollution control installations and from test installations related to road transport testing facilities). Due to a large variety of parameters of industrial processes (characteristics of coal, its initial processing, e.g. milling; technology of combustion (pulverized fuel boiler or fluidized bed boiler), distribution and gradient of process temperatures; air pollution control devices) a large variety of composition, crystal structure and morphology was expected.

In the current contribution we are presenting the results of Mössbauer Spectroscopy X-Ray Diffraction, Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy, Transmission Electron Microscopy, magnetometric and chemical analysis showing an important variety of compositions, structures and morphology of the micro and nanoparticles present in the material under investigation. As can be seen in the figure 1 a and b there is an important correlation between the combustion parameters and the properties of the emitted dust. It is also important to notice the complexity of the internal structure of the micro and nanoparticles (figure 1c) especially when it comes to iron and iron oxides crystallites.

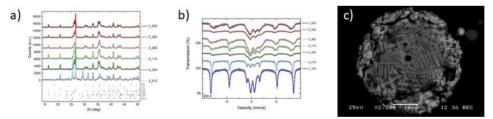


FIGURE 1. X-Ray Diffraction (a), Mössbauer Spectroscopy (b) data obtained form the measurements of the dusts power plant's escape gas system and Scanning Electron Microscopy image (c) of the crossecion of one of the microparticles found showing peculiar iron (and/or iron oxides) structures.

Acknowledgments

J.M.M acknowledges partial support by the National Science Centre in the framework of the MINIATURA 5 founding (grant no.: UMO-2021/05/X/ST10/00975).



Photovoltaic cells based on a three-junction III-V heterostructure grown on Ge: development and characterization in variable conditions

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Vertical heterostructures of the solar cells were epitaxially grown on 6°-off-axis Ge (100) substrates by MOCVD. They consisted of Ge, InGaAs and InGaP p–n junctions separated by AlGaAs tunnel junctions and were capped with an InGaAs layer (Fig. 1a). All layers were lattice-matched to Ge. Tertiarybutylarsine (TBA) and tertiarybutylphosphine (TBP) were used as the As and P precursors, respectively.

Both the back electrical contact to p-Ge and the front contact to n-InGaAs were formed by depositing Ag/Au layers via e-beam evaporation and subsequent rapid thermal annealing in N₂ ambient. Low contact resistivities of $3.8 \cdot 10^{-5}$ and $6.9 \cdot 10^{-6} \ \Omega \cdot cm^2$ on Ge and GaAs, respectively, were determined from prior transfer length method (TLM) measurements. The front electrode pattern was defined by a lift-off process and the cap layer was chemically etched off from the remaining area. The wafers were diced into 5×5 mm chips.

An anti-reflective and passivating layer was obtained by atomic layer deposition (ALD) of 120 nm of Al_2O_3 using trimethylaluminum (TMA) and deionized water as precursors. The oxide was removed by wet chemical etching from the contact pads area.

The fabricated cells were placed in a solar simulator and their I–V characteristics were measured using needle probes (Fig. 1b). Performance parameters of the devices were then extracted from these results. An efficiency of 24.3% and a fill factor of 0.76 were observed at room temperature. The dependence of the characteristics on lighting conditions and temperature up to 80° C was tested.

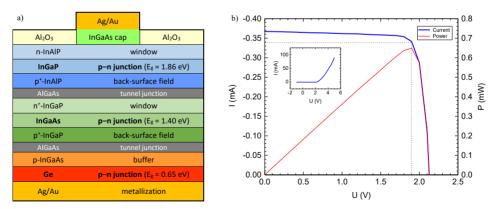


FIGURE 1. (a) Triple-junction heterostructure of the solar cells. (b) Room-temperature I–V characteristic of a 0.25 cm² chip measured in the photovoltaic range under an irradiance of 11 mW/cm² (wide-range plot shown in the inset).

Acknowledgments

The research was funded by Łukasiewicz Research Network within the project "Smart returnable packaging for the e-commerce sector" (e-Pack), contract no. 1/Ł-ILiM/CŁ/2020.



Spectro-electrochemical study of Nickel nano-particle Doped Bismuth Germanate Electrocatalyst

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By introducing metal/metal oxide interfaces and oxygen vacancies through Nickel (Ni) nano particle doping and annealing, the catalytic activity of bismuth germanate ($Bi_{12}GeO_{20}$) single crystal has been significantly increased. The micro-pulling-down method was used to prepare samples. The hydrogen evolution reaction (HER) of these materials was explored in an alkaline electrolyte. The onset potential for hydrogen evolution was observed to be -0.16and -0.12 V for as grown and annealed Bi₁₂GeO₂₀/Ni, which are lower than the onset potential of pure Bi₁₂GeO₂₀ (~-0.31 V). For pure Bi₁₂GeO₂₀, the initial HER kinetics was slow up to -0.78 V, followed by fast kinetics. Similarly, for as grown and annealed Bi₁₂GeO₂₀/Ni, the initial Tafel slope was 31 and 29 mV/dec, but at higher current densities, the slope was measured as 7 and 6 mV/dec. The presence of Ni-based interfaces, oxygen vacancies, and porous structure in as grown and annealed Bi₁₂GeO₂₀/Ni resulted in fast HER kinetics, leading to achieving a 200 mA/cm² current density at \sim -0.79 and -0.62 overpotential. The spectroscopic behavior of Bi12GeO20 were studied by Raman spectrometer and the result reveals the effect of doping and interface which increases after annealing. In conclusion, this study offers new insights into the origins and modifications of the electrocatalytic performance of single crystal-based materials.

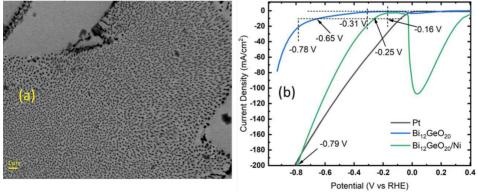


FIGURE 1. (a) FE-SEM image and (b) LSV plot of Bi12GeO20/Ni

Acknowledgments

The authors thank the ENSEMBLE³ Project carried within the Teaming for Excellence Horizon 2020 program of the European Commission (GA No. 857543), and the International Research Agendas Programme (MAB/2020/14) of the Foundation for Polish Science co-financed by the European Union under the European Regional Development Fund and Teaming Horizon 2020 program of the European Commission.



Modification of synthetic knitted fabric with controlled size ultra pure silver nanoparticles

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The development of innovative technological procedures for synthetic knitted fabric modification with controlled size ultra pure silver nanoparticles significantly improves the antibacterial/antiviral properties of such fabric, which is widely used in individual protective masks, medical uniforms and special medical applications.

The undoubted advantages of the "AgNanolfluid"TM product jointly developed by Ukraine-USA JV "MSM" in strategic partnership with V.Bakul Institute of Superhard Materials NASU are: ultra-pure nanosilver, physically implanted by ion-plasma process into food glycerin in vacuum and stabilized in it without any additional chemical reagents Due to the exceptional purity and controlled size of nanoparticles, "AgNanolfluid"TM demonstrated the lowest toxicity and good biocompatibility for humans and animals in combination with high bactericidal/antiviral properties against a wide range of viruses and bacteria.

Our study of textile materials treated with "AgNanofluid"TM under a special protocol proved that biostability of the treated fabric increased by 1.62-4.13 times, depending on the test cultures of microorganisms and fungi All those microorganisms demonstrated significant deformations, surface damage and broken cell integrity compared to the control variants of the test cultures with long-term bactericidal effect [1]. Additional research regarding the activity of nanosilver against the corona-family virus TGEV (gastroenteritis virus, an experimental model of HCoV-19), showed that "AgNanolfluid"TM (50 ppm) effectively suppresses the reproduction of the coronavirus with a selectivity index of 40.0 (the marginal value of it should be min 16.0) [2].

Based on those researches the trade mark "Medical Stream Nano" for modified functional fabric has been registered. Now LTD "Medical Stream" which has produced 2 mln disposable medical masks in 2021 against the order of WHO, created a consortium of researchers and manufacturers for a pilot project to use the be-component Ag-Cu Nanofluid for antibacterial/antivirus modification of military and sport underwear.

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A novel design of electrospun nanofibers of curcumin/HP-βcyclodextrin/pullulan complex with enhanced water solubility and slow release for food technology and drug delivery applications

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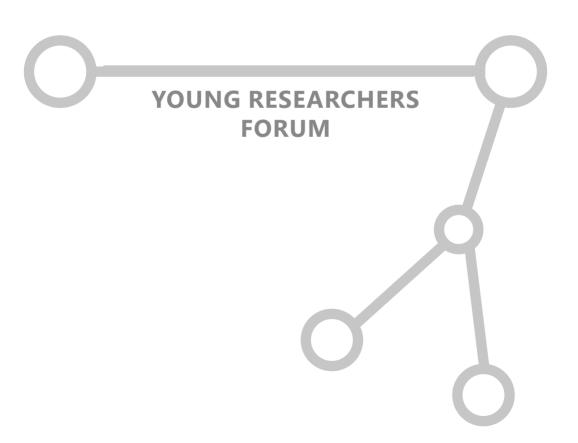
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Curcumin, a hydrophobic drug derived from the rhizome of the plant *Curcuma longa*, is a polyphenol and apart from its utilization as a therapeutic agent, it is widely consumed as a spice, food preservative, flavoring, and coloring agent. It has numerous pharmacological applications for a variety of pathologies including cancer, cardiovascular and Alzheimer's diseases, and inflammatory and neurological disorders owing to the outstanding biological functions such as antioxidant, anti-tumor, and anti-inflammatory activities. Nevertheless, it also exhibits drawbacks like low solubility in water, low bioavailability, and sensitivity to thermal treatments. Additionally, curcumin (Cur) is poorly absorbed in the gut, limiting its bioavailability. Hydroxypropyl-beta-cyclodextrin (HP- β -CD) as a nontoxic and biodegradable cyclic oligosaccharide is capable of forming complex and can be used to increase solubility and enhance the thermal stability of curcumin-based guest molecules.

In this study, Cur/HP- β -CD inclusion complex (IC) incorporated in pullulan were designed via electrospinning using uniaxial and coaxial modes, to obtain high thermal stability and slow-release properties with the aid of curcumin present in the fiber. Cur/HP- β -CD has been mixed with pullulan (Pul), where the former functions as a core material to produce uniaxial nanofibers (Cur/HP-β-CD-IC-Pul-Uni) and the latter as wall material for coaxial mode. The quality of IC was confirmed by X-ray diffraction (XRD) and Fouriertransform infrared spectroscopy (FT-IR). XRD findings have proved the interaction between HP- β -CD and the guest by the disappearance of the characteristic peaks of curcumin molecules. For uniaxial nanofibers (Cur/HP-β-CD-IC-Pul-Uni), small crystalline peaks of curcumin at 8.8 and 17.2° were detected pointing to the remaining uncomplexed active compounds in the sample while there are no crystalline peaks in the coaxial fibers (cCur/HPβ-CD-IC-sPul-Co). The FT-IR and differential scanning calorimetry (DCS) results were correlated with the observations of the XRD analysis and they also indicated that curcumin was fully immersed in the IC of $cCur/HP-\beta-CD-IC-sPul-Co$ coaxial nanofiber whereas there was some amount of uncomplexed crystalline curcumin present in the uniaxial nanofiber (Cur/HP-β-CD-IC-Pul-Uni). DSC findings further demonstrated that inclusion into coaxial nanofibers enhanced the thermal stability of curcumin. After the production of electrospun nanofibers, the melting point of curcumin powder which was initially 174.5 °C, shifted to 279.19 and 291,62 °C for the uniaxial and coaxial nanofibers, respectively.

The studies showed that the curcumin release profile of the Cur/HP- β -CD-IC-Pul-Uni nanofiber is more rapid than *c*Cur/HP- β -CD-IC-sPul-Co nanofiber. The release from both fiber types was found to be significantly enhanced by a diffusion-controlled mechanism when fibers comped to the pristine curcumin. Antioxidant activity and total phenolic content analysis have also been performed to evaluate fiber bioactivity. This novel design can be considered a promising step in food technology and drug delivery systems based on core-shell nanofiber structure, which provides not only slow release but also water solubility for such hydrophobic bioactive molecules.

SECTION A ADVANCED NANOMATERIALS



Persistent luminescence nanoparticles - synthesis and characterization

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Materials emitting light for extended period of time, after irradiation, have been known for many centuries. This phenomenon is known as Persistent Luminescence (PL), and has been extensively investigated in recent years. Therefore PL materials find many applications in daily life materials, e.g., in producing glow-in-the-dark toys and safety signs [1]. However, with the development of nanotechnology, PL continues to be an extensively studied area of research. One of the most promising approaches in this field is the use of Persistent Luminescence Nanoparticles (PLNPs), which have a wide range of potential applications in biosensors, photodynamic therapy, and bioimaging [2]. A great example of PLNPs material is $ZnGa_2O_4$ doped with Cr^{3+} ions. It has been widely investigated due to its long-lasting luminescence and emission band within the first biological window range, making it suitable for multiple biological applications [3].

In this presentation, research results on $ZnGa_2O_4$ nanoparticles doped with various concentrations of Cr^{3+} ions will be shown. The synthesized materials were obtained using two different methods: hydrothermal and sol-gel. We have also examined the decay times of long-lasting luminescence, the excitation and emission spectra of PLNPs, and their changes due to the different synthesis conditions and Cr^{3+} concentration. The structure and morphology of the nanomaterials have been confirmed using powder X-ray diffraction (XRD) and transmission electron microscopy (TEM). The sizes of synthesized PLNPs in aqueous colloids were determined using the dynamic light scattering method (DLS).

Acknowledgments

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YOUNG RESEARCHERS FORUM A

Non-centrosymmetric lanthanide metal-organic frameworks – new approach to luminescence thermometry

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Metal-organic frameworks (MOF) are porous and crystalline materials. During rational synthesis various topologies may be obtained. Particularly interesting are non-centrosymmetric MOFs. Because of lack of center of symmetry they exhibit such interesting properties as second harmonic generation (*SHG*). This nonlinear optics phenomenon in which two photons of the same frequency and polarization combine in a material with a non-centrosymmetric crystal structure to generate a new photon with twice the frequency and half the wavelength of the original photons. SHG's signal depends on the temperature [1].

MOFs are highly tunable materials thanks to their construction from nodes and linkers. If lanthanide ions are used as nodes, we recive materials called as Ln-MOFs. Because of the unique electron configurations of lanthanide ions they exhibit luminescence. Luminescence lifetime or its inteity are ones of many emission features which are dependent on the temperature. In the consequence, luminofors may be used as nanotermometers. During designing new luminescence thermometers it's important to consider thermal stability of material, thermal sensitivity, temperature uncertainity and reaction efficiency.

Combination of SHG and luminescence is possible for Ln-MOFs. It gives possibility to obtain new class of luminescence thermometers [3]. During the presentation there will be presented current results of research on synthesis of non-centrosymmetric Ln-MOFs with erbium (III) and achiral organic linker.

Acknowledgments

Work subsidized under the program "Inicjatywa Doskonałości – Uczelnia Badawcza" "ADVANCEDBestStudentGRANT" nr 075/39/UAM/0026.

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YOUNG RESEARCHERS FORUM A

MXene: a promising titanium carbide material for photocatalytic hydrogen production

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MXenes, the newly emerged two-dimensional (2D) materials, have been targeted towards application in photocatalysis. As one of the most promissing MXene materials, $Ti_3C_2T_x$ is expected to be applied as co-catalyst in photocatalytic systems because of its remarkable properties, such as excellent conductivity, exceptional hydrophilicity, huge active surface, and adjustable structure. Pristine Ti₃C₂T_x MXenes were reported to exhibit photocatalytic activity in dye-sensitized photocatalytic systems [1]. Furthermore, titaniumbased MXenes were proven to act as versatile co-catalysts on various photocatalysts and recognized as an effective way to improve the efficiency of photocatalytic hydrogen production [2]. Regardless of all unique properties, there are some factors that can affect the photocatalytic activity of MXenes. Primarily, their synthesis and subsequent procedures applied for their purification are of high importance. The fractions of MXenes investigated in our study were prepared by the common etching method followed by differential centrifugation with decreasing RPMs. Afterwards, in order to characterize achieved fractions we employed several advanced characterization techniques, namely, scanning electron microscopy, X-ray diffraction, and Raman spectroscopy. All the isolated fractions differed in terms of lateral sizes of MXene flakes, the number of intercalant layers, the amount and the kind of impurities. Secondly, another factor which influences photocatalytic properties of MXenes is their susceptibility to environmental oxidation during their storage. Taking into account all the above-mentioned factors we compared the photocatalytic activity toward hydrogen production of each of the fractions in dye-sensitized systems. It appeared that purification of the sample from a small amount of parental MAX-phase did not influence their activity, whereas a significant reduction of lithium salts in the sample of MXenes led to its notable decrease. It is likely that the degree of oxidation of the sample influences the intrinsic and co-catalytic activity of MXenes in photocatalytic systems in opposite ways: either increasing or decreasing it, respectively. The most active MXene fraction exhibited the hydrogen evolution rate of 89.1 mmol h⁻¹ g⁻¹ for eosin Y /Ti₃C₂T_x/CoSO₄ system. Our work shows huge potential of 2D MXenes used in dye-sensitized photocatalysis for hydrogen evolution.

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This work was supported by the NCN (Grant Number: UMO-2021/43/O/ST5/00137).

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Shape influenced synergistic effect of amino-functional groups on Re nanostructure formation during synthesis of heterogenous nanocatalysts

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A previously recognized [1] prefference of ReO⁴⁻ oxoanion for a "cage-like" amino functionalities structure has been explored [2, 3] in search for improved 4-nitrophenol (4-NP) hydrogenation catalysts. Resins prepared by modifying a copolymer matrix of vinylbenzyl chloride (VBC) and divinylbenzene (DVB) with 1-(2-hydroxyethyl)piperazine (HEP), 1,4bis(3-aminopropyl)piperazine (BAPP) and 1,1'-carbonyldiimidazole (CDI) were submitted to reduction-coupled adsorption of Re, yielding heterogenous nanocomposite catalysts, as demonstrated by **FIGURE 1**. Analyses were conducted using High Resolution Transmission Electron Microscopy (HRTEM) with Selected Area Energy Diffraction (SAED), X-Ray Powder Diffraction (XRD) and UV-Vis spectrophotometry.

The Re@CDI sample has shown superior weight-normalized pseudo-first order kinetic rate constant, conversion rate and stability for the performed 4-NP reduction despite the lowest Re content (5.86 g⁻¹min⁻¹, 90-85%, 11 cycles, ~5%). Nanostructures (NSs) in size range of 1-70 nm consisting of Re⁰ and Re oxides were detected throughout the catalyst, with similar morphology observed in the Re@HEP sample. Determined was a positive influence of the CDI grouping structure on the availability and and stability of ReNS active sites, resulting in increased catalytic activity. Obtained results will aid in future catalyst design decision process.

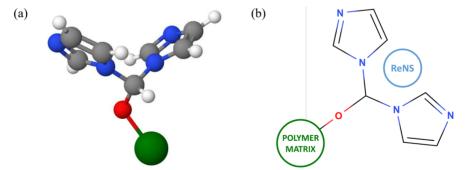


FIGURE 1. (a) 3D vizualisation of CDI-modified resin, (b) schematic of Re@CDI nanocomposite catalyst.

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This work was supported by National Science Centre (Poland) as a part of the research project UMO 2020/39/D/ST8/01352 granted to Piotr Cyganowski.

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YOUNG RESEARCHERS FORUM A

MXenes deposited on paper by vacuum-assisted filtration as effective SERS substrates with increased detection limits

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At present, the noble metal free substrates based on low dimensional semiconducting materials such as graphene, transition metal dichalcogenides, metallic oxides and recently MXene nanoflakes have been studied as promising candidates for Surface Enhanced Raman Scattering (SERS) applications. The main advantages are lower fabrication costs, possibility to tune their electronic properties and biocompatibility. Their Raman signal enhancement is mainly attributed to the photoinduced charge transfer of the chemical mechanism [1].

The Ti_3C_2 , Nb₂C and Ta₂C MXenes based SERS substrates deposited on silicon and glass revealed the detection limit in micromolar range for various dyes [2]. At present, enhancement strategies (new MXene composition and/or specific processing of MXene nanoflakes) are under development to achieve the detection limit comparable with the noble metal SERS substrates. On the other hand, MXene deposition technique affects the effective surface of the active layer and the molecular enrichment strategies could help to increase the amount of the analyte molecules in close contact with the SERS material and increase the detection limit [3].

Here, we present the paper SERS substrates based on Ti_3C_2 MXenes prepared by vacuum-assisted filtration with the ability to detect Rhodamine B as low as 20×10^{-9} M. The Rhodamine B was deposited by vacuum assisted filtration as well. For comparison, spray-coated MXene glass substrates and commercial silver based SERS substrates were used. The detection limit of Rhodamine B on the spray-coated glass did not exceed 10^{-6} M. The Ti_3C_2 MXene-based paper substrates showed comparable SERS enhancement capabilities to commercial noble metal SERS substrates. The latter showed a detection limit of 5×10^{-9} M. The developed Ti_3C_2 MXene-based paper substrates demonstrate an affordable, easy-to-prepare but robust platform for biosensing.

Acknowledgments

This work was supported by the Slovak Research and Development Agency under contract No. APVV-20-0485 and APVV-19-0465, and by the Slovak Grant Agency for Science under contract No. VEGA 2/0117/22 and 2/0046/21.

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YOUNG RESEARCHERS FORUM A

Novel Microwave-assisted solvothermal synthesis of Molybdenum-oxide colloids and what it teaches us about the preparation of transition metaloxide nanoparticles

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Transitional-metal oxide (TMO) nanoparticles are powerful and affordable alternatives to precious metals in various applications (electronics, electrochemistry, photochemistry, catalysis and even medicine). This diverse group encompasses perspective materials ranging from perovskites through zinc, silicon and iron oxides to polyoxometalates. Due to their unique optical tunability [1], non-toxicity [2] and structural flexibility [3], molybdenum-oxides gained significant attention in the development of photothermal nanoplatforms [2, 4]. In nanoscience domain, various techniques are employed to prepare molybdenum oxide nanomaterials ranging from solvothermal and hydrothermal processes [5, 6] to photo-induced synthesis [4].

Recently, we prepared nonstoichiometric MoO_X plasmonic nanoparticles by liquidphase exfoliation (sonication) in a water phase [7]. To better understand their formation, bottom-to-up synthesis route has been developed, employing microwave-assisted synthesis in an organic solvent. This process heavily depends on the synthesis parameters and yields an array of products with decisively different structural, mechanical and optical properties. Herein we present an overview of the characteristics of the products from microscopic (TEM) and spectroscopic (FTIR, UV-vis, Raman) viewpoints and discuss the specific behavior of the molybdenum oxide materials in organic solvothermal process. In particular, variability in nanomaterial structure as well as in oxidation state are explained.

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The effect of periodically corrugated substrate on SERS anisotropy of organic molecules

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Periodically corrugated plasmonic substrates were used for surface enhanced Raman spectroscopy (SERS) of thiophenol molecules. This modulation of corrugated surface can also result in the formation of a photonic bandgap in Surface plasmon resonance frequency [1,2]. Collected Raman spectra of thiophenol molecules revealed enhanced peak intensities of 10³ orders of magnitude compared to the flat substrate. TM polarization enhanced SERS intensity 5 times more than TE polarization. Further, Polarized reflectance analysis on the substrates confirmed that the anisotropy exist due to the excitation of SPP only on the transverse magnetic (TM) polarization. Raman intensities of molecules varied depending on the period of corrugation for different excitation wavelength. Such behaviour could be explained with the use of the model discussed in [3], showing that at selected frequencies a SPP damping changes nonlinearly as a function of corrugation dimensions.

Acknowledgments:

The studies were performed within the LaSensA project carried out under the M-ERA.NET 2 scheme(European Union's Horizon 2020 research and innovation programme, grant No. 685451) and co-funded by the Research Council of Lithuania (LMTLT), agreement No. S-M-ERA.NET-21-2, the National Science Centre of Poland, project No. 2020/02/Y/ST5/00086, and the Saxon State Ministry for Science, Culture and Tourism (Germany), grant No. 100577922, as well as from the tax funds on the basis of the budget passed by the Saxon state parliament and IDUB Mini grant (Support for internationalization of scientific research at the Doctoral School of the Adam Mickiewicz University, grant No. 054/13/SNS/0043)

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Autonomous experiments in materials science exemplified by laser thermal annealing of block copolymers thin films

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The use of advance computing in modern science can save a lot of work, time, and resources. Even before the actual experimental setup is made and the scientist commits to the approach numerical simulations can verify the chances of success. The same tool can be further useful in adjusting the experimental parameters during the main part of the research. Automating strenuous procedures can minimize human error and increase the amount of data collected, shortening the time needed to get sufficient results. At the same time, a scientist is free to analyze the data and change the approach if needed.

We have recently used both simulations and automated algorithms in our work "Unrestricted chiral patterning by laser writing in liquid crystalline and plasmonic nanocomposite thin films ". An idea was to use laser light to recrystallize liquid crystalline thin films in a way that produces large mono-chiral domains. The first step to achieving that goal was to find a right way to illuminate the sample i.e., to control the regular crystallizing front which was needed to avoid creating multiple crystal seeds. Rather than solving 2D partial differential equations for heat transfer with non-trivial power inputs, we used computer simulations. Then we automated the setup, reducing the human interactions to changing the sample and process parameters. This required us to implement machine vision, controlling every device such as motorized stages and laser.



FIGURE 1. The setup for patterning in liquid crystalline thin films.

In current work we would like to convert that approach to rapid thermal annealing of block copolymers (BCP) thin films, combining it with lab-on-chip idea to reduce time and resources spent. Such a setup allows for testing up to 20 different illuminating patterns on a single sample with minimum human interference. Immediately after verifying results a new set of parameters can be checked. Any parameters can be also previously verified by computer simulations. Further plans include adding a simple artificial intelligence subsystem, that can react to any changes in the environment during an experiment. Furthermore, such addition could be immune to imperfections caused by computer simulations that use a simplified model of an experiment.

Acknowledgments

We acknowledge the support from the National Science Center Poland through the Sonata Bis grant 2020/38/E/ST5/00328.

YOUNG RESEARCHERS FORUM A

Photothermal and Photocatalytic Mechanism of Polydopamine Coated Gold Nanorods Towards Rh6G degradation

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Localised surface plasmon resonance (LSPR) presented by gold nanorods (AuNRs) has been proved to be used in different applications such as photoredox catalysis, plasmonenhanced spectroscopy, biomedical technologies, and optoelectronic devices[1]. The combination of AuNRs with Polydopamine (PDA) shells results in a strong photo-thermal effect, making them appealing nanomaterials for biomedical applications. Here, a reproducible hybrid nanoplatform made by an AuNR core surrounded by a polydopamine (PDA) shell has been synthesized by carrying out a seed-mediated growth[2] followed by the further self -polymerization of dopamine (DA) on the surface of the AuNR. Several AuNRs/PDA samples were synthesized with average PDA shell thicknesses going from ≈ 4 nm to ≈ 30 nm showing LSPR values in the range between 920 nm and 800 nm. The effect of the thickness of the PDA shell on the plasmon response of the composite and the photocatalytic performance towards Rhodamine 6G (Rh6G) were examined. Degradation of 54% of Rh6G initial concentration was achieved within 60 minutes of irradiation with a catalyst concentration of 7.4 µg mL⁻¹. Photodegradation kinetics for different initial concentrations of Rh6G was studied with the Langmuir-Hinshelwood model. Finally, using time-resolved spectroscopy, finite-element-method simulations of plasmons show that AuNRs plasmons, coupled with the low thermal conductivity of PDA, provide low thermalization, while enhancing the charge carrier transfer.

Acknowledgments

The authors acknowledge the financial support from the National Science Centre of Poland (NCN) by the OPUS grant 2019/35/B/ST5/00248. D.A.F would like to acknowledge French Government Scholarship for the financial support.

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Realization of a sodium-ion capacitor by pre-metalation of a hard carbon anode using sodium azide as sacrificial cathodic material

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Metal-ion capacitors (MICs) are hybrid electrochemical energy storage systems capable of delivering up to ca. 4 times higher specific energy than electrical double-layer capacitors (EDLCs) ^[1]. This is achieved by combining a battery-type negative electrode (e.g., metalated hard carbon (HC)) with an EDL positive electrode (typically from activated carbon (AC)) in which the electrolyte anions are reversibly electrosorbed. One crucial aspect in the conceptualization, design, and optimization of MICs is the premetalation of the negative electrode, i.e., the formation of a solid electrolyte interphase (SEI) and doping of this electrode. Among the few pre-metalation methods available, the incorporation of a sacrificial material containing a metal ion (M) in the positive electrode is the most attractive one, owing to its cost-effectiveness. The M element is extracted by electrochemical oxidation and transferred to the negative electrode. An optimal sacrificial material for MICs should meet several criteria, including: (i) a relatively low oxidation potential to avoid electrolyte decomposition, (ii) a high irreversible capacity to reduce its amount in the positive electrode, i(iii) stability in the ambient atmosphere for easy electrodes fabrication, and (iv) generation of non-detrimental by-products for optimal device performance. NaN₃ is a rare material that fulfills all these requirements and has already been successfully implemented in sodium-ion batteries ^[2].

In this context, an (+)AC-NaN₃//HC(-) cell equipped with reference electrode was realized, and electrochemical oxidation was conducted to transfer sodium from NaN₃ to HC. The evolving gas during the oxidation process was analyzed with internal pressure measurement (Figure 1a). The result indicates that only a few galvanostatic cycles are needed to completely oxidize the sacrificial material. Subsequently, the electrochemical performance of a (+)AC//Na_xHC(-) laminate Sodium-ion capacitor (NIC) equipped with reference electrode was investigated by galvanostatic charge/discharge cycling. The NIC laminate cell demonstrated a very stable performance during 4000 cycles at 200 mA g⁻¹ (Figure 1b). Furthermore, the discharge tests conducted at constant power revealed that the device maintained an almost constant output energy density of 42.3 Wh kg⁻¹ up to a specific power of 2 kW kg⁻¹ (based on the total active mass of both electrodes). During the presentation, detailed information and results on the fabrication and performance of the laminate cell, including a new design of negative electrodes incorporating novel materials, will be provided.

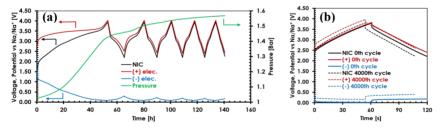


FIGURE 1. 1. a) Evolution of electrode potential, cell voltage and internal pressure during galvanostatic (at C/40) sodium transfer to the anode in an (+)AC-NaN3//HC(-) cell; b) Galvanostatic charge/discharge of the (+)AC/NaxHC(-) laminate NIC during cycling.

Acknowledgments

This work was supported by the Polish National Science Center (NCN) [UMO-2016/22/A/ST4/00092] and the Ministry of Education and Science, Poland [0911/SBAD/2301].

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YOUNG RESEARCHERS FORUM A

Effect of stabilizing agent on the synthesis of ZnO nanoparticles

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ZnO nanoparticles are widely used in opto- and microelectronics for photodetectors and in transparent electronics for TFT arrays [1]. As they are a biocompatible material, they can also be used in medicine.[2]

The purpose of our research was to produce and characterize ZnO nanoparticle suspensions using a stabilizing agent (carboxylic acids) in different proportions relative to the ZnO precursor. The synthesis was carried out according to the following method: zinc acetate was dissolved in ethanol, carboxylic acid was added and heated to boiling, then a solution of tetramethylammonium hydroxide was injected into the reaction mixture, the whole was heated for 2 minutes and then quickly cooled to 0°C. The resulting precipitate was centrifuged, washed with ethanol and finally dispersed in toluene.

The particles obtained were characterized in terms of structure and morphology both as a suspension and as a thin film produced by droplet deposition and by deposition onto a spinning substrate. The following techniques were used for the study: FT-IR and UV-VIS spectrophotometry, as well as an optical microscope (**Fig.** 1) and an atomic force microscope.

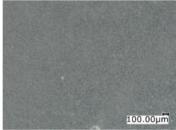


FIGURE 1. Microscopic photo of ZnO layer obtained by droplet deposition method using a slurry obtained from zinc acetate and oleic acid in a molar ratio of 1 to 2

Acknowledgments

We would like to thank the staff of the Department of Molecular Physics at the Technical University of Lodz for their help and valuable advice during the implementation of the Student Research Volunteer Program.

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Biomass-derived HMF upgrading on Co-based MOFs

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Biomass-derived furanic compounds represent a bountiful renewable feedstock for the sustainable production of fuel-additives, biofuels, and chemicals [1]. 5-Hydroxymethyl-2-furancarboxylic acid (HMFCA), for instance, obtained from the oxidation of 5-hydromethylfurfural (HMF), is a valuable building block for the polymer industry as well as the pharmaceutical industry [2]. However, only a limited number of studies focus on the targeted synthesis of HMFCA by applying stoichiometric or catalytic oxidation due to the easy overoxidation to downstream products [3]. Biomass transformation requires updated catalysts or even new materials able to convert this feedstock into valuable products in the liquid phase. In this regard, metal-organic frameworks (MOFs), hybrid organic-inorganic materials, exhibit a unique set of properties that makes them promising alternatives to classic solid catalysts in biomass upgrading processes [4].

In this context, the present study focused on designing and developing Co-based MOF catalysts (i.e., ZIF-67, Co-BTC, Co-BTC-2mim, Co₃O₄@Co-BTC) able to combine high catalytic efficiency with hydrothermal stability in the selective oxidation of HMF to HMFCA with t-BuOOH as oxygen donor and acetonitrile as solvent.

The synthesis was carried out in solvothermal conditions, employing either $Co(NO_3)_2$ or Co_3O_4 as a metal source, together with benzene-1,3,5-tricarboxylic acid (H₃BTC) or 2-methylimidazole (2mim) as linkers, yielding to ZIF-67 (containing Co and 2mim), Co-BTC, and $Co_3O_4@Co$ -BTC materials. Moreover, Co-BTC was used as a precursor in the synthesis of Co-BTC-2mim in a linker exchange process.

The catalytic results indicated that the $Co_3O_4@Co-BTC$ sample was the most efficient catalyst, affording 79.3% HMF conversion and 89.1% HMFCA selectivity using t-BuOOH as an oxidation agent, in acetonitrile as a solvent, at 60 °C and 1 h. Moreover, the recyclability test of $Co_3O_4@Co-BTC$ revealed that the catalyst maintained its performance over four cycles with slight variations in HMF conversion, from 79.6 to 75.2%, and HMFCA selectivity, from 87.6 to 86.1%. Besides, no obvious difference for both the fresh and recovered samples was observed in the XRD patterns, indicating the $Co_3O_4@Co-BTC$ catalyst was stable during the reaction in the liquid phase.

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Modified organosilicon compounds as emulsifying agents

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An emulsion is a system in which one liquid is dispersed in another. It is stabilized by adding emulsifier that reduces the interfacial tension between oil and aqueous phases [1]. Emulsifing agents can be classified as non-ionic, ionic (cationic or anionic) and finely dispersed solids. More recently, derivatives of polyhedral oligomeric silsesquioxanes (POSS) have been also used as emulsifiers [2]. These hybrid silica-based systems have a strictly difined cubic structure. The silica core of POSS can be modified by introduction of various functional groups that enables to change their properties.

The aim of the present research was to check if the modified organosilicon compounds can be applied as emulsyfing agents. Four octaspherosilicates with different ratio of substituents such as 4-allyloxy-2-hydroxybenzophenone and polyethylene glycol (PEG12-20) were synthesized via hydrosililation reaction using Karstedt catalyst. Fourier transform infrared spectroscopy (FTIR) was used to check the progress of the synthesis. The hydrophilicity of the compounds was determined by calculating hydrophilic-liophilic balance value and determining the wetting angle using a goniometer. Next the emulsifing properties of the obtained compounds were studied. Therfore, various types of emulsions consisting of different contents of water, oil and emulsifying agent were prepared. The stability of the obtained emulsions were studied by centifugation test and multiple light scattering method. Each of the prepared emulsions was also analyzed by optical microscope and laser diffraction directly after preparation and after one month.

The results proved that organosilicon compound with higher amount of PEG12-20 groups are more hydrophilic and stabilze emulsions more efficiently compared to compound with higher amount of 4-allyloxy-2-hydroxybenzophenone.

Acknowledgments

This research was financially supported by The National Centre for Research and Development (Poland), grant number LIDER/5/0036/L-12/20/NCBR/2021 "Technology of obtaining high molecular weight UVA/UVB filters for modern cosmetic formulations".

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ZIF-derived carbons for water purification

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Water pollution has serious consequences for the environment, such as biodiversity loss, ecosystem degradation, and human health problems. The main contamination causes are industrial waste, agricultural runoff, sewage disposal, and oil spills. To prevent and reduce water pollution, treating wastewater before discharging it into water bodies is essential for human health and well-being, as well as for environmental protection. The adsorption process is one of the methods to purify water. Efficient porous materials via adsorption can reduce the risk of waterborne diseases, improve the taste and odor of water, and conserve natural resources. Porous carbons consistently represent the dominant group of sorbents with one of the greatest application capabilities due to their high specific surface area, good water and thermal stability. Metal-organic frameworks (MOFs) represent a new type of carbon precursors, which simultaneously act as a templating agent that allows tuning the particle shape [1]. Through the use of diverse metal sources and reaction solvents, it is possible to control the crystallization kinetics of MOFs and develop new structures that can then be used for the preparation of unique carbon materials. One of the challenges is the synthesis of mesoporous carbons derived from the subgroup of MOFs, zeolitic imidazolate frameworks (ZIFs). The properly designed ZIF-derived carbons can be successfully used to adsorb intrusive and globally present contaminants, such as dyes.

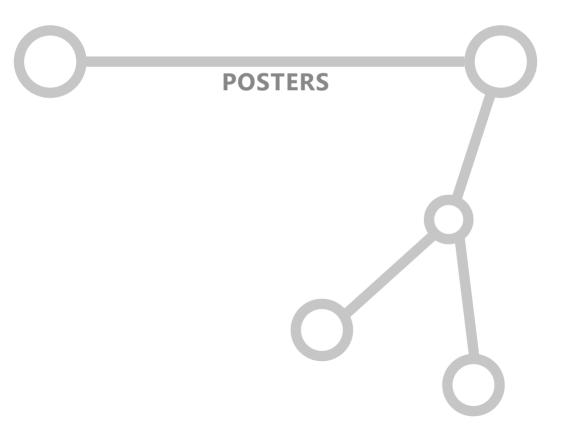
In the conducted research, the preparation of carbon materials with different particle shapes and porosity was developed using zinc-based ZIFs, i.e. ZIF-8 and ZIF-CO₃-1. The 2-methylimidazole, acting as an organic linker, was the main source of carbon and additionally enriched the carbon materials with nitrogen. In turn, salt (zinc acetate) and zinc oxides with different morphologies, spherical and flower-like, were used as metal sources. The materials were obtained by the solvothermal method using dimethylformamide for ZIF-8 and a mixture of dimethylformamide and distilled water for ZIF-CO₃-1. Subsequently, all ZIFs were carbonized at 1000 °C for 1 h in argon flow. The carbon materials were employed in the adsorption processes of tartrazine, brilliant green, auramine O, and rhodamine B.

Analyses showed that the prepared carbons have morphologies similar to ZIFs but differ significantly in porosity. Carbonization of ZIF-8 from salt led to carbon with a polyhedral particle shape and in the case of ZIF-8 built on ZnO, its spherical morphology was reproduced. ZIF-CO₃-1-based carbons, on the other hand, resembled blocks and windmills. The ZIF-8-derived carbons are highly microporous, while a double system of micro- and mesopores was achieved for materials prepared by carbonization of ZIF-CO₃-1. The specific surface area of the samples ranged from 310 to 1155 m²/g. After two hours of adsorption, ZIF-derived carbons demonstrated various dye removal efficiency. Microporous samples adsorbed tartrazine more intensively, while those having mesopores efficiently removed brilliant green from aqueous solutions.

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SECTION A ADVANCED NANOMATERIALS





Influence of the gold nanoparticles on photophysical properties of the hybrid system

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The development of methods and possibilities for the fabrication of nanomaterials imply progress in the improvement and application of new medical procedures. Interdisciplinary research is being conducted on many areas to find effective diagnostic and/or therapeutic methods using metallic nanoparticles [1]. The determination of the photophysical properties of nanoparticles and the study of their interactions with biological material provide important information to create ever better drug or vaccine delivery systems and to identify the occurrence of potential side effects [2,3].

In our study, we synthesized spherical gold nanoparticles coated silica dioxide with a photosensitizer, Rose Bengal, tethered to their surface. Each nanoparticle possesses an identical gold core, but presents a different silica shell thickness. These hybrid plasmonic nanoparticles thus afford a plasmonic nanostructure platform with a source of singlet oxygen generation. The fabrication of the optimal thickness of the shell defines the distance between the dye (donor) and metal nanoparticles (acceptor). That allows determining the optimal conditions for energy transfer in the hybrid system allowing modifying the singlet oxygen generation or dyeing luminescence yield. In our work we compared the influence of the coatings on the singlet oxygen generation process in hybrid systems based on gold nanoparticles. The research allow for the selection of hybrid mixtures indicating the enhancement of photophysical parameters and the optimalization of the interaction between a functionalized nanoparticle and a Rose Bengal. Photophysical parameters relevant to potential applications in photodynamic therapy, diagnostics, or photothermal therapy were determined for synthesized functionalized nanoparticles and their hybrid systems with Rose Bengal.

Acknowledgments

This work was supported by the National Science Center in Poland by the project 2021/41/N/ST4/03017 (P.B).

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Photonic nanojet mediated Raman scattering enhancement of eutectic Metamaterials using a Single Optical Microsphere

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Raman spectroscopy has long been used for molecular identification and analysis [1], but it has limitations when it comes to identifying crystal phases in low-symmetry structures or small crystals [2]. To overcome this challenge, a novel technique has been developed that uses a single dielectric optical microsphere and confocal Raman microscopy to obtain the phase information by enhancing the Raman scattering signal. This method involves placing the microsphere on top of a substrate made of Bi₂O₃-Ag, a plasmon-active multiphase eutectic metamaterial synthesized through the micro-pulling down technique [3]. When laser light is directed onto the silica microsphere, it creates a photonic nanojet (PNJ) which is a highly intense and narrow-focused electromagnetic beam. PNJ is generated due to constructive interference between Mie scattered and incident light and also has the ability to focus light beyond the classical diffraction limit. PNJ helps to enhance the Raman scattering spectra of nano precipitates of γ phase of Bi₂O₃ near Ag nanoparticles, with an estimated enhancement factor of ~ 90. This technique has the potential to significantly improve Raman nanoscopy for chemical and crystal phase mapping, and revolutionize vibrational spectroscopy-based optical nano-characterization.

Acknowledgments

The authors thank the ENSEMBLE³ Project carried within the Teaming for Excellence Horizon 2020 program of the European Commission (GA No. 857543), and the International Research Agendas Programme (MAB/2020/14) of the Foundation for Polish Science co-financed by the European Union under the European Regional Development Fund and Teaming Horizon 2020 program of the European Commission.

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Designing Tunable Near-Perfect Light Absorbers with Ga:ZnO Multilayer Thin Films in the Epsilon-Near-Zero Region

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Strong light-matter interaction in a narrow region of space has many potential uses in photonic circuitry, including ultrafast switching, high harmonic generation, sensing, etc. Transparent conducting oxides such as ITO, AZO, and GZO are often employed in photonic devices to achieve these functionalities. These materials exhibit extreme field enhancement in the near-infrared region, which occurs when their permittivity approaches zero. Such materials, also known as epsilon-near-zero (ENZ) materials, can be incorporated into various platforms such as metamaterials, surfaces, waveguides, and thin films to create devices with a wide range of electromagnetic functionalities[1] [2].

In this work, we explored a novel structure of Ga:ZnO (GZO) multilayers in a ZnWO₄ matrix, which exhibits strong polarization selectivity and resonant absorption. The non-radiating ENZ modes of the constituent GZO layers are excited using end fire coupling. This multilayer structure shows strong polarization selectivity and geometrically tunable resonant absorption/emission. Moreover, incorporating antireflection coating at the facets of the structure enables it to perfectly absorb TM-polarized incident light. The spectral range of high absorption can be tuned by varying the thickness of the GZO/ZnWO₄ layer. We believe that our study will be helpful in the design of photonic components such as modulators, sensors, and other optoelectronic devices based on light absorption/emission.

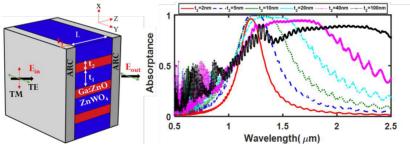


FIGURE 1. Schematic of the considered multilayer structure and the calculated absorption spectra.

Acknowledgments

This work is supported by the ENSEMBLE3 Project (MAB/2020/14) which is carried out within the International Research Agendas Programme (IRAP) of the Foundation for Polish Science co-financed by the European Union under the European Regional Development Fund and the Teaming Horizon 2020 program (GA. No. 857543) of the European Commission

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Relationship between the structural properties of ZnO nanowires and their modulus of elasticity

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Properties of nanowires (NWs), instead of material, are driven rather by effects collocated with dimensions and topology, especially surface-to-volume ratio [1]. In the measurement of NWs, diameter plays a crucial role, as does crystal orientation and the level of crystal defects [2]. Measurement of a single entity in different degree of crystallinity may bring more understanding to the role played by separate factors.

. We present method for a single specimen measurement of the ZnO NWs in different degree of crystallinity. Heat treatment is carried out on the NW attached to the marked substrate in order to measure mechanical parameters on the same element. Measurements were conducted with atomic force microscopy (AFM). The measurements compared the Young's modulus of the NW as the crystallinity of the sample improved. The research is of great importance in establishing the synthesis-structure-property relationships that ultimately lead to the optimization of devices used in fields such as renewable energy (in harvesting devices), medicine (biomedical system), and many others.

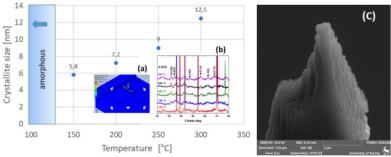


FIGURE 1. Estimated crystallite size determined for samples annealed at temperatures from 100 °C to 300 °C. (a) XRD patterns of anodic films after 2 h of annealing at temperatures from 100 °C to 300 °C, (b) simulation of the case of indentation with 25 nN, (c) monocrystaline conductive diamont tip for nanoindentation.

Acknowledgments

The following research has been conducted with financing from the project 19ENG05 – NanoWires funded from the EMPIR programme (European Union's Horizon 2020).

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Advanced substrates for measurements of nanomaterials

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The dimensions of nanoparticles render them comparable to the surface details of many available substrates. Repeatable measurement of nanoparticles requires a stable, reliable substrate that does not interfere with the measurement of the specimen in any quantity [1]. For topography, that would be realized by surface roughness appropriately smaller than nanoparticle dimensions, etc. Realization of substrates has to simultaneously allow for measurement with microscopic tools and therefore enlarge the contact area of nanoparticles.

We present a series of substrates with surface features prepared specifically for the measurement of nanowires (NWs). Features characterize an elevation of about 500 nm above the substrate, an electrical resistivity of $11 \cdot 10^{-8} \Omega \mu$, and a thermal conductivity of $1,6 \cdot 10^3$ W/K. Details allow for direct placement of NWs, electrical connection, and measurement of a given quantity. They are prepared in a more condensed, less accessible form (Fig. 1a), which has to be accessed with nanomanipulators (e.g., Kleindiek MM3A-EM), or more loosely with electrical connections leading out of the sample (Fig. 1b), allowing for measurement of mechano-electro-thermal properties.

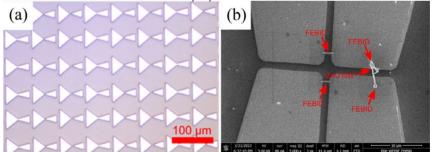


FIGURE 1. Substrates for measurement of nanoparticles: (a) matrix of separated electrically and thermally islands for measurement of nanoparticles imaged with optical microscope, (b) single section of electrically connected setup with nanowire placed imaged with scanning electron microscope.

Acknowledgments

The following research has been conducted with financing from the project 19ENG05 – NanoWires funded from the EMPIR programme (European Union's Horizon 2020).

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Impact of shape and composition of Janus nanoparticles based on ZnS-Ag on photocatalytic hydrogen evolution under visible irradiation

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A series of nanoparticles (NPs) using zinc sulfide (ZnS) and silver compounds with different structures (Janus, Janus-like, and multiheaded) was made through a two-step process involving hydrothermal synthesis and the formation of silver compounds on the ZnS surface. These nanoparticles were then studied for their photocatalytic activity in generating hydrogen under visible light (λ >420 nm). The NPs with Janus morphology showed the highest effectiveness in this process. Various characterization techniques were used to understand the role of surface chemistry in the photocatalytic activity of these NPs. Two possible mechanisms for the photocatalytic reaction were proposed, involving either the excitation of silver particles or the Ag₂S semiconductor. Principal Component Analysis (PCA) was also used to investigate the relationship between the structure of the Janus-like ZnS-Ag NPs and their activity in photocatalytic hydrogen generation under visible light.

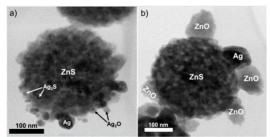


FIGURE 1. TEM images of the most active sample ZnS-Ag-2 (a) and sample with the biggest amount of AgNO₃ added during synthesis ZnS-Ag-10 (b).

Acknowledgments

This work was financially supported by National Science Centre, Poland (Grant no. 2022/06/X/ST4/00176).



Dynamic magnetoelectric effects: generation of spin currents, charge currents and modulation of the spin-wave amplitude

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We show by numerical simulations that the time-varying charge accumulation in the ferromagnetic metal produces spin current while, conversely, the time-varying spin accumulation in the ferromagnetic metal (generated by the inverse spin Hall effect or spin pumping) produces charge current via the dynamic magnetoelectric effects.

For this purpose we developed numerical model that solves Landau-Lifshitz-Gilbert equation coupled with the charge-spin transport equations in Comsol Multiphysics in the s-d approximation. The model takes into account the effects of: spin-transfer torque, spin dephasing, spin pumping, spin-dependent conductivity, spin-dependent potential and voltagecontrolled magnetic anisotropy. Time-dependent as well as eigenfrequency studies are possible.

In particular, simulation reveals that the spin-dependent screening at dielectricferromagnetic metal interface contributes to the spin-polarized current generation in the system subjected to the ac voltage [1]. Then, we show that spin current driven by spindependent screening may be used to modulate spin-wave amplitude in bilayer ferromagnetic system [2]. Finally, we combine ab initio calculations of electronic density of states at MgO/Fe interface with continuous model for charge transport. We show that the voltagedriven electron charge accumulation at MgO/Fe interface leads to the Stoner instability because of the electronic interface resonant states. This instability manifests itself in the spincurrent and spin accumulation femtosecond pulses which are present because of the contribution of the dynamic spin-dependent potential to the spin-polarized current.

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The study has received financial support from the National Science Centre of Poland under grant 2018/28/C/ST3/00052.

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Morphology, thermomechanical, and piezoresistive properties of polystyrene/spherical graphitic shells composite films

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The development of advanced flexible highly sensitive piezoresistive strain gauges that respond to mechanical deformations by changing electrical resistance has recently received much attention. In this work, comparative studies of the effect of spherical hollow graphitic shells (GS) synthesized by chemical vapor deposition (CVD), and commercial multi-walled carbon nanotubes (CNTs) on the morphology, thermomechanical, and piezoresistive properties of polystyrene (PS)-based composites were carried out.

SEM observations revealed that a concentration of 0.25 wt.% of GS was insufficient to achieve uniform distribution of the filler in the PS matrix and to create a conductive path of GS nanoparticles, unlike CNTs, which formed effective connections in the matrix at a concentration of 0.25 wt.%. Application of 0.5 wt.% of both GS and CNTs resulted in composites with conductivity similar to semiconductors, which is highly desirable for piezoresistive strain sensors. The addition of CNTs to PS improved the storage modulus of all CNTs/PS composites, except for the composite with the highest CNTs content (2 wt.%), due to increased stiffness associated with dispersed carbon structures with a relatively high aspect ratio in the matrix. However, the use of GS as a nanofiller in a PS matrix did not show an enhancing effect on the storage modulus; on the contrary, noticeable decreases in the storage modulus values of GS/PS composites were observed compared to pure PS and composites with CNTs. This could be attributed to the local agglomeration of GS nanoparticles in the PS phase, as confirmed by SEM observations. The results of Young's modulus under tensile deformation for the studied composites were in agreement with the dynamic mechanical analysis (DMA) results. The elongation at break values showed improvement for all composites with CNTs, except for the one with 2 wt.% of CNTs, while a reduction in this parameter was observed for all composites with GSs. Piezoresistive tests under bending and tensile stress showed that composites with GS exhibited higher stability of response compared to those with CNTs, which can be attributed to the unique morphology of graphitic shells. The use of hollow spheres allowed for good composite conductivity in the initial state and high sensitivity under deformation, which cannot be achieved using multi-walled CNTs.

Acknowledgments

N.G. acknowledges support from the National Science Center program for scientists from Ukraine (No. UMO-2022/01/3/ST5/00015). This research has been supported by the Centre of Polymer and Carbon Materials of the Polish Academy of Sciences, Poland.



Multi-functional optical sensors of temperature, pressure and laser power

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The control of parameters such as pressure (vacuum), temperature and laser power density are vital in materials science and industry [1]. Therefore, in this work we have developed for the first time a multifunctional sensing platform that allows optical detection of all three parameters, using a sensor based on an inorganic upconverting nanomaterial (NaYF₄:Gd³⁺, Yb³⁺, Er³⁺) emitting in the visible range. To measure these parameters without contact, optical methods based on the luminescence of lanthanides were applied [2]. To develop this sensor, we used the relationship between the local temperature of the material and the luminescence intensity of the thermally coupled levels of Er³⁺, namely the band intensity ratio (525/550 nm) [3]. We believe that this work can inspire new lines of research that allow the development of materials as multifunctional nano-sensors.

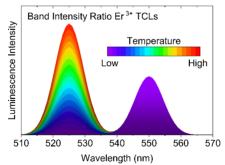


FIGURE 1. Concept of thermally-coupled levels in Er³⁺-doped luminescent material.

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Optical properties of modified MoO_x nanoparticles for local phototherapy

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Light therapy, also called phototherapy, is related to the most promising trends for the medicine of future. This is because it offers high precision, ability to remote control, minimal invasiveness to normal tissues and low systemic toxicity. Light therapy is realised through photoactive agents which optical properties allow to transform light energy to thermal (phototermal therapy) or chemical energies generating reaction oxygen species (photodynamic therapy). Our study is devoted to the design of photoactive agent based on MoO_x nanoparticles, silver and photoactive compounds (berberine, coptisine, hypericin, hyperforin) originated from medicinal plants Chelidonium majus and Hypericum perforatum. MoO_x nanoparticles were used due to their ability to absorb light in near infrared region (biological window I) which is an advantage for phototherapy. Moreover, molybdenum is considered to be an essential trace element for the majority of biological organisms [1]. Silver was chosen due to the ability to improve optical signals and wide bioactive properties, whereas plants Chelidonium majus and Hypericum perforatum are known to contain photoactive compounds and used in folk medicine for treatment of different diseases [2,3]. Our results showed that modified with silver and plant compounds MoO_x nanoparticles reveal novel optical properties, in particular, they are able to emit fluorescence being excited at laser wavelengths 405, 514, 561 and 780 (two photons) nm. Herein, fluorescence emittance at excitation wavelengths 405, 514 and 561 nm is due to the presence of plant photoactive compounds, whereas irradiation by two-photon laser at 780 nm resulted in surface plasmon resonance effect of silver. Moreover, excitation-emission mapping performed for modified MoO_x nanoparticles revealed that, being excited at laser wavelength in the range 240-570 nm, they produce intensive (in comparison with initial MoO_x nanoparticles) Raman signals in the wavelengths 1060-1200 nm. These data allow us to conclude that produced MoOx-based nanoparticles with silver and plant compounds are promising as a photoactive agent.

Acknowledgments

The authors acknowledge the financial support from the National Science Centre of Poland (NCN) by the OPUS 18 - 2019/35/B/ST5/00248. This work was also supported by the Slovak Grant Agency for Science under VEGA 2/0117/22.

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The comparison of physicochemical and sorption properties of modified ordered mesoporous silica materials

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The growth of the human population and the related anthropogenic effects, including water, air, and land contamination require the use of effective treatment processes. Numerous methods for pollutant removal, e.g., oxidation, biodegradation, and coagulation have been applied, although they possess several limitations such as complicated procedures, inefficient elimination, or high energy demands. Adsorption of contaminants holds greater potential due to its high performance, low cost, no generation of toxic by-products, and wide selection of adsorbents. Antibiotics are among the most common water pollutants as a consequence of their large consumption. Since they are removed by excretion, huge amounts of these pharmaceuticals enter the water system. They can accumulate in organisms posing a serious threat to flora, fauna, and people which makes their effective removal an essential matter [1].

The presented work aimed to prepare efficient adsorbents based on silica materials for the removal of tetracycline and ciprofloxacin from water solutions. SBA-15 and KIT-6 obtained from fly ash-based waste solution were subjected to impregnation with lanthanum(III) chloride in the amount required to obtain 5 wt.% La loading. The synthesized samples (5La/SBA-15, 5La/KIT-6) were characterized with X-ray diffraction, lowtemperature nitrogen adsorption/desorption, and the Boehm titration method. The impact of pH (2-9), temperature (RT, 35, 45 °C), and drugs' initial concentration (10-200 mg/L) on the sorption capacities of materials was studied. In order to describe the adsorbent-adsorbate interactions, the equilibrium data were fitted to Langmuir and Freundlich models.

The obtained SBA-15 and KIT-6 possessed 2D hexagonal and 3D cubic structures, respectively. Modification with lanthanum led to a decrease in the intensity of XRD reflexes indicating deterioration of mesoporous structure ordering. The low-temperature nitrogen adsorption/desorption revealed that modified samples have lower specific surface area and total pore volume as well as larger pore size. In the case of La-impregnated adsorbents, both acidic (0.75 mmol/g) and basic (0.75 mmol/g) groups were generated on the surface. Impregnation of SBA-15 and KIT-6 with LaCl₃ causes an improvement in sorption capacities toward tetracycline and ciprofloxacin, which can be ascribed to electrostatic interactions between materials and antibiotics. Depending on the silica material, the adsorption process had an exothermic (the drug was most effectively removed at room temperature) or endothermic (the biggest amount of antibiotic was eliminated at 45 °C) nature. The values of the R² coefficient for the Langmuir model were close to 1, which proved it was the best model to describe the experimental data. The conducted research confirmed that the use of synthesized adsorbents may be beneficial in the treatment of drug-contaminated water.

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Block copolymer templates for plasmonic substrates fabrication

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Gain control over metalic nanostructures assembly remains an important challenge in nanotechnology. Well developed top-down strategies (i.e. photolithography, electron-beam lithography) do provide great structural control, however they become increasingly time-consuming and expensive when it comes to nanoscopic structural motifs reaching the size down to ~ 100 nm and below. Therefore, an alternative bottom-up solutions, involving self-assembling systems are being intensively explored. Development of commonly available and reliable technology of this kind would accelerate the progress made in photonics, plasmonics and allow entering the field of new generation of optical devices based on metasurfaces. In order to fabricate well ordered gold nanostructures we employed block copolymer lithography combined with electron-beam physical vapour deposition. Initially, the poly(styrene-b-ethylene oxide) PS-PEO thin film was spincasted onto thermally reconstructed sapphire substrate and subsequently solvent vapour annealed to get the long-range order of hexagonaly arranged cylindrical domains, oriented perpendicular with respect to the film surface. Afterwards, the reactive ion etching was applied to modify the polymer film surface. Finally, a thin gold layer was deposited using the ultra-high vacuum electron beam evaporation system. Obtained substrates were examined in terms of surface enhanced Raman spectroscopy. Model analyte (thiophenol) was used to monitor the impact of surface topography on signal amplification.

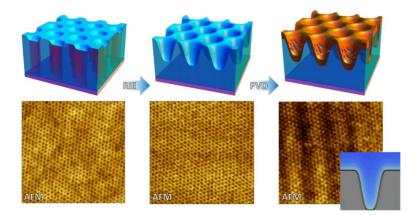


FIGURE 1. Substrate preparation strategy: i) copolymer matrix fabrication, ii) Reactive Ion Etching, iii) Physical Vapour Deposition of Au layer. bottom) AFM images of PS-PEO copolymer based matrix.

Acknowledgments

The studies were performed within the LaSensA project carried out under the M-ERA.NET 2 scheme (European Union's Horizon 2020 research and innovation programme, grant No. 685451) and co-funded by the Research Council of Lithuania (LMTLT), agreement No. S-M-ERA.NET-21-2, the National Science Centre of Poland, project No. 2020/02/Y/ST5/00086, and the Saxon State Ministry for Science, Culture and Tourism (Germany), grant No. 100577922, as well as from the tax funds on the basis of the budget passed by the Saxon state parliament.



Polymer brush length and antibody-antigen rupture force via single molecule force spectroscopy

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Single molecule force spectroscopy (SMFS) is a technique used to study the mechanical properties and interactions of individual biomolecules, such as proteins, polymers at the single molecule level. By applying forces to the molecules and measuring their response, SMFS can provide insights into their folding, unfolding, and binding behaviour, as well as their mechanical stability and elasticity. Here, we showcase two important options of the SMFS technique and its differences in measurement optimization and data processing. We compare the measurement details of establishing the unfolded length of polymer chain, and the force of the mechanical rupture of antigen antibody based binding on living cells under physiological conditions. The polymer chain length was measured on a surface-tethered poly[N-(2-hydroxypropyl) methacrylamide] polymer brush [1], while on the live cell system we established the rupture force of anti-human carbonic anhydrase IX (M75) antibody and carbonic anhydrase IX (CAIX) antigen [2].

Acknowledgments

We gratefully acknowledge the Financial support of the project VEGA 2/0117/22. This work was performed during the implementation of the project Building-up Centre for advanced materials application of the Slovak Academy of Sciences, ITMS project code 313021T081 supported by the Integrated Infrastructure Operational Programme funded by the ERDFW.

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Analysis of graphene quality during the N/MEMS fabrication process

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With the flourishing multidisciplinary field of low-dimensional nanomaterials, including one-dimensional (1D) nanowires/nanotubes and two-dimensional (2D) atomic layers such as graphene/phosphorene, growing interests, and sustained effort have been devoted to creating mechanical devices toward the ultimate limit of miniaturization genuinely down to the molecular or even atomic scale [1].

In the poster, we would like to present the influence of the processes carried out in the initial phase, which directly impact the final results. We are investigating the qualitative analysis of three different graphene monolayers transferred by various manufacturers to the SiO_2/Si surface.

The primary purpose of the work was to suspend a graphene flake between two metal electrodes: drain (D) and source (S) (part of N/MEMS fabrication). The quality of transferred 2D material is crucial. We mainly used SEM, AFM, optical microscopy, and μ Raman spectroscopy to pay attention to its continuity, homogeneity, stability, thickness, and finally, after the stage of wet etching in HF acid: the strength of binding carbon molecules to create a connected, conductive bridge, stretched between D and S.

Acknowledgments

PO WER "Environmental interdisciplinary Ph.D. studies in the field on nanotechnology (POWR.03.02.00-00-1032/16)".

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Cation identity in clay-polyelectrolyte self-assembled hydrogels: NMR study of the polyitaconate-counterion interactions

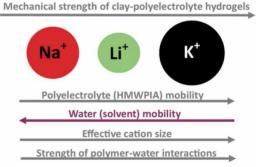
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The clay-polymer ionic interactions, which are affected i.e. by the type of polyelectrolyte counterions in self-assembled nanocomposite hydrogels based on cationic clay (Laponite®) nanoparticles and high molecular weight polyelectrolyte molecules, herein biobased poly(itaconic acid), are directly related to their mechanical properties. The effect of monovalent cations (herein Li⁺, Na⁺, and K⁺) can be predicted according to the Hofmeister series, which relates specific ion effects with the physicochemical phenomena such as self-assembly via ordering of cations from cosmotropic to chaotropic (Li⁺ < Na⁺ < K⁺). Thus, the analogical relation between the effect of poly(itaconic acid) counterions and strength of interactions between individual components of resulting hydrogels was expected. Surprisingly, our study revealed the anomaly of the Hofmeister series concerning the interactions strength in hydrogels indicating the following cations order Na⁺ < Li⁺ < K⁺. Therefore, we focused on the anomalous effect of poly(itaconic acid) counterions on the Laponite®-polyitaconate hydrogels. For this purpose, we applied multinuclear 1D, spin-spin relaxation times T_2 , and diffusion NMR experiments (¹H, ⁷Li, ¹³C, ²³Na, ³⁹K) for an in-depth understanding and explanation of the role of the polyitaconate-counterion interactions in the

Laponite®-polyitaconate hydrogels. Our study revealed that the properties of final result hydrogels are а of initial polyitaconate-counterion interactions in the aqueous solutions of corresponding polyitaconates. In particular, the anomaly of the cation order was successfully correlated to their analogical effect on the mobility of polyelectrolyte and water molecules, effective counterion size, and strength polyelectrolyte-water of interactions¹.



Acknowledgments

This work was financially supported by the Lead Agency bilateral Czech-Polish project provided by the National Science Center Poland (UMO-2020/02/Y/ST5/00021) and Czech Science Foundation (21–07004K).

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New generation of reversible thermochromic pigments – a concept for smart indicator varnishes with an improved environmental profile

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Thermochromic pigments show the ability to change their color as a result of temperature change. Two approaches are known to obtain reversible thermochromic pigments. They are based on the use of liquid crystal technology and leuko dyes. Due to the high cost of synthesis, processing difficulties and toxicity, their use raises more and more objections [1,2]. It is supposed that it is possible to receive reversible, environmentally friendly thermochromic pigments by encapsulating selected organic dyes in a polymer matrix. The resulting micro and/or nano-sized capsules can be used to prepare a range of varnishes based on water/solvent-free binders derived entirely or partially from renewable sources, e.g. from the processing of natural alkylphenols or vegetable oils. This concept is based on the development of new, advanced polymer-polymer composites with an improved environmental profile, acting as temperature sensors, which potential applications include solutions for intelligent construction, electronics or the household appliances sectors. It is believed that the replacement of conventionally used pigments with their green counterparts may contribute to improving the safety of processing and use of varnish products while maintaining the quality parameters of the solutions used so far. The following project, as part of the Implementation Doctorate Program, contributes to the expansion of both theoretical and practical knowledge about new solutions in the field of development of modern paints and varnishes with high application potential.

Acknowledgments

This work was financially supported by the Polish Ministry of Education and Science as part of the Implementation Doctorate Program (Grant no. RJO15/SDW/006-16).

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Synthesizing Au-Pd Bimetallic Alloy Nanowires through Block Copolymer Templating

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Noble metal nanomaterials have numerous potential applications in fields such as catalysis, electronics, and medical biosensors. Platinum, palladium, gold, and iridium exhibit exceptional catalytic properties due to factors like gold's surface plasmon resonance or platinum and palladium's ability to adsorb gaseous molecules on their surfaces. Nevertheless, it has been discovered that utilizing alloyed nanostructures rather than pure metals can significantly enhance the material's catalytic properties since the combined contribution of metallic components modifies their electronic and physicochemical properties. [1]

Our study aimed to produce bimetallic alloy nanowires utilizing an organic matrix of block copolymer (BCP) PS-b-P2VP film that was spin-coated onto a silicon substrate. We optimized the fabrication procedure to generate the most continuous and well-aligned nanowires. We employed an aqueous metal reduction technique, utilizing varying compositions of the solution containing respective gold and palladium metal salts to synthesize the nanowires. The nanowires' elemental composition was evaluated using atomic absorption spectroscopy, and their morphology was examined using scanning electron microscopy. The goal of this research is to assess the catalytic and electrochemical characteristics of the fabricated Au-Pd nanowires.

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Toward the development of paints and varnishes dedicated to electromagnetic radiation absorbers – selection of the polymer matrix and the effect of the amorphous rice starch-dextrin filler on the chosen coating properties

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The constantly growing number of devices and systems which functioning is based on the processing of electromagnetic radiation in the range of radio and microwave frequencies is associated with the emergence of the so-called electromagnetic smog. The appearing reports on the potential harmfulness of the abovementioned factor are a clear signal of the need to start a discussion on this topic and search for new, effective methods of its prevention [1].

Attempts for the development of paints and varnishes that act as absorbers of electromagnetic radiation were done. A set of different polymer matrices characterized by a friendly environmental profile was analyzed for the magnetodielectric properties. The compositions characterized by the most favorable system of magnetodielectric and processing properties, i.e. the water-soluble 2K epoxy system (EMI5) and the solvent-free light-curing composition based on amine modified polyether acrylate (EMI7), were enriched with the addition of an amorphous rice starch-dextrin filler with a 5, 10 and 15 wt%. For the cross-linked samples, hardness, roughness, and surface free energy (based on the measurements of wettability with water and diiodomethane) were determined. Thermogravimetric and dynamic mechanical analyses were performed.

Stable, homogeneous formulas of polymer composites with organic filler were obtained, showing reflection loss in the range between 300 MHz and 2 GHz for 20 mm layer thickness at the level of -2.47 dB and -1.90 dB for EMI 5 and 7 compositions, respectively. The addition of organic filler to the polymer matrix resulted in an increase in the magnetic loss tangent by at least 50%, preferably for EMI5_15% and EMI7_10% samples. Selected compositions with the highest electromagnetic radiation absorption capacity will serve as a matrix for inorganic-organic composites containing hybrid multiferrites nanoparticles with high application potential in protection against electromagnetic smog.

Acknowledgments

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Porphyrin-based material for water pollutant

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One of the most serious problems facing modern civilization is water pollution. Therefore, all strategies that maximize water reuse and contribute to water conservation, as well as those that promote more efficient use of solar energy, are highly desirable to minimize water scarcity and energy demand.

A promising technology for removing pollutants from wastewater appears to be the photocatalytic process. [1] Currently, the most widely used photocatalyst is titanium dioxide, TiO_2 . [2,3] However, the practical application of TiO_2 is limited by the rapid recombination of photogenerated charge carriers and its ability to absorb light only in the ultraviolet (UV) range. Therefore, an attractive approach toward developing more efficient photocatalysts is to modify TiO_2 with photosensitizers, which allow extending the range of action of the photocatalysts toward visible light. Porphyrins, due to their intense absorption in the visible range, are frequently used in both natural and synthetic systems. [4]

The aim of this work was to synthesize and characterize material based on mesotetrakis (p-sulfonatophenyl) porphyrin (TSPP) and titanium dioxide TiO_2 with the ultimate goal of obtaining material with enhanced photocatalytic activity. The two-component system was obtained and tested for photodegradation of the dye rhodamine B.

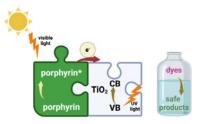


FIGURE 1. Scheme illustrating the process of photodegradation of water pollutants by porphyrin/TiO₂ nanostructures.

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This work was supported by the by AMU "Excellence Initiative - Research University" (054/13/SNŚ/0025).

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Emulsifying properties of difunctionalized octaspherosilicates

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In recent years, new chemical compounds that can act as emulsifiers in colloidal systems have been sought both by scientists and industires [1]. Octaspherosilicates are a group of compounds that can be modified with the selected organic substituents with hydrophobic and hydrophilic properties to obtain the amphiphilic product. So far, organosilicon compounds have found applications in cosmetic industry as ingredients that provide pigment stability, hydrophobicity or even affect the condition of skin and nails [2].

The aim of this study was to obtain and analyze emulsifying properties of three octaspherosilicates modified with polyether groups with three, different polymer chain lengths and UV-absorbing agent, at the same molar ratio. The octaspherosilicates were functionalized with selected olefins by hydrosilylation reactions in the presence of Karstedt catalyst. Next the emulsiyfing properties of compounds obtained were tested. Therefore, the colloidal systmes were prepared and their stability was analyzed by centrufigation test and also by multiple light scattering method for one month to monitor changes occuring in the emulsions. Each formulation was also analyzed by optical microscope and laser diffraction to measure the particle size distribution.

The results enabled determination of the stability factor of the formulations containing novel emulsifer, and then selection of functionalized octaspherosilicate with the best emulsifying properties.

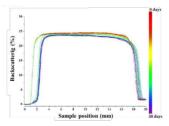


FIGURE 1. The example of backscattering profile of the most stable emulsion.

Acknowledgments

This research was financially supported by The National Centre for Research and Development (Poland), grant number LIDER/5/0036/L-12/20/NCBR/2021 "Technology of obtaining high molecular weight UVA/UVB filters for modern cosmetic formulations"

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Novel ZnFe₂O₄/ZnO core-shell nanofibers with promising photoelectrochemical properties for water splitting applications

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ZnO, Fe₂O₃, and ZnFe₂O₄ possess good physical and chemical stability, sustainability, high energy conversion efficiency, and abundance, which make them promising for photoelectrochemical applications, such as water splitting [1]. One-dimensional core-shell morphology could be used to strengthen materials' photocatalytic activity due to more effective electron access along the axial direction, enhanced light utilization, and expanded active surface area [2]. ZnFe₂O₄/ZnO core-shell electrospun fibers have been synthesized with different ratios of core/shell pumping speeds (200/500, 300/500, and 400/500 μ L/h) and denoted as S1, S2, and S3, respectively. Structure and optical properties have been studied by TEM, XRD and optical spectroscopy. The electrochemical properties of the fabricated nanofibers have been tested in 0.5 M KOH electrolyte using a standard three-electrode configuration. Photoelectrochemical properties have been investigated under irradiation of the samples by a Halogen lamp (power density 25 mW/cm²).

The studied nanostructures demonstrated catalytic activity without applied solar-light radiation. It was found that an increase of the core pumping speed improved the photoelectrochemical properties of the core-shell nanofibers. Incremental photocurrent growth denoted \sim 39%, \sim 42%, and \sim 45% at 1.2 V bias for samples S1, S2, S3, respectively. These samples' calculated photoconversion efficiency values were \sim 1.1%, \sim 1.3%, and \sim 1.9%.

The correlation between fabrication parameters, structure, optical and photoelectrochemical properties was discussed.

Acknowledgments

The authors acknowledge the NCN SONATA-BIS program (UMO -2020/38/E/ST5/00176), H2020-MSCA-RISE-2017 (Project number: 778157), and fundamental and applied research projects of the Latvian Council of Science (Novel core-shell nanofibers formed by co-axial electrospinning for photocatalytic applications, lzp-2021/1-0140).

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Influence of BEA zeolite hierarchization method on their catalytic and adsorption properties

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Zeolites as microporous crystalline materials have been widely employed in a large number of industrial processes as environmentally friendly heterogeneous catalysts, ion exchangers, and adsorbents due to their high surface area, large pore volume, uniform microporous channels, and excellent thermal and hydrothermal stability. However, the microporous channels of zeolites impose diffusion limitations, restrict the transport of reactant or adsorbate molecules within micropores, and therefore limit their applications involving bulky compounds. One of the way to overcome the disadvantages of microporous zeolites is the creation of mesopores within the zeolite crystals to yield a network of connected mesopores and micropores (hierarchical materials) [1].

The aim of the work was a modification of zeolite BEA with various porogeneous agents (NH₄OH, TBAOH, NH₄F) under different modification conditions (heating under reflux, ultrasonic bath) in order to obtain hierarchical zeolite BEA. The influence of the used porogeneous agents and the modification conditions on the crystallinity, textural and acid properties was investigated using techniques such as XRD, FTIR, low-temperature N_2 adsorption, TEM, and termoprogrammed desorption of ammonia (TPD-NH₃). The adsorption properties of the obtained materials were tested in the removal of organic pollutants from water (methylene blue), and the catalytic properties in the acetalization of glycerol with acetone (a reaction for the management of waste glycerol from biodiesel production).

The applied modification conditions allow maintain the Beta structure, but in some modified samples, the crystallinity decreased (XRD, FTIR). N_2 adsorption/desorption measurements confirmed that most of the used modifiers cause the increase of mesopores volume and surface area, especially by modification with ultrasonic bath. TEM images indicated the presence of mesopores that shape depending on the used modifier. The modifications caused small changes in the acidity of the modified samples due to the removal of some framework atoms (NH₃-TPD). The formation of mesopores in the structure of the Beta zeolite increased its catalytic activity in the acetalization of glycerol with acetone for all modified samples. The modified samples also displayed improved adsorption properties which are favorable for purifying water from contaminants such as methylene blue. The adsorption data are described by the Freundlich isotherm model (multilayer adsorption). The obtained results indicate the beneficial effect of the generated mesoporosity as a result of improved diffusion of reagents/adsorbate in the pores and increased access to active/adsorption sites.

Acknowledgements

Natalia Matysiak thanks to ID-UB UAM for financial support of the project (grant no. 076/34/ID-UB/0063).

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In situ Tracked Hybridization Phenomenon of Gold Nanorods in Monolayer Systems

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Gold nanorods (GNRs) exhibit excellent physical, chemical, and biological properties. Their most crucial feature is localized surface plasmon resonance (LSPR). Depending on the preparation conditions, GNRs with different functionalizations exhibit LSPR in various spectral regions. With the Langmuir technique as a base, our aim is to find a competitive technique to study nanoparticles (NPs) on monolayers compared to litography. *In situ* tracking of GNR hybridization allows understanding of GNRs aggregation due to LSPR maximum shift [1-2]. With the use of polyethylene glycol (PEG)-functionalized GNRs, we were able to observe hybridization phenomena in Langmuir monolayers. The experimental results were supported with the use of computational studies of GNRs dimers. Three basic GNRs dimers were taken into account as presented in Fig 1. We have shown that the plasmon coupling of GNRs could be tailored with the PEG alkyl chain and surface pressure. Obtained results could potentially provide a new path for the investigation of NPs in monolayers.

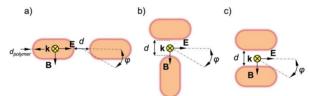


FIGURE 1. Configuration of rod dimers interacting end-to-end (a), in a T-geometry (b), and side-to-side (c) and the incident light vectors applied for all of the configurations.

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This work was supported by the National Science Center in Poland by the project 2019/35/D/ST4/02037.

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Growth of well-aligned ferromagnetic iron oxide nanowires on Cu(410)

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Supported ferromagnetic nanowires attract lots of interest due to their potential applications in magnetic and spintronic devices. One of the important scientific and technological challenges in this field is to develop methods of controlling the mutual alignment of the wires. We have grown well-aligned iron oxide nanowires on a Cu(410) single-crystal substrate. Iron oxides are known for their interesting magnetic properties (ferro- or antiferromagnetic, depending on the oxide phase). Prior to the growth, the surface of the copper substrate was reconstructed using O_2 , which led to the formation of well-aligned narrow atomic steps. Then, Fe was deposited on top of as-prepared substrate and post-oxidized. Scanning tunneling microscopy (STM) and low energy electron diffraction (LEED) revealed that iron oxide grows on Cu(410) in the form of nanowires oriented along the step edges of the support. X-ray photoelectron spectroscopy (XPS) indicated that the nanowires represent the Fe₂O₃ iron oxide phase, while magneto-optical Kerr effect (MOKE) measurements confirmed the presence of a ferromagnetic ordering in the wires with in-plane magnetic anisotropy. All this led to the conclusion, that the wires represent the so-called "gamma" Fe₂O₃ phase (maghemite)

Acknowledgments

The studies were financially supported by the Foundation for Polish Science (First TEAM/2016-2/14 (POIR.04.04.00-00-28CE/16-00) project co-financed by the European Union under the European Regional Development Fund). P.W. would like to additionally express his gratitude towards the European Union for the financial support through the European Social Fund Operational Programme "Knowledge Education Development" grant No. POWR.03.02.00-00-I032/16 "Interdisciplinary PhD studies in nanotechnology". The authors express their gratitude to Luca Vattuone for lending them the Cu(410) single-crystal used at the initial stage of the studies.

Interpreting the ferromagnetic resonance experiments within the Kittel and the Smit-Beljers methods: comparison

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Ferromagnetic resonance (FMR) is an experimental technique used to examine free magnetic energy in magnetic materials. Specifically, this method allows us to find the spatial distribution of magnetocrystalline energy in ferromagnets. The classic method used to interpret FMR experimental data is the Kittel method¹. The resonance condition in the Kittel method is derived from the equation of motion describing the precession of the magnetization vector in a strong magnetic field. Another way to interpret FMR experimental results is the Smit-Beljers method. The Smit-Beljers equation assumes a more natural approach than the previous method, taking into account symmetries of free energy distribution. Comparing these two methods, one can use an analogy that Kittle's approach is equivalent to Newtonian dynamics, where the decomposition of vectors into components is necessary, and the Smit-Beljers method is to some extent equivalent to the Lagrange method widely used in classical mechanics. Specifically, comparing the Kittel's and Smit-Beljers methods, we found that: 1) the first approach requires the decomposition of the equation of motion into components which creates an additional difficulty when transforming equations, for example, describing the demagnetization tensor, 2) in the case of the Smit-Beljers method one has to solve a scalar equation, taking into account that the symmetry of the system is expressed in a more simple and more natural way, and the resonance condition reduces to the analysis of the curvature of the spatial distribution of magnetic energy. The above statements are exemplified by the interpretation of FMR experimental data for a thin layer of GaMnAs magnetic semiconductor².

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Diazonium salt-modified carbons as highly active and recyclable heterogeneous catalysts for glycerol valorization

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The 2030 climate and energy framework of the EU includes wide targets and policy objectives for the nearest period. One of the key goals of the agreement is to progressively reduce the EU's greenhouse gas emissions, which is partially done by using renewable biofuels such as biodiesel (BD) [1]. Biodiesel is typically obtained from vegetable oils via the transesterification process. Importantly, a by-product in the form of glycerol (G) is also formed in this reaction, representing as much as 10 wt.% of the produced BD. From a practical point of view, this by-produced glycerol should be valorized [2].

One of the possible valorization routes of glycerol is its conversion to tert-butyl glycerol ethers (TBGEs). These compounds (especially di- and tri-substituted products) can be used as valuable and sustainable fuel additives that improve fuel properties and decrease the negative impact of fuel combustion on the environment. Furthermore, TBGEs are considered a sustainable alternative to methyl tert-butyl ether (MTBE) additive, whose usage has been limited in some countries [3].

TBGEs can be obtained in the etherification of glycerol with tert-butyl alcohol (TBA) in the presence of an acid catalyst, preferably a heterogeneous one [2]. Although several studies on the use of solid acids in glycerol etherification have been published so far, there is still a need to develop an efficient, recyclable, and inexpensive catalyst for this reaction. In the current work we propose the use of acid carbons obtained in a facile, viable, and sustainable way as catalysts for the production of glycerol ethers.

Carbon materials were prepared from different feedstocks, i.e., glucose (hydrothermal carbon spheres; HTC), phenol-formaldehyde resins (carbon xerogels; CX), and plastic wastes (micro- and meso-porous activated carbons; ACmicro and ACmeso) using low- or high-temperature methods. The samples were then functionalized by an eco-friendly and mild approach using diazonium salt generated in situ (BDS) to endow their surfaces with acidic properties induced by $-SO_3H$ groups. The obtained catalysts were tested in the reaction between glycerol and TBA at 110 °C under self-generating pressure for 24 h.

The sulfonation of carbons by chemical reaction with benzene diazonium sulfonate was an efficient route of functionalization, however, its effectiveness varied depending on the carbon type (ACmicro > ACmeso > CX > HTC). The most effectively SO₃H-functionalized sample was also the one showing the highest activity in glycerol etherification. A high glycerol conversion of ~59% and a combined yield of higher-substituted ethers of ~11% was achieved within 6 h over the modified ACmicro, which exceeded the results obtained for a commercial catalyst Amberlyst-15. Furthermore, the activity of sulfonated ACmicro in subsequent runs was shown to be relatively stable. Importantly, a direct correlation between the content of -SO₃H groups and the activity of the prepared carbons in the tested process was found.

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Modified carbon nanotubes as solid acids for catalytic obtaining of fuel enhancers via glycerol etherification

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Various local and global environmental protection activities have been implemented in recent years to achieve sustainable development goals. Among the suggested ideas, recovering materials from waste streams for recycling or reuse is justified for environmental and economic reasons. A serious challenge is especially tackling a significant glut of by-produced glycerol accumulated on the market due to high worldwide biodiesel production [1]. Glycerol recycling can be, however, also considered a great opportunity.

Due to its reactivity, glycerol has tremendous potential to be transformed into valuable chemicals, such as acrolein, solketal, glycerol carbonate, or acetins. One of the processes recently gaining significant attention is glycerol etherification, which produces tert-butyl glycerol ethers (TBGEs) of significant industrial importance. For example, these compounds can be used as valuable fuel oxygenates, enhancing fuel combustion and reducing exhaust emissions [1]. Therefore, the aim of the current work was to produce TBGEs via glycerol etherification with the use of easy-to-handle tert-butanol (TBA) as an etherifying agent and functionalized carbon nanotubes as solid acid catalysts.

As-received or ball-milled commercial carbon nanotubes (CNTs) were functionalized with sulfuric acid with or without glucose to introduce acidic surface groups to the CNT structure. The obtained samples were thoroughly characterized by elemental and textural analysis, potentiometric back titration, thermogravimetric method, scanning electron microscopy, or XPS technique. The modified CNTs were tested in glycerol etherification in the presence of TBA at 110 °C under autogenous pressure.

The applied modifications enhanced the acidic properties of CNTs compared to the unmodified samples by introducing S- and O-type functionalities. The degree of sample functionalizations as well as the contributions of different surface groups varied depending on the method used. The treatment of the ball-milled CNTs with glucose and fuming sulfuric acid was the most effective method of inducing acidic properties in these samples. This method resulted in a sample showing a significant content of sulfonic groups (0.66 mmol/g) and a high total acidity (2.61 mmol H⁺/g). The above sample gave an improved glycerol conversion and yields of ethers in the tested process compared to a commercial catalyst, Amberlyst-15. The relationship between the -SO₃H contents and the catalytic performance was found. Furthermore, the potential beneficial effect of surface oxygen groups was discovered.

Acknowledgments

K.P. would like to acknowledge her doctoral grant no 017/02/SNŚ/0013 from ID-UB AMU; This work was financially supported by: LA/P/0045/2020 (ALICE) and UIDB/50020/2020 -UIDP/50020/2020 (LSRE-LCM) funded by national funds through FCT/MCTES (PIDDAC); K.M.E. is grateful to FCT for the Junior Researcher grant (no.2021.00535.CEECIND).

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Fabrication of zirconium oxide nanostructures via sequential infiltration synthesis using block copolymer thin films

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Nanometer-sized structures continuously revolutionize various industries by offering efficient and economically competitive solutions to a multitude of problems. Despite years of rapid development in the field, achieving controlled and repetitive synthesis of nanostructures remains challenging. One appealing solution is the utilization of block copolymer molecules that self-assemble into periodic nanoscale morphologies, which can then be converted into inorganic replicas.

Sequential infiltration synthesis (SIS) is a robust technique that involves a gaseous phase selective reaction with a desired chemical moiety to form metal oxide nanostructures. While SIS has been successful for several elements such as Al, Ti, Zn, Sn, In, Ga, etc. [1], the majority of them still require further examination. Among these elements, zirconium oxide (ZrO₂) is particularly interesting due to its properties, including high mechanical and chemical stability, high dielectric constant, and biocompatibility. Thin films of ZrO₂ could find applications in catalysis, microelectronics, or ceramic biomaterials [2].

In our research, we investigated the SIS infiltration process of zirconium (IV) alkylamine and water, which resulted in the formation of a selective inorganic replica of ZrO₂. We overcame initial obstacles hindering the reaction, such as the large size of the zirconium precursor molecule and the polymer's sensitivity to high temperatures, by applying external UV illumination combined with the preservation of the block copolymer (BCP) order. We tested the optimal process parameters and the reactivity of the alkylamine precursor towards functional chemical moieties of a set of homopolymers and diblock copolymers using an insitu quartz crystal microbalance setup. The morphology was investigated using SEM microscopy.

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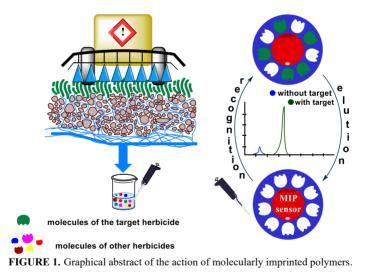
Molecularly imprinted polymers toward metolachlor

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Molecularly imprinted polymers (MIPs) are synthetic sensors that selectively bind to targeted molecules through a "lock-and-key" mechanism [1] S-metolachlor (S-MCh) is one of the most commonly used herbicides in corn, soybean, and sunflower crops. S-Mch is highly poisonous and can be leached into groundwater. The active principle of this herbicide is soluble in water and is absorbed by soil particles. [2] The relatively long half-life of S-MCh translates into more difficult metabolized by soil microorganisms. [3]

Given the above, there is a need to acquire new methods for detecting and monitoring S-MCh concentrations in waters. Novel polymers with a molecular imprint towards S-MCh were synthesized by bulk polymerization using N-isopropylacrylamide and acrylamide as functional monomers, N,N'-methylenebis(acrylamide) as a cross-linking agent, ammonium persulfate and N,N,N',N'-tetramethylethylenediamine as a catalytic system. Polymerization was carried out in an aqueous solution of S-MCh at room temperature, following the rules of green chemistry. The synthesized polymers were capable of selectively sorpted S-MCh from the model and real solutions. The efficiency of the sensors was assessed using two types of polymers with herbicide imprints and without it at different process parameters.



Acknowledgments

The authors wish to acknowledge the financial support of the National Science Centre Poland project Sonata Bis11, 2021/42/E/ST5/00019 (02NB/0002/22).

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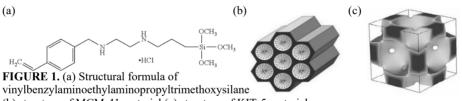
Phase transitions of liquids confined in functional nanoporous silicas

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Nano and mesoporous materials, modified with functional groups, are used as catalysts for chemical reactions. The large surface area of porous materials allows the addition of catalyzing materials to their walls and more efficient chemical reactions. Mesoporous silicas modified with amino groups can also serve as carriers for active substances in the process of their controlled delivery and release. In order to select the appropriate porous structure, it is necessary to know the behavior of the liquid in contact with the porous material and inside its pores. In the following work, we present the behavior of the water and benzyl alcohol in bulk and confined inside silica and carbon nanopores. The carbon samples are form by graphite microcrystals with the void volume of diameter of 0.9 to 4 nm and silica samples have a pores void volume of diameter of 2 4 addition nanomaterials to nm. In silica have been modified by vinylbenzylaminoethylaminopropyltrimethoxysilane (Z6032).



(b) structure of MCM-41 material (c) structure of KIT-5 material For this purpose, tests were carried out using dielectric method and tensiometric method. Experiments with dielectric make it possible to study the behavior of the liquid in the melting process and to determine the phase transition temperature of bulk and the liquid confined in the nanoporous

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determine the wetting energy of liquid inside the pores.

We would like to thank for the financial support to Interfaculty Grant of School of Sciences UAM and National Scientific Centre under the grant of UMO-2016/22/ST4/00092

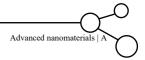
matrices. Tensiometric tests allow us to measure the contact angle inside the porous structure and

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Van der Waals heterostructures and composites based on MXenes with polytriazine imide and graphitic carbon nitride

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Nowadays, one can observe the scientific progress in the synthesis and formation of vdWh (van der Waals heterostructures) and nanocomposites based on previously discovered hexagonal, layered two-dimensional (2D) materials, like graphene, graphitic carbon nitride, hexagonal boron nitride or transition metal dichalcogenides. The vdWh are vertical stacks of few / several crystalline monolayers of different 2D materials, which are held together by weak van der Waals forces. The creation of vdWh with atomically thin interfaces and highly distinct electronic functions allows to obtain functional materials for fundamental studies on structure and the influence of the intrinsic properties of monolayers on each other, such as confinement and transport of charges, excitons, photons and phonons at the limit of single-atom thickness and bandgap tuning. The results could lead to design of a new generation of electronic devices with extraordinary performance and unique functionality [1,2].

MXenes are a novel family of 2D materials, consisting of carbides, nitrides and carbonitrides of early transition metals, which currently are extensively investigated from the point of view of basic sciences and potential applications, such as energy storage systems or nanoelectronics. The most commonly investigated and stable MXene is $Ti_3C_2T_x$, where T_x corresponds to Ti-bonded functional groups (-F, -O, -OH). MXenes form accordion-like porous multilayered structures (m-Ti_3C_2T_x), which can be exfoliated toward graphene-like single-layers (s-Ti_3C_2T_x). MXenes are promising candidates for the fabrication of novel vdWh and nanocomposites. Thanks to the metallic character they could replace graphene in vertical tunneling transistors, light-harvesting and detection devices [3].

This research presents the application of ionothermal synthesis for *in situ* formation of the heterostructures based on $Ti_3C_2T_x$ MXenes with polytriazine imides (PTI).^[4] Two routes were investigated: i) deposition of PTI between the layers of m- $Ti_3C_2T_x$ using impregnation technique and ii) deposition of PTI onto s- $Ti_3C_2T_x$ flakes. The characterization of as-obtained materials by scanning electron microscopy and powder X-ray diffraction proved the successful formation of novel heterostructures.

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This research was financially supported by National Science Centre Poland under Uwertura project - UWERTURA 2018/28/U/ST5/00448.

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Fe₃O₄/CeO₂ "Core/shell"-like Nanocomposites for Perspective Application in Medicine: Fabrication and Characterization

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Multifunctional "core/shell"-like nanocomposites (NCPs) based on the magnetic Fe_3O_4 nanoparticles (MNPs) and cerium dioxide (CeO₂) attract significant scientific interest due to the possibility to combine the simultaneous ability of MNPs to heat up effectively in AC magnetic field with the antioxidant and anti-amyloid activities of CeO₂. Such composites can be promising for biomedical investigations, particularly, in the treatment of age-related diseases caused by oxidative stress, including amyloidoses. The aim of this work was to synthesize "core/shell"-like Fe_3O_4/CeO_2 NCPs, to study, their physical-chemical properties and morphology as well as to analyze their antioxidant and anti-amyloid activity.

A set of Fe₃O₄/CeO₂ "core/shell"-like NCPs with the theoretically calculated thickness of CeO₂-"shell" of 3-, 5-, and 7-nm (*Fe₃O₄/CeO₂-3, Fe₃O₄/CeO₂-5,* and *Fe₃O₄/CeO₂-7* respectively) was synthesized by the precipitation of CeO₂ NPs onto the surface of the Fe₃O₄ MNPs. HR TEM and EELS studies revealed that Fe₃O₄/CeO₂ NCPs consist of Fe₃O₄ NPs core with an average size ~ 23 nm, which is surrounded by CeO₂ NPs with an average size of ~ 3-3.5 nm forming the "core/shell"-like structures. Increasing CeO₂- "shell" thickness is manifested by the increased hydrodynamic diameter of NPs in aqueous suspensions and better stability of NCPs in the suspensions expressed as zeta potential (DLS measurements). *Fe₃O₄/CeO₂-5* and *Fe₃O₄/CeO₂-7* NCPs formed the highly-stable suspensions without any additional stabilizers ($\zeta \ge +30$ mV) unlike bare Fe₃O₄ NPs, which had a zeta-potential value of +18.0 mV. The thickness of the CeO₂ "shell" also affected the heating efficiency of nanocomposites when an AC magnetic field was applied (*H*=9.3 kA/m, *f*=300 kHz). The maximum values of the heating temperature were 40-50°C and they decreased with increasing "shell" thickness. The specific loss power (SLP) values were reduced from 38.8 W/g for Fe₃O₄ NPs to 21.4 W/g for *Fe₃O₄/CeO₂-7* NPs.

The bioactivity of prepared NCPs expressed as the antioxidative and anti-amyloid effect has been examined. All tested NPs significantly inhibited the formation of insulin amyloid aggregates *in vitro*. The anti-amyloid activity was highly dependent on the thickness of CeO₂ layers on the core of Fe₃O₄. The highest ability to inhibit the process of fibril formation was observed for Fe_3O_4/CeO_2 -7 NCPs. The antioxidant activity of Fe₃O₄ and Fe₃O₄/CeO₂ nanocomposites was evaluated by monitoring their catalase- and superoxide dismutase-like activity. *For more detail, please see the presentation submitted by Siposova K. et al.*

Acknowledgments

This work was supported by grants: project No 9918 within Program from The Institute of Electrical and Electronics Engineers (IEEE) Magnetics Society "Magnetism for Ukraine 2022" (project No 9918); grant G5683 within the NATO Science for Peace and Security Programme; Slovak Grant Agency VEGA (No. 2/0094/21; 2/0034/22), Slovak Research and Development Agency (APVV-19-0324) and SAS-MOST JRP 2021/2 (AZCAI).

Pr3+-doped perovskite niobate nano-ceramics towards improving performance of optical temperature sensor by second harmonic generation (SHG) combined with lanthanide luminescence

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Successfully synthesized ($K_x Na_{1-x}$) NbO₃ (KNN) perovskite ceramics doped with Pr^{3+} ions exhibit intense Pr^{3+} down-shifting luminescence and color-tunable second-harmonic generation (SHG) phenomena under pulsed laser excitation. The Pr^{3+} emission bands intensity ratio and the SHG signal were analyzed as a function of temperature, and the ISHG/I610 ratio showed a temperature resolution of 0.07 K. The developed thermometer combines luminescence thermometry and SHG-based thermometry and can be used as a highly-sensitive, dual-mode temperature sensor.

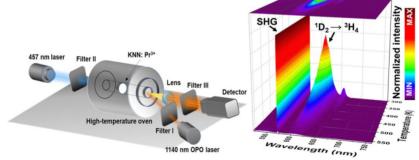


FIGURE 1. Experimental setup for simultaneous measurements of SHG and Pr3+ luminescence as a function of temperature (left) and the resulting emission spectra (right).

Acknowledgments

This work was supported by the Polish National Science Centre (grant no. POWR.03.02.00–00-i020/17, 2019/33/N/ST5/000326 and 2018/31/N/ST4/00684) co-financed by the European Union through the European Social Fund under the Operational Program Knowledge Education Development, and by the EU-FEDER funds. M.R. acknowledges support from Fondo Social Europeo and Agencia Estatal de Investigación (RYC2020-028778-I/AEI/10.13039/501100011033). This investigation was also supported by the Key Research and Development Plan of Zhejiang Province (2022C01229) and the Natural Science Foundation of Ningbo (2021J063).



Cu_xO microwires - optimalization of synthesis and analysis of photocurrent generation

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Copper oxides, due to the location of energy bands, are eagerly studied and modified in terms of photocatalysis. They seem to be very promising in terms of conducting photocatalytic processes in the visible light, because they belong to the group of narrowband semiconductors.

The utilitarian goal of the conducted research was to optimize the electrochemical preparation of a thin layer of copper oxides on the surface of copper plates, in terms of creating structures with a highly developed surface, potentially attractive for the introduction of modifiers. For this purpose, the effect of fluoride anion concentration, applied voltage as well time and temperature of calcination after the process was investigated. The synthesis was carried out in order to obtain uniform, densely and evenly distributed microwires.

The obtained samples were analyzed using the following techniques: SEM, DRS, XRD and their photocatalytic properties were examined by checking the density of photocurrent. Based on the collected results, the mechanism of the formation of thin oxide layers was proposed and some correlations between the changed factor and its effect on the structure of the photocatalyst were observed.

Acknowledgments

This work was founded by the Polish National Science Centre, NCN within the scope of the PRELUDIUM BIS 1 project No. UMO-2019/35/O/ST5/00507, entitled "Novel materials for CO_2 photo-electro-conversion into valuable hydrocarbons"

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Photoelectrocatalytic hydrogen evolution using Pt/perovskite/TNT photoanodes

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Although TiO_2 is widely studied by scientists from around the world, it is still popular in photocatalytic experiments. It is often used as a matrix for the introduction of various modifiers and cocatalysts, which are intended to increase its photocatalytic activity in the wide array of processes.

In the present study, titanium dioxide nanotubes (TNTs) were produced using the electrochemical method on plates made of technical titanium. Subsequently on the surface of which perovskite compounds of the ABO₃ type were deposited by spin-coating. TNT preparation was performed after optimization of TNTs synthesis previously performed by our research group [1]. Namely, the influence of mixing, electrolyte, applied voltage and ultrasonic cleaning after anodization were examined. Perovskites were obtained by the microwave combustion method, which was adapted and modified compared to studies by Ding et al. [2].

The obtained samples were characterized using DRS, XRD and SEM analysis methods. In addition, they have been tested in the process of photo- and photoelectrocatalytic reforming of glycerol (hydrogen generation) under the influence of UV-Vis and Vis irradiation (>420 nm).

Acknowledgments

This work was founded by the Polish National Science Centre, NCN within the scope of the PRELUDIUM BIS 1 project No. UMO-2019/35/O/ST5/00507, entitled "Novel materials for CO_2 photo-electro-conversion into valuable hydrocarbons"

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Breakthrough Control of Intermolecular Interactions Towards the Production of Super-elastic Free-standing Polydopamine Films

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Aggregation of the polydopamine (PDA) molecular building blocks at the air/water interface follows two co-occurring pathways, namely covalent or non-covalent self-assembly. Control of this mechanism could be achieved through the use of the oxidation agents that were successfully applied to the PDA coatings, i.e. Cu^{2+} ions [1] or boric acid [2].

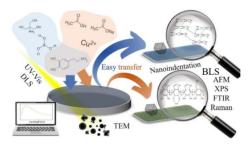


FIGURE 1. Scheme of the experiment – nanoparticles and film growth dynamics observation, followed by examination of the structural, chemical and mechanical properties of the polydopamine free-standing films.

In this experiment, using above mentioned oxidation agents, we have achieved exceptionally high control over the manufacturing process of the ultra-thin PDA free-standing films, i.e. a precise measurement of their thickness growth in real-time, reduction of impurities, the possibility of synthesizing towards the chosen self-assembly mechanism and thus achieving desired mechanical properties, i.e. high Young's modulus.

Acknowledgments

This work was supported by National Science Centre of Poland by the PRELUDIUM20 grant 2021/41/N/ST5/00211 and OPUS grant 2021/41/B/ST5/03038 for the BLS measurements. J.S. is a holder of the a French Government Scholarship and AMU Foundation Scholarsip.

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X-ray diffraction analysis by Rietveld Refinement of Lithium Borohydride doped with Lithium Bromide

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Solid-state electrolytes (SSEs) in lithium-ion batteries (LIBs) are a promising upgrade over traditional liquid electrolytes due to their potential for improved safety, increased energy density, and expanded operating temperature range. Among the promising SSEs, the composite of lithium borohydride and lithium bromide (LiBH₄-LiBr) stands out. This composite has high lithium-ion conductivity, good electrochemical stability, and the potential to enable rapid charging. Understanding the distinction between the hexagonal and orthorhombic phases of LiBH₄ becomes crucial in this context, especially considering the differences in their structure and stability, as well as the lower-temperature phase transition caused by LiBr doping.

The Rietveld refinement method is used to extract detailed information on phase evolution, lattice parameters, crystallite sizes and deformations under different conditions, which is essential for understanding the crystal structure of the material. This in-depth knowledge helps to optimise the LiBH₄-LiBr SSE for the next generation of LiBs, accelerating the shift to safer and more effective energy storage systems.

The results of the Rietveld refinemant analysis are significant in terms of diffusion processes, as the precise determination of the unit cell size directly translates into the prediction of the lithium ion jump distance in the solid electrolyte. This research, which focuses on the solid state electrolytes, lays the groundwork for a thorough investigation of these topics, making it a valuable resource for researchers in this dynamic field.

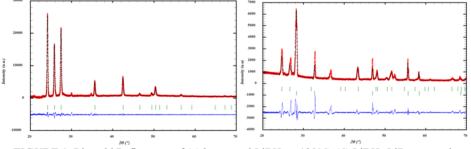


FIGURE 1. Rietveld Refinement of **(a)** hexagonal LiBH₄ at 130°C, **(d)** LiBH₄-LiBr composite at 30°C (0.6:0.4 molar ratio).

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Uniform Array Metamaterials in Porous Thin Films.

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Metamaterials are defined by characteristic negative permittivity and low optical losses allowing highly sensitive light-matter interaction studies. Dispersion relation in hyperbolic metamaterials (HMM) is unique in nature making them ideal candid materials for robust and effective biosensors. Anodic Aluminium Oxide (AAO) provides a versatile platform to develop 1D photonic material. In this research, we synthesised 1D gold nanowire structure via semi-immersed AAO templates in potassium dicyanoaurate-hexacyanoferrate using electrochemical cell [1].

$$[\operatorname{Au}(\operatorname{CN})_2]^- + e^{-} \rightarrow \operatorname{Au}^0 + 2\operatorname{CN}^-(1)$$

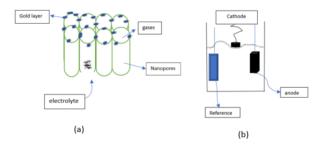


FIGURE 1. (a) AAO template membrane. (b) Electrodepostion cell illustration

Thin films were developed with variable ENZ (epsilon near zero) via controlled metal volume fraction in a dielectric matrix. Nanowire electrodeposition was controlled by *Autolab PGSTAT 30* potentiostat where the work potential was kept at -1.2V and current flow was between -1 to -2mA the experiment was performed at 55°C in 30-minute time intervals for 1 hour. The proposed method opens a unique way to synthesize novel 1D HMMs.

Acknowledgments

We would like to thank National Science Center of Poland (NCN) for the financial support by OPUS grant 2020/37/B/ST5/00576.

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SECTION B NANOBIOMEDICINE



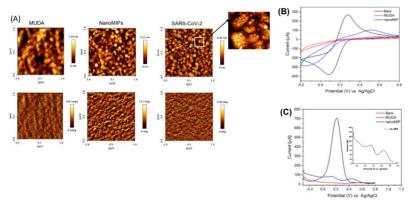
INVITED SPEAKER

Bioinspired Materials: From Sensors to Bioselective Membranes

Zeynep Altintas

Chair of Bioinspired Materials and Biosensor Technologies, Faculty of Engineering, Kiel University, Germany

The occurrence of micropollutants in water sources has been recognized as one of the main environmental problems, and their impact on the environment has been investigated worldwide. These compounds cover a wide range of pharmaceuticals, bacterial and mycotoxins, and human pathogenic viruses, whose certain concentrations in the aquatic environments and foods can lead to major health concerns [1]. We aim to address this problem by designing and synthesizing bioinspired materials for use in high-performance recognition, detection, and purification with the aid of fully integrated sensor platforms and advanced membrane filtration systems [2-6]. The as-synthesized high-affinity bioinspired materials are immobilized on the sensor (e.g., surface plasmon resonance and quartz crystal microbalance) and membrane (e.g., polyvinylidene fluoride and polyethersulfone) surfaces using a variety of covalent and non-covalent conjugation techniques, resulting in target specific-recognition, detection, and removal [2-6]. The computational studies further contribute to the performance of such platforms by improving the recognition properties (e.g., affinity, selectivity, and sensitivity) of the bioinspired polymeric materials [3,5]. In the talk, the sensing and filtration applications of these materials targeting pharmaceuticals and viruses will be covered. The impact of conjugation techniques as well as computational simulations in the ongoing research activities will be discussed.



Acknowledgments

This work was supported by the German Research Foundation (DFG, grant number: 428780268) and the Aventis Foundation (grant number: 80304368).

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Immunoassays with Magnetic Separation for the Detection of Prostate-specific Antigen

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Prostate cancer is the major cause of death in the male population caused by oncologic diseases. Sensitive detection of disease biomarkers, e.g., prostate-specific antigen (PSA), is essential for early-stage diagnosis and effective treatment. Conventional immunochemical methods widely used in clinical analysis are often not sensitive enough for early-stage diagnosis resulting in the need for novel assay formats. Here, we describe the systematic comparison of two kinds of solid phases for biomolecule immobilization in immunoassays utilizing three different labels. The two immunoassay surfaces included conventionally used microtiter plates (MTPs) and magnetic microparticles (MBs). A comparison of the different labels for immunochemical analysis together with the results obtained from conventional and MB-based immunoassays showed that the MBs can serve as a stable support for biomolecules immobilization. The three different immunoassay labels used in this study were horseradish peroxidase (HRP), 5(6)-carboxyfluorescein (FAM), and photon-upconversion nanoparticles (UCNPs); all of them being modified with streptavidin (SA). Among the three different labels used in this study, UCNPs were shown as the most sensitive and stable. The results obtained from conventional and MB-based upconversion immunoassays provided the highest signal-tobackground ratios and the lowest limits of detection (LODs) compared to enzyme-linked immunosorbent assay (ELISA) and fluorescence immunoassay (FIA) performed under the same experimental conditions. The MB-based ULISA carried out with the PSA preconcentration provided the lowest LOD of 0.5 pg/mL achieved in this study. The results demonstrate that using micro- and nanomaterials for PSA detection improved immunoassays sensitivity and working range.

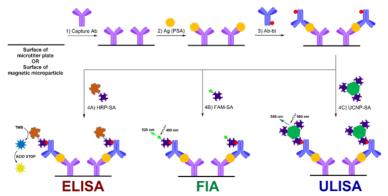


FIGURE 1. General scheme of the used immunoassay strategies. Different label types were used in the last step of each procedure, leading to three different types of readout.



How to help failing heart. Bio- and nanotechnological approaches in postinfarction heart treatment

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Myocardial infarction is a leading cause of death worldwide. Currently used treatment protocols for myocardial infarction led only to the transient improvement of the heart function, but did not provide the clue for full regeneration of the heart tissues. An increasing body of evidence has shown that intramyocardial transplantation of cells may lead to some organ recovery. To this aim, we used the combination of human skeletal myoblasts (huSkM) native or overexpressing gene coding for Cx43 together with mesenchymal stem cells (MSCs) and have shown that MSC enhanced myoblasts homing and retention. In our next studies, we used the same types of stem cells together with PLGA nanoparticles carrying chemoattractant SDF-1 or anti-TGF β . Bioluminescent imaging of post-infarcted mouse hearts revealed prolonged retention of delivered cells (up to 64 days). Additionally, real-time PCR results on left ventricle samples collected from animal hearts, have shown that expression of genes related to the formation of fibrotic scars decreased.

In other studies, we have used IPS-derived cardiomyocytes. We, as well as others, have noticed that these cells, due to their immature phenotype, were not able to functionally couple with surrounding tissue. Therefore, to support the maturation of cardiomyocytes, we proposed to use lipid-liquid crystalline nanoparticles complexed with miR let7g.

Another appealing treatment approach is the development of nanoparticles, which could be used as carriers for anti-apoptotic agents as well as for bioimaging. Here, we tested several candidates (including star polymers, dendrimers, and LLCNPs) complexed with miR 146a. Our primary results indicated that nanoparticles were not toxic to the cells and were able to deliver miR.

Acknowledgments

The research is financially supported by the National Centre for Research and Development-DWM/WPC2/285/2020 and NCN Miniatura 5 2021/05/X/NZ3/01013, Sonata BIS 6 2016/22/E/ST3/00458. M.K. would like to acknowledge National Centre for Research and Development grant no. PBSPBS3/A7/27/2015.



Virus-like particles (VLPs) arrays for biosensing applications

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The COVID-19 (Coronavirus Disease 2019) pandemic has stimulated the scientific world to intensify studies aimed at developing quick and safe ways of detecting viruses in human body and treating the associated diseases. As many viruses constitute a serious threat to human life and health, studies on them can only be performed in certified laboratories that follow strict safety procedures. Due to this, development of "deactivated" virus molecules or safe to use virus like objects that mimic the real virus and allow performing virus related studies in any research unit, constitutes an important scientific challenge. One group of such species are the so called virus like particles (VLPs) in which the capsid of the virus is replaced with a synthetic core to which the real virus proteins are being attached [1,2].

We have developed a method for the preparation of VLPs that imitate the virus responsible for the COVID-19 disease the SARS-CoV-2 (Severe Acute Respiratory Syndrome Coronavirus 2). The particles consist of Au cores surrounded by "coronas" of S1 domains of the real virus's Spike proteins. Besides being safe to use, the VLPs are characterized by the presence of the so called localized surface plasmon resonance (LSPR) in gold cores, which allows utilizing the fabricated particles in biosensing and bioimaging applications [3]. Particularly interesting, from the point of view of our research, is the organization of such VLPs into arrays (linear or 2D) whose geometry and arrangement of particles allows manipulation of their plasmonic properties [4,5].

Acknowledgments

The research was financed through the "Studies on COVID-19" programme from the funds of Adam Mickiewicz University in Poznań and, in part, through the LaSensA project carried out under the M-ERA.NET scheme and co funded by the European Union's Horizon 2020 programme, the Research Council of Lithuania (LMTLT), agreement No. S-M-ERA.NET-21 -2, the Saxon State Ministry for Science, Culture and Tourism (Germany) and the National Science Centre of Poland, project No. 2020/02/Y/ST5/00086.

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INVITED SPEAKER



Calorimetric and computational characterization of amphiphilic dendrons as promising nanocarriers

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Among various delivery systems, self-assembled nanomicelles created with amphiphilic dendrons (ADs) have recently demonstrated higher performance compared to nanovectors utilizing covalent carriers [1]. A crucial point in the development of new, more potent ADs lies in their early-stage characterization in order to i) study the fundamental chemical-physical properties of the AD itself and ii) analyse the morphology, size, strength, and stability of the cargo/AD complex. There are different methods for assessing these properties but Isothermal Titration Calorimetry (ITC) and atomistic Molecular Dynamics (MD) simulation deserve particular attention since they are feasible in order to obtain AD parameters difficult to retrieve with other common techniques, at least at the same level of detail. Specifically, by employing ITC, a detailed understanding of the self-assembly process of AD nanomicelles can be obtained [2-4]. In particular, ITC enables a comprehensive thermodynamic characterization of the nanomicelles, encompassing critical micellar concentration, micelle aggregation number, Gibbs free energy of micellization, and the enthalpic and entropic contributions involved. On the other hand, computer simulations have been established as a fundamental tool in the design and development of new AD nanocarriers. Moreover, the level of detail contained in the information that can be gathered by performing atomistic-scale MD simulations cannot be obtained with any other available experimental technique. MD can be exploited in the different stages of novel dendritic nanocarrier development — from the initial conception to the stage of biological intermolecular interactions [4-7].

Acknowledgments

We acknowledge COST Action CA 17140 "Cancer Nanomedicine from the Bench to the Bedside" supported by COST and National Centre for HPC, Big Data and Quantum Computing. We also acknowledge CINECA Supercomputing Center for awarding us access to Marconi100.

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Liposomes as drug carriers to improve the effectiveness of anti-cancer therapy

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Cancer is the second cause of death worldwide right after cardiovascular disease. Glioblastoma multiforme (GBM) is one of the most malignant primary cancers of the central nervous system. According to the World Health Organization (WHO) the tumor has reached grade 4 malignancy due to its aggressive nature. The standard method of care for GBM patients is removal of the tumor, followed by radiation therapy and adjuvant chemotherapy with temozolomide. Despite current treatment combinations, there has not been a satisfactory therapeutic outcome related to prolonging life in people who suffer from GBM, the median of overall survival is 10 months [1]. Therefore, research is being conducted to improve existing treatments or introduce new techniques to combat this type of cancer.

For many years, our team has been characterizing small-molecule compounds based on styryl moiety. The result of these efforts is the discovery and characterization of the molecular mechanism of action of the styrylquinazolone derivative (IS11) [2]. IS11 derivative exhibits extremely high anticancer activity towards a panel of human glioblastoma cell lines, while maintaining high selectivity against normal astrocyte cells. The multifaceted mechanism of action of IS11 focuses on inhibition of several tyrosine kinases, induction of oxidative stress, cell cycle arrest in the G2/M phase and triggering of a programmed cell death via apoptosis and autophagy. However, the preliminary studies conducted on an *in vitro* blood-brain-barrier (BBB) model using hCMEC/D3 cells revealed limited penetration and reduced anticancer potential of IS11 derivative. Hence, we attempted to encapsulate this compound in drug carriers. We chose liposomes for this purpose due to their several advantages such as biodegradability, biocompatibility, low toxicity, ability to encapsulate hydrophilic as well as hydrophobic compounds and modifying the composition of the membrane [3]. We conducted studies on three types of liposomes: anionic, cationic and neutral. The obtained liposome carriers show stability and good encapsulation efficiency of the tested compound. The in vitro tests indicate the high potential of the IS11 encapsulated in liposome in use *in vivo* studies.

Acknowledgments

This work was supported by KM's grant from the National Science Centre, Poland (2019/35/BNZ5/04208).

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Impact of lipid composition on the protein adsorption of nanoliposomes – a combined *in silico* and *in vitro* investigation

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The fate of liposomes *in vivo* is affected by a wide variety of factors, including lipid composition, size, surface charge, as well as the nature of molecular partners, which can ultimately influence therapeutic efficiency. Upon entering a biological environment, liposomes become coated by a dynamic layer of proteins, known as protein corona, which controls particle transport properties [1]. The aim of the present study is to investigate the behavior of liposomes with different lipid composition in the presence of a model protein, bovine serum albumin (BSA). For this purpose, we employed a combined *in vitro* and *in silico* approach consisting of liposome formulation through thin-film hydration; vesicle characterization through DLS, zeta potential measurements and lipid composition determination; protein corona formation through UV-VIS spectroscopy, polyacrylamide gel electrophoresis (SDS-PAGE) and coarse-grained molecular dynamics simulations.

Six liposomal formulations of DPPC with varying cholesterol content (0-50% mol%) were prepared, and downsizing through mild sonication and extrusion through 200 nm polycarbonate filters led to heterogeneous liposome populations (hydrodynamic diameters ranging from 166±2 nm to 190±2 nm, PDI from 0.08 to 0.12). Cholesterol content was directly proportional with more negative zeta potential values (-16.77±1.5 mV for plain DPPC vesicles to -35.57±2.8 mV for DPPC:CHOL 5:5 vesicles). Both UV-VIS and SDS-PAGE results showed BSA adsorption following 1h incubation at 37°C, regardless of liposome composition. We also found that the used centrifugation protocol for protein-vesicle assembly isolation cannot be applied to liposomes below 130 nm, as they are unable to pellet even at 29,000 x g. However, DLS measurements revealed an increase in size for all initial formulations following protein incubation, both in the pelleted larger liposomes, as well as supernatant (mean increase of 20 nm), suggesting that regardless of size, liposomes adsorb BSA on their surface. We furthermore showed through molecular dynamics experiments that cholesterol facilitates a faster protein adsorption, with the first protein adsorption event occurring in the DPPC:CHOL 6:4 formulation, after approximately 500 ns simulation. Thus, cholesterol does not have a significant impact on the amount of protein adsorbed, but it can influence adsorption kinetics.

Acknowledgments

This work was supported by two grants of the Romanian Ministry of Research, Innovation and Digitalization, CNCS – UEFISCDI: PN-III-P1-1.1-PD-2021-0786 and PN-III-P3-3.6-H2020-2020-0105, within PNCDI III, as well as a H2020 ERA-Chair grant, no. 952390.

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Physical point of view to the problem of antiviral activity of nonfunctionalized nanoparticles

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The antiinfection activity of different nanostructures against of bio-objects are studied intensively for last decades. Particularly, the antiviral activity of 'pure' non-functionalized nanoparticles were observed in lot of experiments held by different scientific teams. This antiviral activity can be explained from physical point of view. The interaction between nanoparticles and virus due to local-field enhancement effect can lead to arising the domains of strong local field (hot spots) on the viral envelope (Fig.1). Thus, the strong gradients of local-field are formed at the surface of viral envelope. The gradients cause the ponderomotive forces acting to the spikes and whole viral envelope. As a result, the molecules-receptors at the spikes are deformed and deformed the envelope up to its destroying. This deformation is the reason of lost of infection activity of viruses. The antiviral activity of non-functionalized nanoparticles does not strongly depend on the material from which the nanoparticle is fabricated. Because the near-field interaction is the reason of arising of antiviral activity of nanoparticles, the activity significantly depends on the size and shape of the particles and is manifested against of different viruses. The results of various experiments performed by the scientific group of Authors and other scientific groups can be explained in the frame of the proposed mechanism.



FIGURE 1. Ponderomotive forces acting to the virus surface due to strong gradients of local field.

Acknowledgments

This work was supported in part (V.L. and N.R.) by Grant N_{2} 225 Φ 07-01 awarded by Ministry of Education and Science of Ukraine.

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Strategies for surface functionalization of hyaluronic acid-based hydrogels – a platform for myocardial infarction treatment

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Due to dysregulated cellular mechanisms, myocardial infarction (MI) causes serious damage to the heart that leads to ongoing damage and unfavorable tissue remodeling that cannot be adequately repaired by the body. Various delivery systems were already presented in the area of MI treatment, including nano- and microcarriers, hydrogels, and implants loaded e.g. with growth factors, chemokines, nucleic acids and stem cells. Moreover, more advanced approaches, which favour synergistic effects of MI treatment with enhanced targeting and release are also being currently investigated in this topic. When hydrogels are used in MI treatments, there are numerous options for therapeutic intervention from both the encapsulated biologics and the delivery method itself. [1]

Hyaluronic acid is a biologically active glycosaminoglycan biopolymer that is primarily found in the extracellular matrix. The unique physicochemical and biological characteristics of this biopolymer, which is non-toxic, reproducible, and biodegradable, include receptor-specific binding and the ability to regulate macrophage activation via the cell-surface receptors of hyaluronic acid in order to modulate inflammatory responses. [2] Using hydrogels to deliver biologics, notably those containing hyaluronic acid, is still fraught with difficulties. The first and most important issue is the straightforward reality that water takes up the majority of a hydrogel's volume. This has the important effect of producing a relatively modest volume to enclose biologics. Additionally, the hydrophilicity of hydrogels frequently causes biologics that are encapsulated to leak in bursts. To improve the release rate control, we can either modify the biological agents, or modify the hydrogel itself. In order to obtain desired properties, such as appropriate hydrophobicity (for long-term and target-specific drug delivery), viscoelastic properties (to serve as injectable materials), and thermoresponsivity (to be able to undergo a sol-gel transition by raising the temperature if a thermo-responsive moiety with a lower critical solution temperature is grafted onto it), there is a great need for simple functionalization methods.

In this work, we show effective methods for functionalizing hyaluronic acid in order to achieve the previously described functionalities, including β -cyclodextrin-, litocholic acid-, and pNIPAM (poly(N-isopropylacrylamide))- functionalized hyaluronic acid hydrogels along with its characterization.

Acknowledgments

Project number DWM/WPC2/285/2020, entitled "Construction of Multifunctional Nanosystems for Theranostics of Ischemic Heart Diseases", funded from the National Centre or Research and Development is kindly acknowledged. Moreover M.K. would like to acknowledge project ID-UB 076/34/UAM/0070 funded by Adam Mickiewicz University.

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Exploring cationic amphiphilic drugs as RNA delivery enhancers

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The clinical approval of the first RNA interference (RNAi)-based medicinal product Onpattro® (patisiran) in 2018 and the more recent clinical success of the SARS-CoV-2 messenger RNA (mRNA)-based vaccines (Comirnaty® and Spikevax®) underscore the potential of RNA-based drugs. Lipid nanoparticles (LNPs) have become a well-established platform to package, protect and deliver various nucleic acid cargos into the cytosol of cells. However, despite recent advances in LNP design and manufacturing, only limited endosomal escape efficiencies (~1-4%) are reported for state-of-the-art LNPs. This abstract describes the repurposing of a specific class of cationic amphiphiles, i.e. low molecular weight cationic amphiphilic drugs (CADs), to improve cellular delivery of RNA therapeutics. A variety of pharmacologically diverse CADs was identified to promote cytosolic delivery of siRNA from the endolvsosomal compartment through the transient induction of (phospho)lipidosis, lysosomal swelling and lysosomal membrane permeabilization (LMP) [1-5]. More recently, exploiting their ability to integrate in lipid membranes, CADs have been repurposed as both structural and pharmacologically functional components of LNP-like formulations, termed CADosomes and CAD-LNPs, for local delivery of both siRNA and mRNA [6]. As CADs maintain their pharmacological activity upon LNP integration, these formulations provide opportunities for drug combination therapy for the treatment of a variety of pathologies.

Acknowledgments

B.B. is a doctoral fellow of the Research Foundation-Flanders (1S75019N, FWO, Belgium). K.R. and C.M. acknowledge the FWO for funding through research grant G039419N. K.R additionally acknowledges the European Research Council (ERC) for funding received under the European Union's Horizon 2020 research and innovation program (ERC Consolidator Grant agreement No. 101002571).

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INVITED SPEAKER

Nanoparticles: exquisite tools to improve radiation based therapies

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Radiotherapy, one of the main treatments in cancer, can be improved by the use of heavy atoms, as radiation enhancers. Many investigations are conducted in this area. The challenge is to increase the radiation damage on tumor whilst preserving healthy tissue by improving targeting. Recent developments in nanotechnology brought new perspectives by using nanoparticles, which can be specifically functionalized. We have shown that metal based nanoparticles strongly enhance complex molecular damage induced as well by carbon ions, as by protons or gamma rays. This effect is not due to the nature of the incoming radiation but explained by the auto-amplification of electron cascades into the nanoparticles. This work aims at evaluating the efficiency of the NPs, understanding the biological mechanisms underlying these effects and findings the action sites. These results allow us to measure how the use of heavy nanoparticles could improve treatments by enhancing efficiency into the tumor.



Tracking the biological fate of silica nanoparticles in senescent cells

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Silica nanoparticles (SiNPs) have shown to be highly stable and non-toxic when used for cell applications. They can be engineered to penetrate cells and serve as vehicles for drug transport. Numerous studies have indicated that cell division reduces the concentration of internalized SiNPs. Utilizing senescent cells, which do not divide, offers a different approach for examining the cellular uptake and retention kinetics over extended periods [1]. In the presentation, I show the data for rhodamine-labeled SiNPs detected in senescent cells at three days and beyond using confocal laser scanning microscopy (CLSM) and flow cytometry techniques [2]. SiNPs, when internalized, remain in the cytoplasm for the long term and do not exit. Most studies about SiNPs have focused on their mechanisms in cancer cell lines. However, exploring the functions of SiNPs in senescent cells could reveal new potential applications. This research lays the groundwork for developing NP-based tools capable of detecting and targeting senescent cells for therapy.

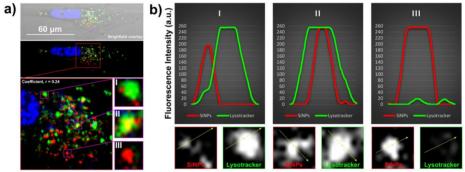


FIGURE 1. Co-localization of 200 nm SiNPs with lysotracker inside a senescent cell. (a) Live imaging of senescent cells using CLSM. Staining with Hoechst 33342 (blue) and lysotracker (green) shows the nucleus and acidic cell compartments, respectively, in the same confocal plane as SiNPs (red). Colocalization analysis found overlap between lysotracker and SiNPs for the cell in the image with a Pearson's correlation coefficient, r = 0.24. SiNPs are categorized as I, II, and III based on their correlation with lysotracker. (b) Quantification of the fluorescence images shown in (a) using a line analysis. The fluorescence channels were first split using Image J software and transformed to binary formats. The signals along the yellow line drawn for examples I, II, and III were plotted as overlaid histograms.

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This study was supported by grant OPUS 17, 2019/33/B/ST5/01495 from the National Science Center, Poland.

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Plant-produced HBV virus-like particles as vaccines and carriers

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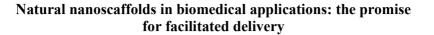
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Plants are efficient producers of Virus-Like Particles (VLPs), including chimaeric VLPs with heterologous epitopes, constitute basis of numerous vaccines. VLPs are also used as versatile cargo vehicles for delivery of drugs, various biopharmaceuticals and nanoparticles. VLPs assembled by HBV (Hepatitis B Virus) antigens: S- and M-HBsAg (small, medium HB surface Antigen) and HBcAg (HB core Antigen) were produced in transgenic plants and via transient expression. S-HBsAg in lyophilised plant tissue was used as a low-dose oral booster vaccine [1] whereas purified M- and S-HBsAg were used as injection vaccines [2], and all triggered immune response comparable with a commercial vaccine [1,2]. Plant-produced HBcAg administered as an injection-oral vaccine induced significant mixed Th1/Th2 immune response, required for treatment of chronic hepatitis B (CHB) [3,4]. Purified HBcAg VLPs were also successfully used as an envelope for assembly of complex bionanoparticles with SPION (Super Paramagnetic Iron Oxide Nanoparticles) cores [5] for possible hyperthermy. Preliminary studies enabled us to exploit plant-expressed HBcAg as an epitope carrier for future veterinarian vaccine [6] and CHB therapy purposes.

Acknowledgments

The studies were supported by: Grant No. N302 157837 from the Polish State Committee for Scientific Research and Projects No. 2016/23/B/NZ7/01288, 2019/35/B/NZ6/04002 and 2020/37/B/NZ6/02334 from the National Science Centre.

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Viruses are inherently organized supramolecular structures, designed by nature for viral genome packaging and delivery. Instances of virion application in biomedicine, bio- and nanotechnology have been substantiated during the last decade. However, the recent advances are neither exhaustive nor fulfilling the needs of healthcare and nanoengineering; particularly missing are safe, universal and multipurpose delivery systems. For facilitated cargo transfer, we employ intrinsic yeast viruses by the development of bionano scaffolds.

The yeast is a prominent model system, highly relevant for human research, further supported by granting of Saccharomyces cerevisiae a GRAS (Generally Regarded As Safe) status. Yeast viral systems feature unique combination of simplicity and robustness. Doublestranded RNA viruses are uninfective and exclusively intracellular. Deep integration into the metabolism presumes virus significance for host survival in diverse ecosystems, including the human body environment. S. cerevisiae L-A virions are genuine packing system of viral genome: the only capsid protein associates into 60 assymetric dimers, forming a relatively loosely packed yet firmly structured 39 nm diameter particle. The expression of sole capsid protein in virus-naive host leads to spontaneous formation of genome-free VLPs (virus-like particles), ready for complexation of cargo molecules. We cloned and sequenced all to date known S. cerevisiae - and many alike - dsRNA viruses from natural yeast. Gene engineering of both outer and inner shells of capsid has been demonstrated to be compatible with nanoscaffold structure, conferring both the modification and targetting options for a particle. The proof-of-principle of cargo loading was demonstrated by assembling of VLPs carrying external nucleic acids and peptides, so confirming the perspectives in packing of the different payload.

The bioengineering of intrinsic benign yeast viruses is performed to prepare versatile nanoscaffolds with precise addressability option. The proposed range of bionanoparticles with augmented targeting significantly expands the repertoire and beneficial properties of current transfection agents. The development of structures highly compatible with human body will open new horizons in bioengineering and production of fine materials with unseen yet functionalities and functions. Once developed, it presumes a great potential for outreach into healthcare by expanding into preparation of nanomaterials with prominent drug delivery option.

Acknowledgments

This research is funded by Research Council of Lithuania under the Project P-MIP-23-415.



Polysulfone membranes with nanoadditives for safer CRRT.

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Continuous renal replacement therapy (CRRT) is a way to treat acute renal injury (AKI). To reduce the risk of adverse reactions associated with therapy we need membranes with high biocompatibility, which can be achieved by increasing their hydrophilicity [1].

The aim of the study was to obtain nanocomposite membranes based on polysulfone (PSU) modified with various nano additives by wet phase inversion. Based on the antifouling and hydrophilic properties described in the literature, as a nanofiller were used commercially available nanoadditives: carbon nanotubes (MWNT-OH, Nanostructured & Amorphous Materials); mesosilica SiO₂ (Sigma-Aldrich) and a SiO₂ nanopowder (Zoosorb, Biomedix); graphene and graphite (Ferro Carbon).

Nanocomposite membranes were obtained by nonsolvent-induced phase separation (NIPS) base on system: polysulfone-dimethylformamide-water (Sigma-Aldrich). Pores morphology were characterized by scanning electron microscopy (SEM, Nova NanoSEM). Physicochemical properties of the membrane surface were reflected by wettability and surface free energy (SFE, Kruss 25). The test showed that all of the nanoadditives, except mesosilica, increased membranes hydrophilicity by reducing a wetting angle below 90°. Total volume porosity was determined by considering the volume of water (V_{water}) in the membrane relative to the geometric volume of the membranes ($V_{membrane}$) and the best results were observed for nanocomposite with mesosilica (Figure 1). The membranes were also exposed to a static transfer test with E. coli bacteria to assess the retention of bacteria cells. The collected material was studied after cultivation on an agar medium. All five types of additives increased the total porosity of the material while blocking the passage of bacteria cells. However, not all chosen additives increased membrane hydrophilicity. Further studies are needed to assess the hemocompatibility of designed materials.

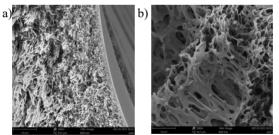


FIGURE 1. SEM image of membrane cross-section. (a) PSU membrane, (b), PSU+mesosilica.

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Nanoenhanced membranes for biomedical applications

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Polymeric materials have a huge potential for biomedical applications. However, there are still many studies necessary to improve their final properties. The primary barrier is the time and cost spent to fabricate biocompatible constructs while maintaining their mechanical strength and surface properties [1].

The regulatory safety aspects and membrane life cycle must be investigated before any of these membrane systems are used in the clinic. Especially the aspects related to the interactions of polymeric materials with body fluids are particularly relevant. A critical issue to consider is the degradation of the polymer-based system in the human body [2,3].

Modifying polymer membranes with nanomaterials can improve their physicochemical properties and biological activity but also may cause various adverse effects on the immune system. For instance, accumulations of nanoparticles in tissues and organs may induce mutagenesis and carcinogenesis [4]. Thus, to ensure perfect biocompatibility of polymeric materials, nanoadditives should be covalently bound to the polymer matrix.

Acknowledgments

This work was supported by the National Science Centre under research Grant number DEC-2017/01/X/ST5/00108.

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INVITED SPEAKER

Targeting extracellular proteins for rapid and efficient ovarian cancer cell capture: Role of nanoparticle properties in efficient capture and culture of ovarian cancer cells

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The development of specific and sensitive immunomagnetic cell separation nanotechnologies is central to enhancing the diagnostic relevance of circulating tumor cells (CTCs) and improving cancer patient outcomes. The limited number of specific biomarkers used to enrich a phenotypically diverse set of CTCs from liquid biopsies has limited CTC yields and purity. Ultra-high molecular weight mucin, MUC16 has been shown to physically shield key membrane proteins responsible for activating immune responses against ovarian cancer cells and may interfere with the binding of magnetic particles to popular immunomagnetic cell capture antigens. CA125, the antigen binding site of the mucin MUC16, is a gold-standard ovarian cancer clinical biomarker detectable in 52% of early-stage and 90% of late-stage ovarian cancer patients. We demonstrate that cell bound CA125 is an effective target for rapid immunomagnetic extraction of expressor cells with near quantitative yield, high purity and viability from serum. The results provide a mechanistic insight into the effects of nanoparticle physical properties and immunomagnetic labelling on the efficiency of immunomagnetic cell isolation. The growth of ovarian cancer cells has also been studied after separation and we demonstrate for the first time that nanoparticle size significantly impacts cell-particle behavior and growth rate. These results present the successful isolation of 'masked' CTCs and strategies for improving immunomagnetic separation and cell culture properties of ovarian cancer cells.



"Core-shell"-like Fe₃O₄/CeO₂ particles: physical-chemical properties vs. bioactivity

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Reactive oxygen species (ROS) are formed as a natural by-product of cellular aerobic metabolism. Because of their highly reactive nature, ROS can irreversibly modify proteins, nucleic acids, and lipids. Their ability to be scavenged is important in combating aging and oxidative stress-related diseases, such as cancer, diabetes mellitus, and neurodegenerative diseases, including Alzheimer's disease. Cerium dioxide nanoparticles (CeO₂ NPs) due to their antioxidative properties are perspective nanoscale material in the study of the processes accompanying oxidative-stress-related diseases, including amyloid-related pathologies [1-4]. In turn, magnetic Fe₃O₄ NPs have drawn increased attention thanks to their remarkable properties that allow the generation of heat (hyperthermia) under alternating magnetic fields and to be guided via an external magnetic field.

Magnetic Fe_3O_4/CeO_2 nanocomposites (NCPs) were prepared by the precipitation of CeO₂ NPs on the surface of previously cryochemically obtained Fe₃O₄ NPs. Newly fabricated Fe₃O₄/CeO₂ NCPs with different thicknesses of shell were tested and compared by their bioactivity; the antioxidant and anti-amyloidogenic activity were evaluated. The obtained results showed that all "core-shell" NCPs exhibit the anti-amyloid activity expressed as the ability to inhibit fibril formation. In addition, all NCPs were able to partially disassemble preformed amyloid fibrils. The extent of anti-amyloid activity exhibits a size-dependent efficacy to alter protein amyloidogenesis and points to the both, importance of the presence of a magnetic (Fe_3O_4) core and the interplay between NCP size and surface chemistry. For a more detailed view of bioactivity, i.e. to assess the impact of size/redox state, we analyzed also the pseudo-enzymatic activity of NCPs by monitoring the SOD-, oxidase- and catalase-like activity. Our results demonstrate well-defined valence- and size-dependent pseudo-catalytic activity. We can assume that the major catalytic activity arises from the shell of NCPs, however, the involvement of the magnetite core cannot be excluded, as the XPS analysis revealed the coexistence of two redox-ion couples: Fe³⁺/Fe²⁺ and Ce³⁺/Ce⁴⁺. The coupling of both, Fe_3O_4 and CeO_2 led to higher catalytic activity than either of them, perhaps due to synergistic catalytic mechanism [1-6].

Acknowledgments

This work was supported by grants: the NATO Programme (G5683), MVTS AZCAI (JRP 2021/192), VEGA (No. 2/0094/21, 2/0034/22), and APVV-19-324.

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Synthesis, characteristics, and effect of zinc oxide and silver nanoparticles on the regeneration and metabolite profile of chrysanthemum shoots

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Studies on the effect of nanoparticles on plants are relevant for horticultural purposes. The aim of this study was to test, for the first time, the effect of zinc oxide submicron particles (ZnO SMPs), zinc oxide nanoparticles (ZnO NPs), and zinc oxide nanoparticles combined with silver nanoparticles (ZnO+1%Ag NPs) on the *in vitro* regeneration and biochemical activity of adventitious shoots in *Chrysanthemum* × *morifolium* (Ramat.) Hemsl. 'UTP Burgundy Gold' and 'UTP Pinky Gold'.

The original microwave solvothermal synthesis procedure was applied for the synthesis of material samples. The ZnO NPs sample and the ZnO+1%Ag NPs sample were characterised by homogeneity of particle shape and size. The average particle sizes calculated on the basis of the specific surface area results for the ZnO NPs sample and the ZnO+1%Ag NPs sample were 25 ± 2 nm and 27 ± 2 nm, respectively. Internode explants were cultured on the MS medium with 0.6 mg·L⁻¹ 6-benzylaminopurine (BAP) and 2 mg·L⁻¹ indole-3-acetic acid (IAA), and treated with the tested material samples at the concentrations of 100 and 500 mg·L⁻¹. After nine weeks of culture, the regeneration efficiency was evaluated and the regenerated adventitious shoots were analyzed in terms of phytochemicals content.

In chrysanthemum 'UTP Burgundy Gold', shoot regeneration did not occur on the control internodes in contrast to the treatments with all tested material samples. The highest regeneration efficiency was obtained for 100 mg·L⁻¹ ZnO SMPs and 500 mg·L⁻¹ ZnO NPs treatments (6.50 and 10.33 shoots per explant, respectively). Shoots from these combinations also had high or moderate content of chlorophylls and carotenoids. On the other hand, in 'UTP Pinky Gold', the highest number of shoots was produced in the control object (12.92), after the treatment with 500 mg·L⁻¹ ZnO SMPs (12.08), and 500 mg·L⁻¹ ZnO NPs (10.42). These shoots had increased ratios of chlorophylls (*a+b*) to carotenoids. Interestingly, in the latter cultivar, the application of ZnO SMPs and ZnO NPs decreased the accumulation of phenolic compounds. ZnO SMPs and ZnO NPs have more beneficial effects on the induction of shoot regeneration compared to ZnO+1%Ag NPs.

The results are important for the improvement of micropropagation protocols used in chrysanthemum production and/or breeding, especially for cultivars recalcitrant to adventitious organogenesis.

SECTION B NANOBIOMEDICINE



Development of Bioselective PVDF and PES Membranes using Various Functionalization Strategies and Epitope-Mediated Virus Receptors

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Waterborne viruses are a public health concern due to relatively small infection doses [1]. The hepatitis A virus (HAV), which is transmitted mainly by direct contact with contaminated water, is a leading cause of acute viral hepatitis worldwide [2]. The development of bioselective membrane technologies is crucial to control outbreaks of waterborne diseases in point-of-care settings. This study aims to develop functionalized bioselective membrane by epitope-mediated polymeric nanoparticles (nanoMIPs) for specific recognition and removal of HAV virus.

Results and Discussion

Computational simulations were employed to design polymeric receptors with highest affinity towards HAV particles. HAV epitope imprinted nanoMIPs were synthesized via solid phase synthesis method using the computationally derived recipe. The nanoMIPs were conjugated on the polyvinylidine fluoride and polyethersulfone filtration membranes following three different surface functionalization methods. Surface topography, phase distribution and surface morphology were evaluated with atomic force microscopy and scanning electron microscopy. The membrane performance was evaluated by filtration experiments in terms of permeation flux, membrane fouling and virus quantification.

Conclusions

A sensitive and selective assay for recognition and removal of hepatitis A virus established with the use of bioselective PVDF and PES membranes using HAV-specific nanoMIPs..

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This research was financially supported by the German Research Foundation (DFG) under the project number 428780268.

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The elucidated effects of inorganic nanoparticles on the structure, properties and functioning of bacterial cell membranes

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In conjunction with the growth of the population and the demand for innovative technological and industrial solutions, the dynamic development of nanotechnology revolutionised the last decade by offering solutions to the problems of the modern world. Nanomaterials (NMs) are beneficial for multiple purposes, including the fight against pathogenic microorganisms. However, their commonly known and widely recognised antimicrobial properties may become problematic when they exhibit such effects beyond their original purpose through their entry into various environmental compartments [1,2]. Despite advanced and intensified research on the abstruse NMs and bacteria interactions, knowledge regarding their biological activity and potential toxicity is still partial and contradictory and insufficiently elucidates the overall toxicity profiles [1]. Therefore, examining the properties of their biological activity is essential for their safe and controlled future utilisation whilst reducing environmental risks.

This study aimed a multifaceted analysis of the influence of inorganic nanoparticles (NPs), including Ag-NPs, Cu-NPs, ZnO-NPs and TiO₂-NPs, on the structure and properties of *Escherichia coli*, *Bacillus cereus* and *Staphylococcus epidermidis* cell membranes. The performed experiments included the permeability of outer cell layers, cytoplasmic leakage, ATP levels and fatty acid profiling of the cells exposed to NPs. The results confirmed the negative and significant impact of particular NPs on the tested parameters in all bacteria. Predominantly the alterations in the membrane permeability were positively correlated with cytoplasmic leakage and negatively correlated with total ATP levels. Interestingly, the established fatty acid profiles were unique for each strain and concerned various changes in the percentages of hydroxyl, cyclopropane, branched and unsaturated fatty acids. The results have contributed to a comprehensive explanation of NPs biological activity and provided insight into their prominent interactions with bacterial cell membranes.

Acknowledgments

This research was funded in whole by the National Science Centre, Poland, grant number 2021/41/N/NZ9/02506. The presented results are part of "Undesirable consequences of the metallic nanoparticles action on the properties and functioning of *Escherichia coli*, *Bacillus cereus* and *Staphylococcus epidermidis* membranes" (doi: 10.1016/j.jhazmat.2023.130728) article.

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Alkylated derivatives of hyaluronic acid as kartogenin carriers

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Cartilage diseases progress with age and result from making them a dominant problem in orthopedic surgery. To reduce the need for surgical interventions, searching for new methods and preparations for inducing and supporting cartilage regeneration is essential [1, 2]. The main goal of the research is to improve delivery of kartogenin (KGN), the small molecule with chondroprotective properties and potential of chondrogenic differentiation of mesenchymal stem cells. Therefore this biologically active substance can be used to repair cartilage tissue. The KGN structure determines its hydrophobic properties, which causes a decrease in the activity of the drug substance and its removal from the body too quickly. In order to reduce this negative effect, various novel carriers were fabricated and examined. The research premise was to receive structurally diverse hyaluronic acid. This polymer was modified using carbon chains of various lengths and in varying ratios to obtain different grades of substitutions. Properties of composed derivatives were investigated using spectroscopic methods and other advanced analytical methods. The obtained derivatives formed the basic components of the polyelectrolyte aggregates, which were used as KGN carriers. The final step was to assess the biological activity of the composed systems regarding their cytotoxicity towards stem cells. The resulting polymers are effective carriers for kartogenin molecules, and could have a great potential in cartilage tissue repair.

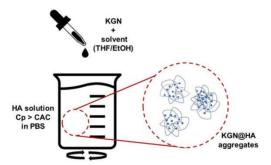


FIGURE 1. Scheme of KGN@HyCx_L/H aggregates production.

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In Vitro Study of Biomimetic and Paramagnetic Nanoparticles for Targeted and Efficient Treatment of Liver Cancer

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Liver cancer is one of the most common and lethal cancers worldwide. Traditional cancer treatments like chemotherapy, radiotherapy, and surgery have limitations and can cause severe side effects. Theranostic nanosystems combine therapeutic and diagnostic properties, enabling simultaneous detection and treatment of cancer. In this study, we aimed to develop a drug delivery system (DDS) based on biomimetic and paramagnetic nanoparticles to enhance the targeted and efficient treatment of liver cancer [1].

Polydopamine (PDA) nanoparticles have received considerable attention for their biocompatibility and photothermal properties. PDA nanoparticles can be loaded with chemotherapeutic drugs, enabling combined therapy [2]. Furthermore, the addition of Fe to PDA nanoparticles can increase their photothermal response and tumor-killing ability [3]. However, the poor targetability and short circulation time of nanoparticles in the bloodstream limit their therapeutic potential. To overcome these limitations, we utilized a biomimetic approach to coat drug-loaded PDA-Fe nanoparticles with membranes extracted from HepG2 cells.

We successfully developed a DDS based on biomimetic and paramagnetic nanoparticles for the targeted and efficient treatment of liver cancer. We synthesized PDA-Fe nanoparticles using a simple one-pot method. The particles were then loaded with doxorubicin, a potent chemotherapeutic drug. The drug-loaded PDA-Fe nanoparticles were successfully coated with HepG2 cell membranes, resulting in a stable DDS. The nanoparticles showed excellent biocompatibility and enhanced cellular uptake compared to uncoated nanoparticles. The coated nanoparticles also showed effective targeting to homotypic cancer cells. In addition, the nanoparticles exhibited significant cytotoxicity towards HepG2 cancer cells and increased cell death by apoptosis. Furthermore, the nanoparticles showed contrast enhancement in MRI imaging, making them promising theranostic agents for liver cancer treatment.

Acknowledgments

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The importance of process parameters screening in the synthesis of polysaccharide-based nanoparticles using solvent displacement method

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There are two main approaches toward the polymeric nanoparticles preparation – solvent displacement method and emulsification-diffusion method [1]. Although both ways require at least two solvents (mostly, one of them is organic and the other is water or buffer), the difference is in the miscibility criteria. While the solvent displacement method requires media that mix freely one with another, emulsification-diffusion does not necessarily meet this criterion. Each process parameter (e.g., temperature, organic solvent character, solvents' volume ratios, stirring method and power) can significantly impact the properties of obtained nanoparticles [2].

Screening these process parameters should be considered as important part of research on nanoparticles preparation. This gap in the literature can be well seen, especially in the synthesis of polysaccharide-based nanoparticles. In this study, we evaluated the solvent effect's impact on basic nanoparticles' characteristics: size and zeta potential. Measurements were conducted on ZetaSizer Nano-ZS (Malvern).

Obtained results indicated that not only the variation in process parameters (temperature, solvent type, polymer concentration) influence the particle size, but also the concentration of the sample during the measurement.

As a result, we could observe that the particle size was changing together with the type of organic solvent applied (tetrahydrofuran, dimethylsulfoxide, dimethylformamide) as well as the concentration. On the other hand, the water phase temperature (0°C, 22°C, 40°C and 70°C) during the addition of the organic phase barely does not affect the size of nanoparticles in the screened range.

In light of this study, it is essential to emphasize the importance of a clear description in papers, not only the nanoparticles preparation conditions but also the sample preparation condition before the size distribution analysis.

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Designing GMO/GML/F127 Lipid Liquid Crystalline Nanoparticles with Antibacterial Activity by Central Composite Design

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During the design of new nanocarriers, it is crucial to have knowledge of and control over their physicochemical properties in order to obtain an optimized system with desired features [1]. In the presented studies, a full two-level factorial design and a central composite design were applied to acquire the objective functions of hydrodynamic diameter, polydispersity index, zeta potential, and optical density at 660 nm of a new glyceryl monooleate (GMO)/glyceryl monolaurate (GML)/Pluronic F127 lipid liquid crystalline nanoparticle system. Monolaurin and monolauric acid exhibit antibacterial activity attributed to destructive effect on bacterial membrane [2], therefore optimized system is anticipated to inherit aformentioned bioactivity. Accordingly, obtained system was tested for antibacterial activity agains Gram-negative *Escherichia coli* and Gram-positive *Staphylococcus aureus* bacterial strains. Moreover, to assess usefulness of the composition for biological systems, WST-1 proliferation test on HeLa and MSU 1.1 cells was conducted.

The conducted studies demonstrated the usefulness of the central composite design in optimizing the synthesis conditions of the LLCNPs, resulting in a stable GMO/GML/F127 dispersion with a mass ratio of 26,5:3,5:1,5. Physicochemical studies confirmed the presence of a structure with cubic inner symmetry, with a hydrodynamic diameter of $136,5 \pm 6,2$ nm and a strongly negative zeta potential. Additionally, biological studies proved antibacterial activity against *Escherichia coli* and *Staphylococcus aureus* strains.

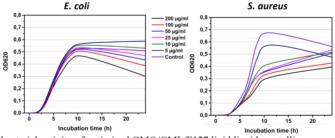


FIGURE 1. Antibacterial activity of optimized GMO/GML/F127 lipid liquid crystalline nanoparticles against *Escherichia coli* and *Staphylococcus aureus* stains evaluated over 24h period.

Acknowledgments

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Streptavidin-biotin interaction simulated by steered molecular dynamics: methodology based on dynamic force spectroscopy

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Protein-ligand interactions, including one of the strongest known, i.e. between streptavidin and biotin, are a key research topic regarding biomolecular functions. Understanding them is crucial in virology, cancer treatment, and understanding genetic diseases in multitude of organisms including human, livestock, and endangered species.

One of methods of in vitro protein-ligand interaction investigation is dynamic force spectroscopy (DFS), analysis of force spectra (distribution of unbinding forces) under external force of load varying by several orders of magnitude. Accompanying computer calculations consist of modelling the complex, molecular docking, and multiple unbinding events simulation with steered molecular dynamics (steered MD or SMD). Exemplary workflow for unbinding simulations is shown on Fig.1.

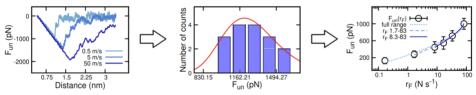


FIGURE 1. Exemplary flow of the SMD-DFS simulations leading to DHS model fit.

Such calculations, including multiple low-cost runs allow for efficient usage of computational power, embracing embarassing parallelism of the method and provide multiple benefits over single, high-cost runs like quantum mechanical MD. The benefits include lack of efficiency loss associated with multi-core usage and possibility for heterogeneous cloud computing [1]. We assess limitations and possibilities of the method, including lifelike and experiment-like receptor restraints, and application of various thermally activated unbinding under external force models, including Dudko-Hummer-Szabo (DHS) model [2]. The final goal is to extract energetic and kinetic parameters describing streptavidin-biotin interaction with high accuracy. The current literature presents multitude of comparable data, yet, there is plenty of room for improvement in uderstanding mechanics of this specific bond.

Acknowledgments

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Senescent Cells as a Model for NanoBioMedical Research

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Cellular senescence is a type of response to various stressors which triggers a series of molecular events that ultimately lead to growth arrest but with continuous metabolical activity [1]. Due to that and other features, senescent cells can be considered a great model in nano research for intracellularly analyzing and monitoring the fate and kinetics of nanoparticles or nanocarriers [2]. Many protocols deliver scattered information about the process of senescence induction with various information about the results and efficiency. Those protocols are not providing the crucial information to use those cells as a model for further experimentations, which is the number of senescent cells obtained by described methods.

During this study, the protocol of senescence induction by using doxorubicin was prepared and performed on W138, and A549 cell lines, based on available articles, and confirmed by various senescence markers that obtained cells were senescent. The main goal of this study is to obtain quantitative data on the efficiency of the protocol with the approximate number of senescent populations. Also, to study their morphology changes by confocal microscopy and the possible model application window. Additionally, the fate of nanocarriers will be demonstrated by flow cytometry technique and kinetics of release of senolytic, the drug that can kill senescent cells. Overall, our studies are a preliminary step towards a more complex model but are very important in future in-situ models and studies, opening various possibilities for further development in many fields, such as biomedicine and materials sciences.

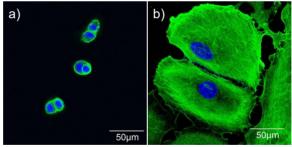


FIGURE 1. Comparison of morphology between control (a) and senescent cell (b) after induction A549 cell line with doxorubicin.

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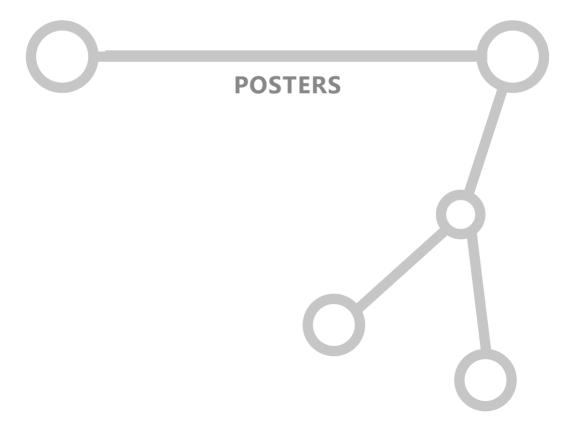
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SECTION B NANOBIOMEDICINE



Confocal Raman microscopy as a versatile tool for *in vitro* label-free interaction studies between nanomaterials and live cells

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Confocal Raman Microscopy (CRM) is a multifaceted analytical method for noninvasive livecell analysis and nanomaterial-cell interaction studies. *In vitro* label-free CRM of live cells enables the detection of bioconjugated nanoparticles in the intracellular space in real time at a submicrometric resolution, as well as the differentiation of individual cell compartments. Previously we have shown the potential of this methodology for the intracellular localization of graphene oxide [1], MoS_2 [2], Fe_3O_4 [3], MoO_x and MXene [4] nanomaterials conjugated with active targeting agents, monoclonal antibody M75 and RGD peptides. Moreover, we used this method to assess the HaCaT human keratinocyte cell line morphological changes induced by essential oils encapsulated in poly(\Box caprolactone) nanocapsules [5]. Here, we employed label-free live-cell CRM for the localization of Au and MoO_x based nanoparticles conjugated with plant extracts – *Silibinin, Chelidonium majus* and *Hypericum perforatum*, within cancer and healthy cells. Comparison of the Raman signal with regard to active targeting agent based inorganic nanoparticle conjugates is given.

Acknowledgments

This work was supported by the Slovak Research and Development Agency under contract No. APVV-20-0485 and by the Slovak Grant Agency for Science under contract No. VEGA 2/0116/22 and 2/0117/22.

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The influence of zinc oxide and zinc oxide nanoparticles on the growth of various plant pathogens *in vitro*

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ZnO NPs exhibit a broad antifungal and antibacterial action and could be applied to control the spread of and infections caused by a variety of plant pathogens [1-2]. The aim of this study was to investigate and compare the effects of ZnO submicron particles (ZnO SMPs) and ZnO NPs on the response of various plant pathogens: *Botrytis cinerea*, *Fusarium oxysporum* and *Alternaria alternata* in *in vitro* culture. ZnO NPs were produced by means of the microwave solvothermal synthesis. As a reference sample, ZnO SMPs, produced using the indirect French process, were used. ZnO NPs were characterized by a homogeneous spherical morphology, with an average size of 30 ± 2 nm. ZnO SMPs had a heterogeneous morphology and a wide size distribution ranging from 100 nm to 2000 nm, with an average particle size of 240 ± 30 nm.

In the experiments, all pathogens were inoculated on the PDA medium (DifcoTM Potato Dextrose Agar) with the addition of ZnO SMPs or ZnO NPs at the following concentrations: 0, 100, 200, 500, 1000, 2000 mg·L⁻¹. Mycelium disks were cut from seven-day-old pathogens cultures and placed on the medium in the center of each Petri plate. The plates were then incubated at 23 °C. The mean diameter (mm) of mycelial growth of the fungi was measured every 24 hours until complete overgrowth of the plate occurred in one of the combinations (for each pathogen separately).

It was found that the addition of ZnO NPs and ZnO SMPs to the medium significantly inhibited the growth of mycelium in all tested pathogens. However, regardless of the concentration used, the advantage of ZnO NPs over ZnO SMPs in inhibiting the growth of mycelium has not been demonstrated. The minimum inhibitory concentration (MIC) was defined as the lowest concentration of the compounds that inhibited mycelium growth and can indicate the potential use of these compounds in plant protection. Interestingly, the smallest tested concentrations (100 mg·L⁻¹) caused a significant reduction in the growth of mycelium in *F. oxysporum* and *A. alternata*. On the other hand, in *B. cinerea*, only the concentration of 500 mg·L⁻¹ and higher limited the growth of mycelium. Further research will include *in vivo* tests on plant material.

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Fabrication and characterization of Gd₂O₃ hollow spheres for potential bioapplication

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Multifunctional nanomaterials present great interest in the scientific research fields due to their unique properties. These materials are able to combine several functions in one nanosystem, which allows to use it in different scientific areas. For example, the combination of luminescent and magnetic properties enable for obtaining potential nanomaterials for biomedical applications, mainly for diagnostic analysis, magnetic resonance imaging (MRI), and fluorescent labelling [1]. The combination of magnetic and fluorescent properties yields dual-imaging probes that can provide bifunctionalities of high sensitivity/resolution fluorescence imaging, as well as noninvasive and high spatial resolution MRI for real-time monitoring. Gd-based materials due to the high magnetic moment of Gd, are one of the two most popular contrast agents (another one is iron oxide) used in MRI [2]. Gd₂O₃ is a well-known single-phase multifunctional material - crystallophosphor with intensive green emission and high paramagnetic performance [3]. At the same time, Gd ions like all rare earth elements can possess toxicity. The hollow structure of nanoparticles could significantly reduce the possible toxicity of Gd ions in comparison to bulk oxides or Gd-based chelates. Moreover, hollow structures can be a great base for drug loading.

The main goal of the present study is the simple synthesis approach of Gd_2O_3 hollow nanospheres with controlled shell thicknesses for potential drug carriers and contrast agents for MRI. The Gd_2O_3 spheres formation process, phase composition, and crystal structure, as well as, morphology and relaxivity, were investigated in detail.

 Gd_2O_3 hollow nanospheres have been successfully prepared using the hydrothermal template-directed method, where carbon spheres were as sacrificed templates. A homogeneous precipitation method was used to fabricate Gd_2O_3 hollow spheres with a controlled mesoporous shell using urea as a precipitating agent and following heat treatment. Results showed that obtained Gd_2O_3 spheres are monodisperse and have hollow structures with mesoporous shells of controlled thicknesses. Spheres (size ~150 nm) are highly crystalline with high phase purity. The studies of NMR relaxivity showed that obtained hollow Gd_2O_3 spheres could act as contrast agents for magnetic resonance imaging especially at low magnetic field. Furthermore, Gd_2O_3 hollow spheres could significantly reduce the

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Studies of selected carbon nanomaterials with amyloid beta peptides

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Alzheimer's disease (AD) is a disorder of central nervous system (brain), that slowly destroys nervous cells, memory and thinking skills, and finally the ability to perform basic tasks. It is the most common cause of dementia among older population. According to the amyloid hypothesis, in AD, the processing of the amyloid precursor protein (APP) by β - and γ -secretases enzymes results in the formation of several variants of amyloid β peptides usually containing 40 or 42 amino acid residues [1]. They exhibit a tendency to form aggregates and amyloid deposits, which accumulate in the brain, disrupt nerve signaling pathways, and lead to the degradation of neurons.

Previous data indicate that various nanoparticles can inhibit the aggregation processes of $A\beta$ peptides [1,2], therefore, the systematic studies of these nanosystems can lead to the development new concepts for effective diagnostic tools or therapies. Since many years carbon nanoparticles (eg. carbon nanotubes or fullerenes) are studied as promising nanostructures for nanomedicine. They may exhibit useful biomedical applications, due to their unique physicochemical properties, such as small size (below 100 nm), high active surface and ability to cross the blood brain barrier [3].

The goal of our studies was an analysis of interactions between $A\beta$ peptides and selected carbon nanoparticles using various biophysical methods. We focus on visualization the process of the formation of amyloid deposits using spectrofluorimetry and microscopy. Close view of the mechanics of pathological aggregation of $A\beta$ peptides should help in better understanding of neurodegeneration processes. This research was supported by Study@Research grant.

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Antioxidant effectiveness of silver nanocolloids in combination with cloves

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Free radicals cause many diseases like cancer or dementia. They are also responsible for food spoilage during its storage and processing [1].

Spices like cloves are known for their antimicrobial activities and antioxidant properties. Studies have shown that cloves can help to reduce inflammation and improve digestion. Silver nanocolloids are antibacterial. By combining the antibacterial properties with the health benefits of cloves one can improve their efficiency [2].

This study investigated the antioxidant properties of cloves and silver nanocolloids using electron paramagnetic resonance (EPR). The antifungal properties of silver nanocolloids were also checked.

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Interaction of lipid drug carriers with protein studied at nanoscale

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Lipid-based drug delivery systems (LBDDS) have contributed to significant achievements in the pharmaceutical industry and in developing new therapeutic strategies [1]. Liposomes are the most common and well-investigated LBDDS however recent years witnessed emerging growth of interest in other formulations which overcome the limitations of conventional approaches. Upon administration, lipid drug carriers experience various physicochemical phenomena, depending on the administration route. In the case of intravenous drug administration, the interaction of lipid carrier with blood proteins is crucial for the distribution of the bioactive molecules in the bloodstream and reaching the target tissue. Therefore the surface properties of LBDDS have been identified as considerable factors influencing the pharmacokinetic profile (PK) of the intravenously administered drugs.

In this work we explored the interaction of serum albumin with three-component lipid monolayer build of palmitoyloleoylphosphatidylcholine (POPC), sphingomyelin (SM), and cholesterol (Chol). Using wide range of lipid compositions and various concentrations of serum albumin we identified the factors governing the lipid-protein binding behavior. Our study revealed that albumin can penetrate selectively the monolayers of POPC/SM/Chol. This behavior may lead to the increase of the size and charge of the lipid carrier and affect the drug transport throughout the bloodstream. The results of this work provide essential physicochemical data that can be used for predicting the pharmacokinetic profile of lipid-based formulations.

Acknowledgments

This work was financially supported by the Ministry of Science and Higher Education in Poland. M.W. acknowledges the Ministry of Science and Higher Education in Poland for financial support within Project No. 0512/SBAD/2120.

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Zeolite-based composites possessing anti-amyloidogenic activity as promising drug-released carriers

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One of the most attractive approaches in biomedicine and pharmacy is the application of multifunctional materials. Zeolites, both, natural and synthetic possess a micro-mesoporous crystalline aluminosilicate structure of a 3D tetrahedral framework of oxygen-sharing AlO₄ and SiO₄ groups. Due to their unique properties, such as precisely defined pores and channels, high thermal stability, expanded surface area, high ion-exchange capacity, and strong acidic sites, zeolite, including clinoptilolite (CZ) may be used in different areas such as industrial, environmental, biotechnological, and biomedical applications. One of the relatively unexplored but potential applications of CZ particles is to detect, monitor, and treat amyloid-related diseases, which are characterized by the presence of stable, ordered, filamentous protein aggregates, commonly called amyloid aggregates or fibrils. Previously we observed that CZ particles exhibit anti-amyloidogenic effects on the protein amyloid aggregation in a dose- and temperature-dependent manner [1,2].

In the present work, we focus our attention on improving the anti-amyloid activity of CZ-zeolites using three selected dyes, namely aluminum phthalocyanine (SAP), zinc porphine (ZnP), and hypericin (HYP). Fabricated CZ-composites with incorporated dyes have been tested and the anti-amyloidogenic activity, biocompatibility, and biodistribution of individual dyes and zeolite-dye composites have been examined. The results revealed the anti-amyloid activity of all tested dyes and CZ-dye composites. It was shown, that the incorporation of dyes into CZ particles enhanced anti-amyloidogenic activity in comparison to pure CZ particles. In addition, all studied fluorescent dyes incorporated in zeolites are promising photosensitizers with applications in photodynamic therapy.

Thus, the results confirmed that newly prepared zeolite-dye composites can be used as a biocompatible carrier model for targeted drug delivery with controlled release.

Acknowledgments

This work was supported by grants: MVTS AZCAI (JRP 2021/192), VEGA (No. 2/0094/21, 2/0034/22), and APVV-19-324.

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Gold nanoparticles reduce the intensity of *Hypericum perforatum* L. plant defense against *Agrobacterium tumefaciens*

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Agrobacterium-mediated transformation is a promising tool for functional genomic studies and crop improvement. However, several important plant species remain resistant to Agrobacterium infection due to the induction of plant defenses. We have previously shown that intracellular reactive oxygen species (ROS) increase rapidly in Hypericum perforatum L. cells when co-cultured with Agrobacterium, resulting in a complete loss of Agrobacterium viability within 12 hours of treatment [1]. Here, we show that the Agrobacterium-induced plant defense response in H. perforatum can be suppressed using gold (Au) nanoparticles (NPs). In brief, H. perforatum cells were co-cultured in the presence and absence of 25 ppm Au NPs, and the intracellular ROS production in the H. perforatum cells and the viability of Agrobacterium tumefaciens were tested. The results showed that the presence of Au NPs reduced the intensity of intracellular ROS production (Fig. 1A) and subsequently increased the viability of Agrobacterium mediated transformation methods for recalcitrant plant species such as H. perforatum.

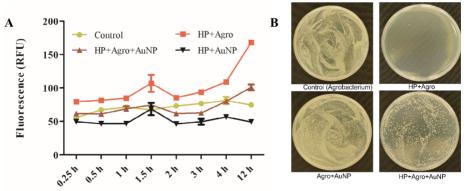


FIGURE 1. (A) Intracellular ROS production. (B) Viability of *Agrobacterium* after 12 h co-cultivation [HP: *Hypericum perforatum*, Agro: *Agrobacterium tumefaciens*, AuNP: Gold nanoparticles]

Acknowledgments

This work was supported by the National Science Centre (NCN), OPUS project no Reg. No 2017/25/B/NZ9/00720 and the NANOPLANT project, which received funding from the European Union's Horizon 2020 research and innovation program under grant agreement no. 856961.

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Synthesis and characterization of iron-based drug carriers for anti-migraine therapy

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Migraine is a chronic, disabling disease that affects approximately 15% of the population. One of the most common factors responsible for migraine attacks is stress which is the trigger of tension-type headaches and occurs very often during an intense lifestyle. Migraine is also associated with a deficiency of many nutrients – vitamins (B2, B3, B12) or minerals such as magnesium [1]. Unfortunately, the effectiveness of well-known drugs used in migraine treatment (i.e., ketoprofen, naproxen sodium, diclofenac) is limited. Drugs must pass the way through the gastrointestinal system before they can be absorbed [2]. Hence, there is a need for a novel and safe delivery system that will allow the drugs to reach the action site for fast and effective acute treatment of migraine. Metal–organic frameworks (MOFs) are porous and crystalline materials that have found varied applications in several fields. They are known for their high specific surface area and pore volume, facile synthesis, high drugloading capacities, and controlled release [3]. MOFs containing iron are most often selected as drug carriers, due to their biocompatibility and low cytotoxicity.

The aim of the study was the synthesis, characterization and application of Fe-BTC materials as drug delivery systems. FeCl₃·6H₂O and trimesic acid were applied as the precursor of metal ions and linker, respectively. The synthesis of materials was performed in distilled water, ethanol, and water–ethanol mixture with different ratios at 130 °C for 72 h. The materials were characterized with the use of X-ray diffraction, low-temperature nitrogen adsorption/desorption, thermogravimetric analysis, and scanning electron microscopy. Samples were tested in adsorption processes of a diclofenac/vitamin B12 mixture, which were conducted for 2 h at room temperature. Then, the drug release processes in phosphate buffers simulated intestinal (pH 6.8) and rectal (pH 7.7) fluids were carried out.

Studies have shown that depending on the solvents used during synthesis, Fe-BTC materials exhibit different textural parameters. The sample synthesized in a 10:1 ratio of water–ethanol mixture was found to have the largest specific surface area $(222 \text{ m}^2/\text{g})$ and pore volume $(0.34 \text{ cm}^3/\text{g})$. In turn, Fe-BTC material obtained in water is more stable at high temperatures. Fe-BTC samples are promising adsorbents of diclofenac and vitamin B12 from aqueous solutions. The results confirmed that materials have better sorption capacity towards diclofenac than vitamin B12. The adsorption mechanism of these pharmaceuticals includes hydrogen bonds, van der Waals forces, and electrostatic interactions with MOF surfaces. An *in vitro* experiment of drug release revealed that the diffusion process occurs in a controlled manner. Diclofenac and vitamin B12 were liberated with greater efficiency in a phosphate buffer of pH 7.7.

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HAp+Ag-SiO₂ as a new kind of biocompatible coatings improved the NiTi applications in implantology

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Metallic alloys are widely used in implantology due to their excellent mechanical properties and good biocompatibility. However, under the conditions prevailing within the body, these materials can release heavy metals into the surrounding tissues, which can have adverse health effects. Therefore, continuous efforts are being made to develop new methods to modify such alloys and reduce the release of heavy metal ions while improving their biocompatibility. One promising approach uses coatings made from bioactive materials such as ceramic phosphates (CaP) and silica glasses (SG). Extensive research is being conducted on both CaP and SG coatings. CaP provides osseointegration, but it has high brittleness and poor adhesion properties. On the other hand, SG can form chemical bonds between different materials.

This research aimed to develop new multifunctional coatings based on hydroxyapatite (HAp) and a silver-silica nanocomposite to enhance the properties of NiTi alloy and its biocompatibility. The coatings were deposited on the alloy surface using the electrophoretic deposition approach (EPD) at different ratios of HAp+Ag-SiO₂ (1:1, 5:1, 10:1). Several parameters, including surface roughness, wettability, surface free energy, and a comparison to reference coatings (HAp and silica), were determined for all coatings. Additionally, the antibacterial properties of the coatings against two strains of bacteria (*Escherichia coli* and *Staphylococcus aureus*) were evaluated. It has been shown that all HAp+Ag-SiO₂ systems exhibited significantly better antibacterial properties compared to the control systems. Furthermore, the viability and cell adhesion of two normal cell lines, named human fibroblasts (NHDF) and human osteoblasts (HOB), were investigated. No significant differences in cell viability were observed for both cell lines compared to the control coatings. Similar observations were made regarding cell adhesion on the coating's surface.

In summary, the $HAp+Ag-SiO_2$ coatings, particularly the 5:1 ratio, demonstrated superior physicochemical and biological properties compared to the reference coatings. The research indicates that incorporating Ag-SiO₂ into the coating material leads to the development of new biocompatible implant materials.

Lipid liquid crystalline nanoparticles as potential carriers of biologically active substances supporting regenerative therapy

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Myocardial infarction and following complications are one of the leading causes of mortality worldwide. Despite intensive attempts to develop a therapy using cardiomyocytes obtained from pluripotent induced stem cells (IPSc), full regeneration of heart tissues has not yet been achieved [1]. One of the reasons for the failures is seen in the fetal phenotype of the obtained cardiomyocytes. So far, the proposed solutions for improving the maturity of cardiomyocytes have included extending the cell culture time or supplementation of the culture medium with hormones. Recently it has been shown that non-coding RNAs may have a positive effect on cardiomyocyte maturation by regulating PI3K/AKT/Insulin pathway, however, the reports on using nanoparticles as their carriers have been very limited.

In this study, we present a strategy toward lipid liquid crystalline nanoparticles (LLCNPs) complexed with miR let7g, thus developing new nanocarriers for targeted RNA delivery. The aim of the research was to synthesize LLCNPs with glycerol monooleate (GMO) as a structure-forming lipids, modified with DODMA cationic lipids in various concentrations. GMO/DODMA/F127 was synthesized using a top-down approach. The effect of the DODMA on the physicochemical properties of lipid nanoparticles, such as particle size, colloidal stability, and morphology, has been investigated.

Next, they were copmlexed with miR by incubation for 1.5h at RT. Their uptake, cytoand genotoxicity on human cardiomyocytes, as well as effects on reactive oxygen species production and mitochondrial membrane potential, were investigated. The changes in expression of genes related to metabolic switch and markers characteristic for mature cardiomyocytes were assessed by real-time PCR.

Obtained results revealed that GMO/DODMA/F127 nanoparticles were efficiently taken up by cells, they were not geno- or cytotoxic toward the cells. Moreover, LLCNPs-miRlet7g had the potential to positively impact PI3K/AKT/Insulin signaling pathway.

Acknowledgments

The research is financially supported by the National Science Centre Poland Miniatura 5 2021/05/X/NZ3/01013 and National Centre for Research and Development DWM/WPC2/285/2020.

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Dendrimer Functionalized Polydopamine Nanoparticles For Multimodal Therapy of Glioblastoma

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Glioblastoma is one of the most aggressive and difficult-to-treat cancers. Traditional anticancer treatments are ineffective; a life expectancy following diagnosis is only 12–18 months. Brain tumor cells overexpress a number of proteins that play a crucial role in tumor progression and may be used as therapeutic targets. A down-regulation of an extracellular matrix glycoprotein - tenascin-C (TN-C) by RNA interference (RNAi) is a very promising strategy in cancer treatment. However, the efficient delivery of naked double-stranded RNA (dsRNA) complementary to TN-C sequence is problematic due to rapid degradation by nucleases and poor intracellular uptake. Polydopamine (PDA) coated nanoparticles functionalized with polyamidoamine (PAMAM) dendrimers may be used for gene silencing therapy and as a drug delivery vehicle. PDA, a nature-inspired polymer, is characterized by high biocompatibility and a simple functionalization process. Moreover, the photothermal properties of this polymer allow its application in photothermal therapy (PTT), which is a great alternative for cancer treatment.

The aim of this study was to synthesize and characterize PDA nanoparticles (NPs) functionalized with PAMAM dendrimers for therapeutic dsRNA and DOX delivery. PDA@Dendrimer NPs could be further used in combined drug delivery, gene silencing and photothermal therapy. NPs were characterized in terms of physicochemical and photothermal properties as well as their cytotoxicity using human U118-MG cell line derived from a glioblastoma multiforme was assessed. The results show that the synthesized NPs may be potential non-viral vehicles for dsRNA delivery and as photothermal agents for PTT in glioma treatment.

Acknowledgments

The research was financed by The National Science Centre (NCN), Poland under project number 2018/31/D/ST8/02434.



Electrochemical biosensor for rapid detection of SARS-CoV-2 antibodies based on 1D ZnO nanorods

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The coronavirus disease (COVID-19) caused a significant impact on the world's health and economy. The significance of a diagnostic tool is purely influenced by the type of test, testing accuracy, and time it takes to receive the results [1]. Although the reverse transcription polymerase chain reaction (RT-PCR) is still the standard method for detecting severe acute respiratory syndrome coronavirus-2 (SARS-CoV-2), antigen rapid detection tests are frequently used to identify the viral proteins. Despite being less sensitive than molecular tests, antigen rapid detection tests have the advantages of being inexpensive and providing results quickly at the point of care. In order to reduce the spread of the virus, it is necessary to develop diagnostic tests that can rapidly identify the infected individual. Owing to their high sensitivity, portability, selectivity, fast response, and cost-effectiveness the electrochemical biosensors are recently considered as a promising tool for SARS-CoV-2 detection [2,3]. Additionally, they can detect target analytes with low low concentrations which makes them advantageous for early diagnosis of the disease.

In this work, we present 1D ZnO nanorods used as the template for electrochemical biosensor application for the detection of SARS-CoV2-2 antibodies. In comparison with traditional methods of antibody detection, the present work offers several advantages such low-cost portability, and high accuracy. With continuous research and development, the 1D ZnO based electrochemical sensor will play an important role in rapid and sensitive diagnostic tools for the monitoring of infectious diseases.

Acknowledgments

The financial support of Marie Skłodowska-Curie Research and Innovation Staff Exchange (CanBioSe 778157) is gratefully acknowledged. The authors also acknowledge the financial support from the National Science Centre of Poland (NCN) by the SONATA-Bis grant 2020/38/E/ST5/00176.

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MgAl Layered Double Hydroxides Nanohybrids as Effective Carriers for Controlled Release of 5-Fluorouracil: Effect of Experimental Conditions on the Release Behavior

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Layered double hydroxides (LDH) are very suitable nanomaterials to host different drugs, which are then released in a controlled manner under appropriate experimental conditions. In this study, 5-fluorouracil (5-FU) trapped in Mg-Al LDHs was achieved by co-precipitation method at low suprasaturation using chloride salts, as metal precursors, and NaOH as alkaline conditions. The molar ratio of Mg/Al in the brucite like layers is 2, while the Al³⁺/FU ratio is 1. The amount of loaded FU was controlled by the hydrothermal conditions, as drug incorporation decreased with increasing temperature. XRD results confirmed the layered structure of the MgAl LDH nanohybrids while FTIR spectra displayed the absorption frequencies of 5-fluorouracil, indicating the incorporation of the drug within the LDH nanocarrier. To observe the release control of 5-FU from LDH, dialysis bag method was employed. The effect of the various conditions on the release behavior was assessed. Thus, tests in phosphate buffer solution at different pH values, to simulate physiological and extracellular tumor environment, were performed. To evaluate the role played by the cations found in blood in the drug release from a nanocarrier, tests in PB enriched in cations were carried out. To observe how the amount of the nanodrug controls the release behavior, tests using different solid/liquid ratios were performed, as well.

The results revealed the impact of the pH on the controlled release in the sense that acidic pH was less favorable to the release, effect attributed to the lower solubility of FU in slightly acidic medium and/or formation of a complex between the FU and the released cations. The presence of the salts (Mg^{2+} , Ca^{2+} , K^+ , Na^+) in the phosphate buffer at a concentration similar to those in the bloodstream had no effect on the release of FU. Yet, changing the amount of solid in the dialysis bag while keeping the volume constant positively affected the controlled release, as the amount of solid increased, and the release rate was slower. In addition, the experimental results showed an effect of the interactions between drug and LDHs as well as of the geometric constraints due to the tridimensional organization of the nanoparticles on the release rate. To understand the complex relationship between the pH and the release behavior, the samples recovered after controlled release were subjected to XRD and FT-IR analyses. The experimental results showed an ion exchange between the FU and PO_4^{2-} anions of the release medium for the release at physiological pH while at lower pH values, the dissolution of the inorganic component came together with the ion exchange mechanism. These correlations are helpful to predict and optimize the behavior of the delivery systems based on LDHs.

Aacknowledgments

This work was supported by a H2020 grant – ERA-Chair, no 952390 and a grant from the Ministry of Education and Research, CNCS/CCCDI - UEFISCDI, project number PN-III-P3-3.6-H2020-2020-0105/35/2021.



Targeting Cellular Senescence with Silica Nanoparticles

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Nanotechnology is one of the most promising fields of research, especially when it comes to new imaging properties and therapies for diseases. In addition, nano-based tools offer efficiency, specificity, and sensitivity. The delivery of drugs based on nanoparticles (NPs) utilizes their unique characteristics, such as their relatively small size (10-1000 nm), shape, and modified surface area, to improve therapeutic efficiency. However, few studies have investigated the use of NPs in studying cellular senescence. Cellular senescence is implicated in the pathogenesis of various age-related diseases, such as cancer, as well as in normal tissue development and regeneration. Therefore, understanding the mechanisms underlying cellular senescence is an important area of research in the field of aging and disease prevention.

Our previous research showed that senescent cells tend to accumulate silica nanoparticles (SiNPs) while proliferative cells can dilute them with each division [1]. To test the hypothesis that **senescent cells take up more SiNPs compared to normal cells**, we incubated native cultures of WI-38 fibroblasts with rhodamine-labeled SiNPs. Our findings indicated a positive correlation between commonly used senescence biomarkers (SA- β -gal, SAHF, and growth arrest) and a negative correlation with proliferation markers. These results suggest that SiNPs could be a promising tool for targeted therapy against senescent cells, and could pave the way for further research in this field.

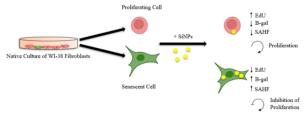


FIGURE 1. WI-38 fibroblasts uptake of silica nanoparticles (SiNPs). The native culture was incubated with 25 μ g/ml of 200 nm rhodamine-labeled SiNPs for 2 hours and then washed with HBSS three times. After 24 hours, the cells were stained for the proliferation marker (EdU), the activity of β -galactosidase (β -gal), and the nuclei for senescence-associated heterochromatin foci (SAHF).

Acknowledgments

This study was supported by grant OPUS 22 2021/43/B/NZ3/01454 from National Science Centre, Poland.

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Mobile-based electrochemical enzymatic and non-enzymatic sensors for glucose monitoring

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Mobile-based electrochemical sensors for glucose monitoring are a rapidly advancing technology that allows individuals to conveniently and accurately measure their blood glucose levels using their smartphones or other mobile devices. These sensors take advantage of the ability to enzymatically or non-enzymatically measure glucose in a variety of solutions [1].

These sensors work on the principle of electrochemical detection, where the concentration of glucose in a biological sample (such as blood, serum or infusion fluids) is converted into an electrical signal. This signal is then measured and analyzed by the mobile device to determine the glucose level [2]. Moreover, these sensors provide real-time glucose monitoring, allowing individuals to track their glucose levels continuously throughout the day. This feature is particularly useful for individuals who require tight glucose control or have fluctuating glucose levels [3].

Herein, we present the non-enzymatic and enzymatic sensor for glucose detection. The systems were constructed based on a hybrid nanomaterial. The enzymatic system was based on the system of hybrid material, which served as a platform for the immobilization of the enzyme - glucose oxidase (GOx) from *Aspergillus niger*. A non-enzymatic system that uses the electrocatalysis of copper oxide to oxidize glucose. A number of physicochemical analyzes were performed to accurately characterize both systems including transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), atomic force microscopy (AFM), Fourier transforms infrared spectroscopy (FT-IR). The most important analytical parameters of the sensor like sensitivity, detection, selectivity, time-stability were determined. The systems were also used for tests on real solutions, i.e. human serum or human blood. Finally, the most important properties of enzymatic and non-enzymatic systems were compared.

Acknowledgments

This work was financed and prepared as part of a research project supported by the National Science Centre Poland, no. 2017/27/B/ST8/01506. Dr. Artur Jędrzak is also grateful to the Foundation for Polish Science (FNP) for its support through a START scholarship.

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The influence of selected nanocolloids on aging processes - EPR study

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Excess of free radicals in human body can cause many diseases, for example inflammations or cancer. They can also accelerate the aging process of the skin. There are a lot of products on the market that contain various forms of metals with antioxidant properties.

Despite their small size, nanocolloids have a large active surface. They are characterized by better antifungal and antibactericidal properties than traditional colloids. Nanocolloid gold has a soothing and rejuvenating effect on the skin. It has a positive effect on skin elasticity and increases the penetration of active ingredients contained in cosmetics into the deeper layers of the skin. Silver nanocolloids have anti-inflammatory and antibactericidal properties. Nanocolloids of copper and platinum also neutralize reactive oxygen species (ROS) [1,2].

Electron paramagnetic resonance (EPR) allows to test the antioxidant properties of nanocolloids of various metals and helps to assess the effectiveness of neutralizing free radicals. The aim of the study is to examine the effect of selected nanocolloids on skin aging processes using EPR. The properties of the studied materials, such as hydrodynamic diameter and zeta potential were assessed using dynamic light scattering approach.

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Green-inspired silver nanoparticles (AgNPs) show antimicrobial activity against rapeseed pathogen *Sclerotinia sclerotiorum*

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Oilseed rape is a crop of great economic importance in Poland, but its production is constantly affected by the fungal pathogen *Sclerotinia sclerotiorum*, which causes white mold [1]. Fungicides are used to control it, but they pose risks to the environment. The development and use of "green-inspired nanopesticides" has the potential to be not only effective and targeted, but also sustainable and with lower toxicity to non-target organisms [2]. We synthesized silver (Ag) nanoparticles (NPs) using plant extracts and tested them against *S. sclerotiorum* [Figure.1]. The inhibitory effect of AgNPs on the growth response of *S. sclerotiorum* was tested *in vitro* using different concentrations of NPs. Our results show that green AgNPs inhibit the growth of *S. sclerotiorum* in a concentration-dependent manner, reaching 100% at the highest concentration tested. Further studies are being conducted to test the effects of green AgNPs on plant growth, physiological status and overall development. This will contribute to strategies for using green nanomaterials for disease control and overall improvement of smart/sustainable agriculture.

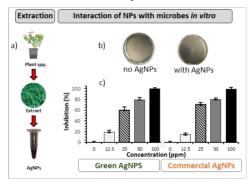


FIGURE.1 Green synthesis of AgNPs and their *in vitro* testing against *S. sclerotiorum*. a) Extraction of AgNPs from plant, b) growth inhibition tests of fungal *S. sclerotiorum* on agar plates, and c) % inhibition compared to the control.

Acknowledgements

This work was supported by the NANOPLANT project, which received funding from the European Union's Horizon 2020 research and innovation program under grant agreement no. 856961.

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Synthesis and characterization of a new material based on 5, 10, 15, 20 tetrakis (m-hydroxyphenyl) chlorin and graphene oxide with potential application in cancer phototherapy

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In dynamic phototherapy (PDT), tumor cells are locally killed by reactive oxygen species (ROS), such as singlet oxygen ${}^{1}O_{2}$ produced by a photosensitizer (PS) under illumination and in the presence of oxygen. Widespread use of known photosensitizers is limited due to prolonged dermal photosensitivity, poor water solubility, and insufficient selectivity [1,2]. Fortunately, the above problems can be overcome by emerging two-dimensional layered materials (2DLMs) with versatile properties. 2DLMs have great prospects for application in PDT due to their large specific surface area and abundance of functional groups that can serve as a carrier for PS, and in addition, 2DLMs can help enhance the dispersibility of PS in physiological environments [3 – 5].

Through non-covalent functionalization of dye molecules (m-hydroxyphenyl) chlorine) (THPC) with graphene oxide (GO), a new nanomaterial has been created, which has been fully characterized by spectroscopic methods, and the properties of the hybrid material toward phototherapy, including singlet oxygen generation, have been investigated.

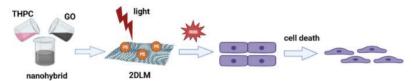


FIGURE 1. Representation of the synthesis and a simple photothermal protocol for PS/2DLM materials.

Acknowledgments

This work was supported by the by AMU "Excellence Initiative – Research University" (054/13/SNŚ/0024)

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Structural aspects and computational approach to the nanocomposite complex of EMAP II cytokine with TiO₂ nanoparticles

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Protein drugs are a distinctive and adaptable class of biotherapeutic agents, known for their high biological activity and specificity. Many proteins have demonstrated remarkable antitumor properties and are now considered viable alternatives to cytotoxic chemotherapeutic agents in cancer treatment. Recent advancements in biotechnology have made it possible to produce selected proteins in a reproducible and large-scale manner. Among the diverse range of biological applications, TiO2 nanoparticles have emerged as a particularly promising means of delivering biologically active substances to specific targets [1]. However, it should be noted that ingestion of TiO2 nanoparticles may result in accumulation within the body, leading to

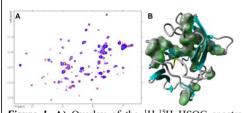


Figure 1. **A)** Overlay of the ${}^{1}\text{H}{}^{-15}\text{H}$ HSQC spectra recorded for the EMAP II protein without (red) and with (blue) TiO2 nanoparticles. **B)** The residues reveled large *csp* values visualized on 3D structure of the EMAP II.

potential toxic effects, including DNA damage, infiltration of inflammatory cells in the colon, alteration of the gut microbiome, and increased intestinal wall permeability.

In this study, we utilized NMR spectroscopy to examine the structural changes that occur in the human AIMP1 (p43) protein upon interaction with 20 nM TiO2 nanoparticles (NP). The addition of TiO2 NP caused chemical shift perturbations (csp) that enabled us to identify the specific residues involved in the binding interface between the protein and

NP. Our data indicate that the addition of NP to the solution led to significant changes in several residues, namely Gly39, Leu56, Ile65, and Lys92 (Figure 1A), which are located in the same plane and likely facilitate the surface responsible for the protein-NP interactions (Figure 1B). In the next stage, we aim to develop a computational model of the nanocomposite complex.

Acknowledgments

LK acknowledge to FEBS Ukrainian Short-Term Fellowship. IZ is partially supported by a research grant (2021/41/B/ST4/03807) from National Science Centre (Poland). DL and AK acknowledge to Complex interdisciplinary research program of the National Academy of Sciences of Ukraine "Fundamental bases of molecular and cellular biotechnologies".

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Functionalization of hyaluronic acid materials for post-heart attack therapy of the cardiac muscle

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Coronary artery disease, also known as ischaemic heart disease, is the most prevalent cardiovascular disease. It is a significant clinical, social, and economic problem. Despite tremendous advancements in medicine in recent years, the incidence of myocardial cell hypoxia leading to heart failure and heart attack continues to rise. This is primarily due to the aging population and an increase in the number of individuals exhibiting risk factors for cardiovascular diseases. Heart failure refers to structural and functional abnormalities of the heart that ultimately result in inadequate delivery of oxygen and nutrients to the tissues [1].

A promising approach for cardiac repair in regenerative medicine is the use of injectable hydrogels, e.g. based on hyaluronic acid. Hyaluronic acid is a natural anionic polysaccharide with a wide range of physicochemical and functional properties, making it highly useful as a drug delivery platform [2]. It can be characterized by biodegradability, non-toxicity, and the ability to modify its properties through the chemical conjugation of functional groups [3].

The study's main objective was to design and develop functional nanoparticles based on hyaluronic acid as drug delivery systems for cardiac muscle post-heart attack therapy. To achieve this, potential therapeutic systems were prepared in the first stage of the research. They possess an increased active surface area, drug-loading capability, long lifespan, the ability for cellular internalization, and ease of transport within the body [2]. In this way, we prepared three kinds of hyaluronate-based nanoparticles: pure sodium haluronate (SH-NP), and hyaluronates modified with litocholic acid (HA-LCA) and β -cyclodextrin (HA-CD). The structure and composition of the obtained nanomaterials were confirmed using nuclear magnetic resonance spectroscopy (NMR), infrared spectroscopy (IR), and thermal analysis was performed using differential scanning calorimetry (DSC).

In many applications of injectable hydrogels, it is desirable to match the physical properties of the hydrogel to the site of implantation to minimize adverse side effects such as mechanical damage [4]. The physical parameters of hydrogels are crucial for their drug delivery capabilities. The received systems should possess physical properties similar to living tissue, which makes them suitable for further research as conjugates of pseudo-dendrimers Bis-MPA PEG functionalized with Apelin-13 polypeptide, forming intelligent systems for selective drug delivery.

Acknowledgments

Project number DWM/WPC2/285/2020, entitled "Construction of Multifunctional Nanosystems for Theranostics of Ischemic Heart Diseases", funded from the National Centre or Research and Development is kindly acknowledged. Moreover M.K. would like to acknowledge project ID-UB 076/34/UAM/0070 funded by Adam Mickiewicz University.

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Engineered nanoparticles interferes with primary metabolism of *Hypericum perforatum* L. cell cultures

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We have recently reported the changes in secondary metabolism of Hypericum perforatum L cell suspension cultures in response to treatment with metal and metal oxide nanoparticles (NPs) [1]. Here, we show that treatment with metal and metal oxide NPs differentially affects primary metabolism in Hypericum perforatum L cell suspension cultures. Briefly, H. perforatum cell suspension cultures treated with 25 ppm of various NPs (Ag, Au, Cu, Pd, CeO2, CuO, TiO2, and ZnO) for 72 h were analyzed using UPLC-HESI-HRMS/MS for changes in primary metabolite profile. Results showed changes in 70 annotated primary metabolites that either decreased or increased in cells after treatment with metal NP, whereas they remained unchanged during treatment with metal oxide NP. The content of carbohydrates, amino acids and nucleotides decreased after treatment with Ag, Au and Cu, but the accumulation of some carboxylic acids and fatty acids increased after treatment with Ag NPs. All the tested metal NPs also decreased the content of some low molecular weight antioxidants (e.g., glutathione, ascorbic acid, their hexoside) by 2-5 times. On the other hand, the content of some primary metabolites with chelating properties, such as ornithine, lysine, citric acid, oxalosuccinate, and nucleotides, was increased after treatment with Ag and Cu NPs in the media. In conclusion, NPs have the ability to inhibit or stimulate primary metabolism of plant cells, depending on their type.

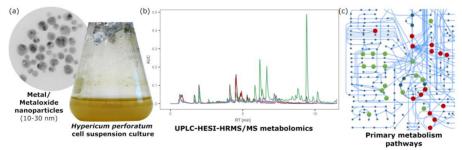


FIGURE 1. General experimental design: (a) treatment of *H.perforatum* cells with metal or metal oxide nanoparticles, (b) untargeted metabolomic analysis, (c) analysis of primary metabolic pathways.

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This work was supported by the NANOPLANT project, which received funding from the European Union's Horizon 2020 research and innovation program under grant agreement no. 856961

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The development of a new drug delivery system based on silk spheres targeting VEGF receptors for oligotherapeutics delivery

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Small interfering RNA (siRNA) shows high efficacy in the silencing of the target gene expression; however, its delivery to the cells is very limited. Bioengineered silk is a biocompatible and biodegradable material with great potential in drug delivery. It can be functionalized with a specific recognizing peptide or nucleotide-binding domain, allowing to target specific cells and enabling the delivery of nucleic acids. The tumor microenvironment consists not only of cancer cells but numerous types of cells, including endothelial cells of the vascular system. Angiogenesis is a process based on the formation of new blood vessels, which plays an important role in tumor development. Thus, targeting the VEGFR1 and VEGFR2 receptors overexpressed in cancer and endothelial cells to deliver an angiogenesis-inhibiting oligonuctleotide is a promising cancer treatment strategy.

The aim of the study is to generate and characterize newly developed VEGFRs-targeting silk spheres.

Five bioengineered silk proteins able to target cancer and endothelial cells were constructed. The functionalized silks were based on the MaSp1 spidroin sequence of *Nephila clavipes* fused to VEGFR1 and VEGFR2 receptor-binding peptides: VE1MS1, VE1bMS1, VE1cMS1 (recognizing VEGFR1), and VE2bMS1, VE2cMS1 (recognizing VEGFR2). MS2KN silk, a MS2 variant based on the MaSp2 silk protein functionalized with nucleic acid binding domain KN, was used to prepare blends with VEGFR-targeting silks. Bioengineered silks were expressed in the large scale bacterial expression system and purified using the thermal extraction method. Obtained proteins were analyzed with SDS-PAGE. Next, proteins were processed into nanospheres by mixing different functionalized silk variants and their blends with high concentration of potassium phosphate buffer. Spheres morphology and size were analyzed with SEM imaging, ImageJ software, and Nanoparticle Tracking Analysis (Nanosight). Agarose gel electrophoresis was performed to determine oligonucleotides binding to the silk proteins. Sphere binding to the VEGFR-positive endothelial (HUVEC) and lung cancer (H1975, HCC4006) was evaluated with flow cytometry.

VEGFR-targeting silks were successfully produced and purified. Mixing of functionalized spheres with potassium phosphate allowed to acquire of spherically structured nanoparticles. Agarose gel electrophoresis determined the high efficiency of oligonucleotides binding to the blends of VEGFR-functionalized silks with MS2KN. Flow cytometry analysis indicated that VEGFR-targeting silk spheres bound to the VEGFR-positive cells with high efficiency, compared with control MS1 particles without binding domain. VE1MS1 demonstrated the highest affinity to VEGFR1, while VE2bMS1 toward VEGFR2.

The results indicated VEGFR-targeting silk spheres as a promising tool for the effective delivery of drugs, including oligotherapeutics, to the VEGFR-overexpressing cells.

Acknowledgments.

The study was supported by The National Science Centre (2021/43/D/NZ7/00622).

Role of cell membrane constituents in transport of potential hemoglobin effectors studied by molecular docking

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Inositol hexakisphosphate (phytic acid, IP6), and inositol trispyrophosphate (ITPP) have been shown to increase oxygen transport in erythrocytes through lowering the hemoglobin-oxygen affinity. It provides hope in treating hypoxia and tumor cell normalization [1]. Red blood cell membrane is known to exhibit high selectivity in transcellular transport towards ITPP over IP6 and the transport mechanism is related to band 3 anion exchanger protein, known as AE1 [2].

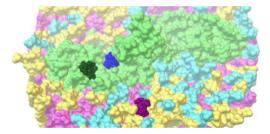


FIGURE 1. Top view of AE1 transport protein (light green) embedded in the cell membrane. Exemplary adsorption site (purple) and two binding sites in the pocket at the channel entrance (green and blue). Cholesterol, sphingomyelin, and other phospholipids are coloured in light colours.

We optimized all possible geometrically inequivalent inositol phosphates using density functional theory (DFT) approach. Then, we performed molecular docking of the molecules in the AE1 active site and adhesion centers on the cell membrane built around the transport protein and equilibrated with use of molecular dynamics (MD) in CHARMM36 force field. As a result the Gibbs energy difference between bound and unbound state of the molecules was determined. The lipid composition of the adhesion centers influences the energy of adhesion on the lipid bilayer in direct vicinity of AE1. Based on the results and known facts about distinct phospholipids (sphingolipids and phosphatydylinositols) and choloesterol distribution in the erythrocyte cell membrane, we draw conclusions about possible mechanisms of inositol phosphates transport selectivity.

Acknowledgments

We acknowledge financial support of Polish Ministry of Education and Science under grant number DI2017/007947 in Diamond Grant programme and grant number 0512/SBAD/2320. The work on the inositol phosphates conformation-picking scheme development has been cofinanced by the National Science Centre Poland under the decision DEC-2018/30/E/ST3/00267.

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Surface modified Metal-Organic Frameworks Nanoparticles for improved stability in physiological conditions

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Nanoparticles (NPs) of Metal-Organic Frameworks (nanoMOFs) are of great importance for drug delivery, especially due to their specific characteristics, such as a large surface area with a high drug loading capacity, controlled drug release, lack of toxicity, and easy-to-tune size, shape, and surface[1]. Among nanoMOFs, Zeolitic Imidazolate Frameworks-8 (ZIF-8) NPs are of special interest in the field of drug delivery and cancer treatment due to their pH-responsive character of degradation. Tumor targeting requires NPs to have long blood circulations, without accumulation in the liver or spleen. However, ZIF-8 NPs often suffer from a lack of stability in the physiological conditions, resulting in the early NP degradation, and "burst" release of the entrapped drugs. To overcome these limitations, modification of the outer surface of nanoMOFs is necessary.

In this study, we first synthesized the ZIF-8 NPs by the different synthesis methods, leading to the formation of NPs of different sizes (20-80 nm) and shapes (nanospheres, nanocubes, and rhombic dodecahedra nanoparticles). To avoid the early degradation of NPs in physiological conditions, we proposed to modify the surface of ZIF-8 NPs with lipid coating (DOPC). MOF@lipid NPs should have benefited from the properties of both porous particles and liposomes [2]. Lipids coated around nanoMOFs improve the stability of the NPs and help to control the release of the desired entrapped drugs. In addition, MOF@lipid nanoparticles were previously demonstrated to be significantly more stable than liposomes, which have an aqueous core instead of a porous MOF core [2]. We successfully coated the DOPC lipid on the ZIF-8 NPs of different morphology. Moreover, the stability and degradation of coated NPs in physiological conditions were improved compared to unmodified NPs (verified by e.g. XRD, TEM, DLS, IR). Presented nanoparticles are suitable for further tests in drug delivery applications.

Acknowledgments

The authors thank the National Science Centre of Poland for the financial support through the Opus grant, project number 2019/33/B/ST5/01495.

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In vivo evaluation of the toxicity of MS2-type silk spheres designated for oligonucleotherapeutics delivery to treat cancer

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Nowadays, a widely developed direction of cancer therapy is the use of drugs based on nucleic acids. However, the application of oligonucleotherapeutics *in vivo* is limited due to the activity of endogenous nucleases. Drug delivery systems can successfully overcome these limitations and allow for effective and safe delivery of nucleic acids to tumor. We constructed a drug delivery system based on spheres made of MS2-type spider silk functionalized with the KN peptide, which binds nucleic acids. Spider silk can be used for the production of biomedical nanocarriers due to its high biocompatibility and biodegradability. Regardless of these properties, any nowel drug carrier should be carefully tested for potential toxicity.

The aim of this study is to investigate whether a systemic administration of MS2-type nanocarriers can induce toxicity in mice.

The sequence encoding the MS2 protein and its counterpart functionalized to deliver nucleic acids (MS2KN) were introduced into a bacterial expression system and the proteins were produced at a semi-large scale in a bioreactor. Proteins purified by the thermal method were mixed with 2M potassium pohosphate buffer to form spheres. The research was carried out on 3 variants of spheres made of MS2-type proteins: MS2, MS2KN, and MS2KN spheres with bound oligonucelotides (MS2KN/ODN). In order to investigate acute toxicity 3 doses (5, 10, and 20 mg/kg b.w.) of spheres were applied to mice and behaviour of mice was observed. To study the subacute toxicity, spheres at a dose 20 mg/kg b.w. were applied to mice 3 times. The blood samples for the analysis of biochemical markers were collected on the 1st, 7th, and 14th day. The immunogenicity of MS2-type spheres was determined by intravenously administration the spleens were collected. The isolated splenocytes were then restimulated with an agent that was administered previously to mice. After 72h, splenocyte proliferation and the level of released cytokines was analysed using flow cytometry. Morover, the potential anty-silk antibody production was analysed in mice sera using ELISA-type assay.

The highest tested dosage of silk nanospheres (20mg/kg) was not lethal and did not affect the mice behavior. The application of silk nanoparticles did not affect the modification of biochemical markers in the sera, indicating no damage to internal organs. Splenocytes collected from mice after treatment with MS2-type spheres did not demonstrate increased proliferation or secretion of immune-related cytokines after specific stimulation. There was no presence of antibodies against spider silk protein in sera collected from mice after administration of MS2-type spheres.

The results did not indicate systemic toxicity in mice after the application of MS2-type spheres. Due to the demonstrated biocompatibility, the spheres presented in the study can act as carriers of nucleic-based drugs. In future studies, we plan to use this MS2-type drug-delivery system for *in vivo* application of oligonucleotherapeutics to cancer models in mice.

Acknowledgments. The study was supported by The National Science Centre (2020/37/B/NZ6/03435).

Versatile, Antioxidant, and Anti-amyloidogenic Cerium Oxide Nanoparticles

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Oxidative stress reflects the imbalance between reactive oxygen species formation and cellular antioxidant capacity due to enhanced ROS generation and/or dysfunction of the antioxidant system. Oxidative stress has been recognized as a contributing factor in aging and the progression of multiple age-related neurodegenerative diseases characterized by the presence of amyloid aggregates. Among various substances, cerium dioxide nanoparticles (CeO₂ NPs) due to their unique properties derived from shielded 4f-electrons and low redox potential of the Ce³⁺/Ce⁴⁺ redox couple seem to be applicable in the study of the processes accompanying oxidative-stress-related diseases, including amyloid-related pathologies.

This study aimed to examine the antioxidant and anti-amyloidogenic activity of newly prepared CeO₂ NPs with various physicochemical properties controlled during synthesis. We analyzed the effect of CeO₂ NPs on insulin amyloidogenesis and anti-oxidant properties expressed as pseudo-catalytic and pseudo-superoxide dismutase (SOD) activities. The size-depended activity of CeO₂ NPs to inhibit the amyloid formation of insulin was demonstrated. Although the interaction of CeO₂ NPs with insulin was strong enough to reduce the fibrillization process, the interactions of nanoparticles with mature fibrils seem to be incapable to cause fibril disassembly. The antioxidant activity of CeO₂ NPs was evaluated by monitoring their catalase- and SOD-like activity. We observed that CeO₂ NPs are capable of effectively dismutase the superoxide anion into H₂O₂ (SOD-like) and via catalase-like activity decomposing H₂O₂. Our results demonstrate well-defined valence- and size-dependent catalase- and SOD-like activity of CeO₂ nanoparticles. On the other hand, the larger particles having the lowest percentages of Ce³⁺ ions at the surface, display the higher catalase-like activity [1,2].

We demonstrated that the method of synthesis significantly affects the final physicochemical properties of nanoparticles, such as the size and ratio of Ce^{3+}/Ce^{4+} on their surface and thus also their resulting bioactivity [1,2]. Analysis of the published and current results allows us to predict the anti-amyloidogenic properties of CeO_2 nanoparticles based on size and surface chemistry which can be controlled by the adjustment of synthesis conditions.

Acknowledgments

This work was supported by grants: the NATO Programme (G5683), MVTS AZCAI (JRP 2021/192), VEGA (No. 2/0094/21, 2/0034/22), and APVV-19-324.

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Design of Ibuprofen-loaded microemulsions and NMR characterization

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Cancer is a disease often accompanied by inflammation, and anti-inflammatory agents have been shown to help reducing the cancer risk or improve the effectiveness of anticancer drugs. In developing new therapeutic routes for cancer treatment, several colloidal-system-based cancer therapies have been discovered lately. A microemulsion (ME)-based delivery system for anti-inflammatory and anticancer drugs has several advantages, including enhanced solubility, targeted drug delivery, reduced systemic toxicity, and higher treatment efficacy [1].

Ibuprofen-loaded ME is a promising drug delivery system that can overcome the limitations of ibuprofen, such as its low solubility and poor bioavailability. Furthermore, ibuprofen has been shown to enhance the efficacy of other anticancer drugs when combined [2].

This study aimed to develop ibuprofen-loaded MEs, which are suitable for tailoring the treatment of cancer types accompanied by the inflammation process. MEs were prepared using the phase titration method, with Maisine CC - oil phase, Tween 20 - surfactant, and ethanol - cosurfactant. The total drug content was 1 and 3%. In order to verify the type of ME encapsulating the drug, and the drug distribution in the ME's matrix, the obtained formulations have been assessed by ¹H NMR and diffusion-ordered NMR spectroscopy (DOSY). Prior to NMR, samples were characterized by DLS. The results revealed average sizes between 139 and 180 nm, depending on composition, in line with previous reports. Analysis of the DOSY spectrum, together with the calculation of the self-diffusion coefficient, led us to the conclusion that the type of prepared MEs is oil-in-water while the ¹H NMR spectra confirmed the presence of IBU in the MEs. The controlled release of IBU was investigated by dialysis method for 96 h and the released amount was determined by HPLC. The release results for ME with 1% IBU showed a slow and controlled release in the first 24 h and sustained up to 96 h while the ME with 3% IBU release is slow and controlled in the 96 h, requiring a longer time for the release.

Acknowledgments

This work was supported by an H2020 grant – ERA-Chair, no 952390 and a grant of the Ministry of Education and Research, CNCS/CCCDI - UEFISCDI, project number PN-III-P3-3.6-H2020-2020-0105/35/2021.

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Synthesis and Characterization of Magnesium-Aluminium Layered Double Hydroxides for 5-Fluorouracil Delivery in Cancer Treatment

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Cancer treatment remains an intensely researched field, with a focus on developing novel and efficient drug delivery technologies. In this study, we focused on the synthesis and characterization of magnesium-aluminium layered double hydroxides (LDH) loaded with 5-fluorouracil (5-FU) to obtain nanomaterials with potential applications for cancer therapy.

The synthesis of LDH was accomplished using the rationally controlled coprecipitation method, followed by the intercalation of 5-FU into the layered structure. In order to control the physico-chemical properties, different conditions of temperature and time were used for the hydrothermal treatment following the co-precipitation step. Confirmation of the LDH composition and structure was performed using advanced analytical techniques, that is, atomic absorption spectroscopy (AAS), X-ray diffraction (XRD), thermogravimetry (TG), and Fourier-transform infrared spectroscopy (FTIR). XRD analysis revealed the typical layered structure of the synthesized LDH with well-defined crystallites for both purely inorganic and 5-FU loaded LDHs. The intercalation of 5-FU into the LDH matrix was confirmed by FTIR and TG based on changes in the absorption spectra, and mass loss depending on the temperature, respectively.

To evaluate the drug delivery capacity, *in vitro* release studies were conducted using the dialysis bag method under experimental conditions simulating the physiological environment, e.g., pH 7.4, 37 °C, and mild agitation speed. The results demonstrated a gradual and controlled release of 5-FU from LDH, suggesting that these nanomaterials could be effectively utilized in targeted drug delivery for cancer therapy.

Further characterization of LDH included morphology and particle size analysis using scanning electron microscopy (SEM) and textural properties through nitrogen physisorption measurements. SEM images exhibited well-defined nanoparticles with a quite homogeneous size distribution and particles agglomeration depending on the conditions used for thermal treatment. N_2 physisorption analysis revealed a high specific surface area and adequate porosity for drug adsorption.

In conclusion, we successfully synthesized magnesium-aluminium LDH loaded with different amounts of 5-FU and controlled morphology. The physico-chemical characterizations confirmed their suitable structure and properties for controlled drug delivery which exhibit great potential for cancer treatment.

Acknowledgments

This work was supported by a H2020 grant – ERA-Chair, no 952390 and a grant of the Ministry of Education and Re-search, CNCS/CCCDI - UEFISCDI, project number PN-III-P3-3.6-H2020-2020-0105/35/2021



Delivery of novel photosensitizer by functionalized silk spheres to HER2overexpressing cancer cells

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Introduction: H2.1MS1 is a bioengineered spider silk functionalized with a human epidermal growth factor receptor 2 (HER2) binding peptide. Nanospheres made of H2.1MS1 silk are biocompatible and biodegradable, and can specifically deliver drugs to HER2-overexpressing cancer cells. Photodynamic therapy (PDT) is a clinically approved cancer treatment with high efficacy and minimal systemic adverse effects. Nevertheless, a photosensitizer (PS) should be specifically delivered to the cancer site prior to its photoactivation. H2.1MS1 spheres can be used for targeted delivery of PS to HER2-overexpressing cancer cells.

Objective: To develop a targeted delivery system for a novel photosensitizer based on bioengineered silk spheres functionalized with a HER2-binding peptide.

Methods: Functionalized spider silk was produced in E. *coli* strain BLR and purified using the thermal method. The H2.1MS1 spheres were formed using 0.5 mg/mL H2.1MS1 protein and 2 M potassium phosphate buffer in a micromixing device. The 100 μ g of spheres were loaded with 500 nM of metal-free porphyrins, PS3 or PS4 for 24 h by diffusion. PS3 and PS4 were spectrofluorometrically measured at λ_{em} of 665 nm. The ovary (SKOV3) and breast (MDA-MB-231) cancer cell lines were seeded at a density of 10,000 and 15,000 cells/well, respectively, cultured for 24 h, and then treated with 31.25, 62.5, 125, 250, 500, and 1000 nM of PS3 or PS4. After 24 h, the cells were irradiated with 2, 5, or 10 J/cm² or not-irradiated (control) using a lamp emitting light at 425 nm. After 24 h, the cell viability was measured using an MTT assay.

Results: H2.1MS1 silk was biotechnologically produced and purified. The morphology of H2.1MS1 spheres was spherical and their size was approximately 250 nm of a diameter. The nanoparticles were loaded with the metal-free porphyrins, PS3 and PS4, with yields of 289 and 412 nM, respectively. The PS3 and PS4 exhibited dose-dependent cytotoxicity after irradiation of 2 to 10 J/cm² in both SKOV3 and MDA-MB-231 cancer cell lines. The IC₅₀ of PS3 and PS4 at 10 J/cm² irradiation for SKOV3 cell line was 190 nM and 230 nM, respectively. Whilst IC₅₀ of PS3 at 10 J/cm² irradiation was 76 nM for MDA-MB-231 cell line. Importantly, both non-photoactivated PS3 and PS4 did not show cytotoxicity.

Conclusion: H2.1MS1 spheres were successfully loaded by both metal-free porphyrins, PS3 and PS4 at high concentrations. PS3 and PS4 exhibited promising toxicity after irradiation and when not-photoactivated were not toxic for both HER2-overexpressing (SKOV3) and control (MDA-MB-231) cancer cell lines. In further experiments, the cytotoxicity of PS3 and PS4 after loading into H2.1MS1 spheres will be tested and compared between HER2-overexpressing and control cancer cell lines.

Acknowledgments

The project was funded by National Science Centre, Poland, grant no. 2021/43/B/NZ7/02476.

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Star polymers complexed with miR 146a as a potential tool that regulates cardiomyocytes apoptosis after myocardial infarction

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Star polymers and copolymers with cationic charges can interact with negatively charged particles through electrostatic interactions. Among polymeric systems with carrying properties, dendrimers have the advantage of well-defined structure, size, stability, and biocompatibility. However, their application is limited due to their multistep synthesis, laborious purification, and thus their high preparation costs. Recently, due to the development of controlled radical polymerization [1], the preparation of a wide variety of complex macromolecular architectures is possible. The Atom Transfer Radical Polymerization (ATRP) [2] process, developed by Matyjaszewski, is the most effective and widely used method for controlled radical polymerization (CRP). In our studies star polymers complexed with miR 146a were used as a tool that may regulate cardiomyocyte apoptosis.

The star polymer having a cationic, degradable core for encapsulation and release of miRNA 146a, with a well-defined size (between 10 and 50 nm in diameter) was prepared by the ATRP method. The star polymer was complexed with micro RNA by incubation for 3h at RT. The efficiency of miR binding was assessed by gel electrophoresis. The uptake of nanoparticles and intracellular delivery of fluorescently labeled miR were assessed by confocal microscopy. Cytotoxicity and genotoxicity of star polymers (pure polymers and complexed with miR) toward cardiomyocytes were tested using WST-1 and comet assay, respectively. Flow cytometric analysis and staining of live cells with Mitosox revealed that cells incubated with star polymer did not enhance reactive oxygen species production.

In conclusion, star polymers complexed with miR 146a were not toxic to human cardiomyocytes. In the next step, functional assessment of their impact on hypoxia-induced cardiomyocytes should be investigated.

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The research is financially supported by the National Centre for Research and Development-DWM/WPC2/285/2020.

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A facile One-Pot Synthesis of Versatiles PEGylated Platinum Nanoflowers and Their Application in Radiation Therapy

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Nanomedicine has stepped into the spotlight of radiation therapy over the last two decades. Nanoparticles (NPs), especially metallic NPs, can potentiate radiotherapy by specific accumulation into tumors, thus enhancing the efficacy while alleviating the toxicity of radiotherapy. Water radiolysis is a simple, fast and environmentally-friendly method to prepare highly controllable metallic nanoparticles in large scale. In this -project we used this method to prepare biocompatible PEGylated platinum nanoflowers (Pt NFs). These nanoagents provide unique surface chemistry, which allows functionalization with various molecules such as fluorescent markers, drugs or radionuclides.

Epitope-mediated plastic antibodies for mass-based detection of pathogenic viruses

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The contamination of water resources with pathogenic viruses poses a large threat to health, especially in communities with limited resources. Rapid, cost-effective, and accurate biosensing platforms are needed for sensitive detection of viruses in point-of-care applications as the current gold-standard of virus monitoring methods are limited due to time-consuming, expensive, and laborious detection procedure. The majority of the biosensing platforms targeting viruses utilizes antibodies as receptors which are costly and prone to denaturation. On the other hand, plastic antibodies tailored for the analyte via molecular imprinting technology can be employed as recognition units in biosensors thanks to their specificity, selectivity, and high stability under various environmental conditions. Hepatitis A virus (HAV) is a waterborne human pathogenic virus causing liver inflammation [1]. Herein, we synthesized epitope-mediated polymeric nanoparticles (nanoMIPs) as plastic antibodies for specific detection of HAV using quartz crystal microbalance (QCM) sensor.

The template to be imprinted (i.e., epitope) was selected from the outer region of HAV capsid to ensure the accessibility during recognition. The epitope was imprinted using solid-phase synthesis method [2]. The nanoMIPs were immobilized on carboxyl functionalized quartz crystal microbalance (QCM) sensor using carbodiimide coupling chemistry (Figure 1). The nanoMIPs and the nanoMIPs-QCM sensor were characterized by dynamic light scattering and fluorescence microscopy respectively. The mass-sensitive detection of templated epitope was investigated for a concentration range of $10 - 1000 \,\mu$ M showing a detection limit of $10 \,\mu$ M. The HAV recognition was confirmed for a wide detection range of $0.00135 - 13.5 \,\text{IU} \,\text{mL}^{-1} \,\text{HAV}$. The selectivity of the sensor was confirmed with control assays employing nanoMIPs synthesized for another epitope of a different protein (i.e., cardiac Troponin I). Furthermore, the nanoMIP-QCM sensing platform exhibited low cross-reactivity against other pathogenic viruses.

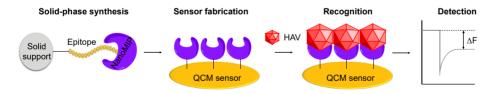


FIGURE 1. Synthesis of nanoMIPs and sensor fabrication steps.

Acknowledgments

This research was financially supported by the German Research Foundation (DFG) under the project number 428780268.

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Time- and dose-dependent digestive enzyme activity in *Acheta domesticus* after exposure to AgNPs or GO

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The dynamically developing nanotechnology provides many valuable solutions for industry and medicine. Still, at the same time, it creates a real problem of unintentional exposure of organisms from various ecosystems to nanoparticles [1]. Contamination of food with various nanoparticles can lead to impaired function of the digestive tract, affecting the availability of nutrients and the final condition of the organism.

The study aimed to investigate the activity of selected digestive enzymes in a model organism (*Acheta domesticus*) after exposure to silver nanoparticles (AgNPs) and graphene oxide (GO). Animals were exposed to AgNPs (4, 40, and 400 μ g/g of food) or GO (2, 20, and 200 μ g/g of food) throughout adulthood. The activity of selected enzymes (protease, amylase, α -glucosidase, β -galactosidase, and lipase) was measured in the first five days of exposure (to capture early compensatory changes and possible symptoms of hormesis) and on days 16 and 21 (in individuals with marked signs of aging).

The nanoparticles (AgNPs or GO) stimulated the activity of the part of tested enzymes. This effect was more pronounced in the case of amylase, lipase, and α -glucosidase. The stimulating impact in amylase and lipase was dose-dependent, being more intense as the dose increased. In general, AgNPs showed a more significant potential to alter the tested enzymes' activity. Both nanoparticle types inhibited protease activity and had no clear influence on β -glucosidase and β -galactosidase. Surprisingly, the effect of lipase and α -glucosidase stimulation was more visible in the old insects (at 16 and/or 21 days of exposure).

The obtained results clearly show that both types of nanoparticles modify the functions of the digestive tract in *A. domesticus*. The intensification of the activity of some enzymes is probably related to the attempt to obtain more energy needed to defend the organism. It should be remembered that animal digestive functions result from the gut activity and the microbiome inhabiting the gut. Thus, the influence of stress factors on microorganisms should also be considered [2]. Inhibition of protease activity, especially in aging specimens, indicates less importance of protein utilization at the end of life. This is consistent with the physiology of this species. However, the phenomenon is intensified in the groups exposed to nanoparticles. Generally, aging is associated with an altered physiological state, most likely accelerated by stress factors.

The impact of nanoparticles on digestive functions is associated with a potential disturbance in the amount of available energy for proper development, growth, and reproduction of an organism and a defense against stress. However, considering the results obtained, we can assume that the disturbances can be compensated to some extent, or even some hermetic mechanisms can be visible, improving individuals' survival odds.

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Study of the impact of protective creams containing physical (nano) filters and chemical (nano) filters on minimizing negative effects of the UV radiation using EPR spectroscopy

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There are many products on the market that are designed to protect the skin from the harmful effects of the UV radiation. We distinguish chemical and physical filters that differ in their properties and mode of action. In the description of creams, we can see the annotation of "nano", which tells us about the particle size of a given ingredient. Nano filters have become more and more common, and they bring many advantages as well as controversies.

Although the filters should prevent the negative effects of ultraviolet radiation, the nano form of some physical filters can cause the proliferation of free radicals. In addition, the size of the particles carries the risk of the substance entering the body and, as a consequence, undesirable interactions with the organs [1]. Nano substances are also used to reduce the negative effects and neutralize free radicals [2].

Electron paramagnetic resonance allows to examine the antioxidant properties of sunscreens, which are designed to protect the skin, e.g. from the photoaging process. The aim of the study is to compare the effect of a cream with a physical filter and a chemical filter on the formation of free radicals after exposure to UV radiation using the EPR method.

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Self-emulsifyng systems in antibiotics delivery

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Due to their stability, relative simplicity of composition and preparation method, the use of self-nanoemulsifying drug delivery systems (SNEDDS) is particularly promising for low soluble pharmaceuticals. However, it is necessary to use emulsifiers in these systems, increasing the stability of emulsions and ensuring a reduction in droplet size, which also means an increase in the mass exchange surface between the lipid and aqueous phase, and consequently more efficient drug release from the lipid phase. In the SNEDDS research, synthetic surfactants as well as plant oil derivatives such as monoglycerides have so far attracted the main attention. In the light of these facts, there is a question about the use of other surfactants for the drug-loaded nanoemulsions. These compounds should be both effective emulsifiers and exhibit bioactivity. These expectations are met by saponins, natural surfactants of plant origin.

The aim of the research was to investigate the impact of saponins, on physical properties of SNEDDS containing antibiotics. The research involved optimizing the composition of SNEDDS, based on measurements of the size distribution of emulsion particles and their zeta potential. The effect of the addition of saponins on in vitro lipolysis and on the biocidal properties of the emulsions was also studied. The realized research made it possible to conclude that emulsions containing digitonin among the saponins had the most favorable physicochemical properties. For further studies, SNEDDS compositions were used, in which the content of the drug and digitonin was 5% (w/w). Moreover, it was found that the addition of digitonin accelerated the process of lipolysis compared to SNEDDS containing no added saponins. Studies with *Candida albicans* and *Candida krusei* strains showed that the introduction of klimbazole into the emulsion system of SNEDDS preserves its biocidal properties (compared to samples where the drug was administered directly into solution). The collected data allow us to expect that saponins will find application in emulsion delivery systems for these drugs, where rapid release of the drug from the lipid phase into the surrounding continuous-aqueous phase is important.

Acknowledgments

The research was supporter by Ministry of Education and Science (Poland). Wojciech Smułek was a recipient of the Mieczysław Bekker Program funded by the National Agency for Academic Exchange (Poland).

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In vitro Drug Release Evaluation of Fluorouracil - MgAl Layered Double Hydroxides Nanohybrids on Glioblastoma Model Systems

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Glioblastoma (GBM) is a highly heterogeneous primary tumor with an almost organ-like structure spread through a high proportion of the brain [1]. Currently, treatment for GBM involves maximal resection followed by radiotherapy and/or chemotherapy, but this therapeutic protocol has an extremely low efficiency due to tumor cells survival to initial therapies, resulting in tumor regrowth/recurrence [2]. In the recent years, nanodrugs have been becoming a promising area of drug development for invasive tumor such as GBM [3]. Herein, GBM susceptibility to fluorouracil (FU) loaded MgAl layered double hydroxide (LDH) nanostructures with different morpho-structural properties is investigated. Free and FU-loaded LDH with Mg/Al molar ratio of 2 were synthesized by coprecipitation at low supersaturation followed by hydrothermal treatment. To control the properties, particularly the crystallites' size and the amount of the drug in the samples, the temperature and time were adjusted. The main physico-chemical properties of LDHs (composition, structure, texture, hydrodynamic diameter and surface charge) were evaluated by corresponding techniques. The ability to release the drug, the cytotoxic properties and the probable mechanism, particularly ROS production, were assessed on two GBM cell lines, that is, U87 and T98G, which exhibit different genetic alterations and morphologies. In addition, modulation of the cellular response to the administrated FU - MgAl LDHs can be observed. T98G cells were grown in EMEM medium and U87 cells were grown in RPMI-1640 medium, both media being supplemented with 10% FBS and 1% PS. Twentyfour hours post seeding, the cells were exposed to FU – MgAl LDHs (100µg/ml and 300µg/ml) for different intervals of times $(2 \rightarrow 72 \text{ h})$. Cellular viability and intracellular level of ROS were determined using specific assays. The nanodrugs, showing very good physico-chemical properties, significantly impaired viability of GBM cells, greater effects being observed on U87 cell line. However, FU – MgAl LDHs did not influenced intracellular levels of ROS in a relevant manner.

Acknowledgments:

This work was supported by a H2020 grant – ERA-Chair, no 952390 and a grant of the Ministry of Education and Re-search, CNCS/CCCDI - UEFISCDI, project number PN-III-P3-3.6-H2020-2020-0105/35/2021.

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Methacrylic bone cements modified with CAPTISOL-Eugenol complex

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Bone cements are biomaterials designed to stabilize complex fractures, as well as fix implants. Among the many materials used in orthopedics, methacrylic cements are widely used. These materials are two-component systems (powder phase and liquid phase) based on poly(methyl methacrylate), which are cured *in vivo* by polymerization reaction. The incorporation of an endoprosthesis or bone cement during surgery may cause infection, therefore bone cements are modified with the addition of an antibiotic [1]. Nowadays, however, unconventional antibacterial agents are sought, which is why in this research eugenol is used. Essential oils, among them eugenol, are safer and more reliable than synthetic drugs [2]. Eugenol is hydrophobic and not soluble in water, thus to change that, it was encapsulated with Cyclodextrin-Captisol® [3].

The aim of this work was to obtain Captisol®-Eugenol (CP-EU) complex, its incorporation into bone cement and investigation the properties of the obtained materials: doughing time, maximum temperature, setting time and compressive strength as well as the release of eugenol from modified bone cements. Moreover, the course of the polymerization (rate of polymerization and degree of double bond conversion) was investigated. Bone cements were prepared by mixing powder phase composed of two methacrylic co-polymers, Captisol®-Eugenol complex (CP-EU) and initiator (benzoil peroxide). The liquid phase was prepared by mixing 2-hydroxyethyl methacrylate, methyl methacrylate and triethylene glycol dimethacrylate with co-initiator (N,N-dimethylaniline).

Modification of methacrylate bone cement with CP-EU complex significantly influenced its properties. An increase in compressive strength was observed, with Young's modulus approaching that of commercial bone cement when the compressive strength was even higher. Moreover, a decrease in the maximum curing temperature, as well as a high level of release of eugenol, was obtained.

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The study was funded by the Ministry of Education and Science - 0912/SBAD/2303

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In vitro efficiency of appoferritin-based transport nanocarriers for drug delivery application to leukemic cells

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To achieve the most effective therapeutic results in the treatment of tumor diseases, the selective delivery of drug compounds into the cell seems to be relevant, which makes it possible to reduce the risks of mortality during therapy. There is a growing interest in the development of efficient and selective drug delivery systems (DDS) based on various nanocarriers. In recent years, protein cages (hollow protein nanoparticles) have been taking center stage as DDS into tumor cells. Ferritins are a classic type of such protein nanoparticles due to good biodegradability, ability to accumulate in highly vascularized tumors, and internalization by tumor cells through transferrin receptor 1.

The purpose of current work was to evaluate the redox state (a test for determining the content of low molecular weight antioxidants, LMWA) and the physical state of the lipid bilayer of B- and T-lymphoblastic human blood cells (cell lines IM-9 and MOLT-4, respectively) during their incubation with chemotherapy drugs that used in leukemia treatment (vincristine (Vincr) and dexamethasone (Dex)), and synthesized nanosystems based on appoferritin (a form of ferritin without iron) with Vincr (Apf-Vincr) and Dex (Apf-Dex) encapsulated inside.

It was shown that Vincr and Dex at concentrations close to therapeutic after incubation with human leukemic cells during 24 h shifted the cellular redox balance towards prooxidants, at the same time, the effect of Apf-Dex and Apf-Vincr also led to a decrease in LMWA cytosol level, but in lesser degree than under pure Vincr and Dex action. It should be noted that Apf-Vincr and Apf-Dex nanocages practically did not affect to the membrane lipid bilayer microviscosity during incubation, while the use of pure Vincr and Dex changed its fluidity. Moreover, it was found that the percent of died cells IM-9 and MOLT-4 after 48 h incubation with Vincr and Dex was more compared to the effect of transport systems Apf-Vincr and Apf-Dex on cellular viability.

Thus, synthesized nanosystems based on appoferritin has good loading efficiency and controlled drug release properties.

Acknowledgments

The work was supported by NCN the OPUS grant 2020/37/B/ST5/00576 and the SCST international grant M21ARMG-003 (2021–2023).



Preparation and Validation of Photo-curable Resin-Based Composite with Active Pharmaceutical Ingredient

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Active pharmaceutical ingredient (API) based composites are used for such purposes as drug delivery, tissue engineering, wounds healing [1] and more. One of the modern methods of obtaining such composites is a 3D printing method - digital light processing (DLP) classified as an additive method using UV radiation projected with use of digital micromirror device (DMD). Properly selected printing parameters allow to produce samples with a resolution of several tens of µm. In the DLP process, liquid resins are used, making it possible to obtain printed composite materials by adding filler directly to the liquid resin. Conventional photocurable resins are insoluble in water and do not degrade upon contact with the human body, making it necessary for them to be able to migrate the API in the resin structure and release it. However, it is important to ensure safe conditions for the active pharmaceutical ingredient by avoiding phase transformations associated with, for example, changes in temperature or preventing chemical reactions with the components of the resin during the composites obtaining process. In addition, the selected constituents of the composite have to be compatible enough to provide the desired physical and chemical properties and, at the same time, have an affinity for each other at a low level that allows the release of the drug from the matrix. The study conducted focused on composites made of acrylic resin with a pharmaceutically active ingredient in the form of caffeine. The composites were tested to examine properties such as surface energy, tensile strength and Young's modulus in order to evaluate the effect of caffeine on resin properties. Nano-scale tests were also performed on the hardness and Young's modulus, which were obtained in the nanoindentation tests. The results present the potential of the applied DLP method for manufacturing biocomposites containing API due to the properties of the obtained composites comparable or better to the samples made of pure resin.

Acknowledgments

The work was performed as a result of the research project no. 2021/42/E/NZ7/00125 (ID: 526262) financed by the National Science Centre (Poland).

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Antimicrobial activity assessment of silver nanoparticles synthesized by the microbiological method

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Silver nanoparticles are one of the most exploited nanomaterials. Due to the specific qualities and proven antimicrobial potential, they can be employed in medicine and various industries, e.g. pharmaceutical, textile, chemical or cosmetics. There are three routes of silver nanoparticles synthesis: chemical, physical and biological. Among them, the biological method seems to be the most beneficial. The lack of the hazardous chemicals use, no toxic waste generation and considerable cost-effectiveness cause that this ecoffriendly method is continuously being improved. Biosynthesis of silver nanoparticles can be performed with the use of different organisms or products of their metabolism. Because of the fast growth rate, ease of cultivation and variety of produced compounds, filamentous fungi have arisen as the most appropriate choice for the silver nanoparticle synthesis on a big scale ^[1].

The aim of this study was to evaluate the antimicrobial activity of silver nanoparticles synthesized by the microbiological method using two soil filamentous fungi strains.

The first stage of the study was to isolate filamentous fungi strains capable of silver nanoparticles synthesis from a soil sample. Then, silver nanoparticle synthesis was performed with the use of two selected strains that occurred to be the most effective. After the synthesis, the antimicrobial activity of the obtained nanoparticles was tested against common human pathogens: bacterial strains *Escherichia coli* ATCC 25922, *Staphylococcus aureus* ATCC 29213, *Pseudomonas aeruginosa* ATCC 27853 and *Streptococcus pyogenes* ATCC 19615. The microdilution method according to M07 CLSI norms was used and the tested silver nanoparticles concentration ranged from 0,098 to 100 µg/ml.

The conducted study proved that filamentous fungi capable of effective silver nanoparticle synthesis are possible to find in the environmental samples. Moreover, the antimicrobial potential of newly synthesized silver nanoparticles was confirmed. The *Pseudomonas aeruginosa* strain was found to be the most vulnerable to the action of both types of synthesised silver nanoparticles among the tested bacterial strains. Here, the bacterial growth was completely inhibited in the AgNPs concentration of 1,56 µg/ml. The least vulnerable strain was *Staphylococcus aureus* with the minimal inhibitory concentration of 6,25 µg/ml for both AgNPs types.

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Nanotechnology in chrysanthemum breeding – evaluation of the biochemical, genetic, and phenotype variation of shoots regenerated from leaf explants treated with silver nanoparticles

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Despite many perspectives and benefits arising from the enormous progress in nanotechnology development, nanomaterials at higher concentrations may also have unexpected effects on plants that have not yet been sufficiently explored during the implementation of innovative agronanotechnologies in crop improvement. Therefore, the study aimed to test the applicability of silver nanoparticles (AgNPs) in chrysanthemum breeding. The research hypothesis assumed that AgNPs, as a chemical mutagen added onto the micropropagation medium, can cause changes at the molecular level in the explant cells, and the emerging variation may be useful in chrysanthemum breeding.

Chrysanthemum × *morifloium* (Ramat.) Hemsl. 'Lilac Wonder' and 'Richmond' leaf explants were cultured on the MS medium with 0.6 mg·L⁻¹ 6-benzylaminopurine (BAP) and 2 mg·L⁻¹ indole-3-acetic acid (IAA) and treated with AgNPs at the concentration of 50, and 100 mg·L⁻¹. AgNPs were produced by the seeded-mediated growth method (Nanoparticles Innovation NPIN s.c., Łódź, Poland). The size and size distribution measured by STEM (Nova NanoSEM 450, FEITM, Hillsboro, OR, USA), were 20 ± 3 nm. The biochemical response of leaf explants during three successive weeks of *in vitro* culture was analyzed. The effectiveness of adventitious organogenesis was evaluated after 10 weeks. Produced shoots were rooted *in vitro*, acclimatized and cultivated *ex vitro* in glasshouse. At the full flowering stage chrysanthemums were subjected to phenotype verification. The genotype stability was evaluated using genetic marker systems: randomly amplified polymorphic DNA (RAPD) and start codon targeted polymorphism (SCoT).

AgNPs strongly suppressed the ability of leaf explants to form adventitious shoots and the efficiency of regeneration. The content of metabolites (chlorophyll *a*, chlorophyll *b*, total chlorophylls, carotenoids, anthocyanins, phenolic compounds), and the activity of enzymatic antioxidants (superoxide dismutase and guaiacol peroxide) in leaf explants, varied depending on the AgNPs treatment and age of culture. Phenotype variations of *ex vitro* cultivated chrysanthemums, covering the color and pigment content in the inflorescence, were detected in one 50 mg·L⁻¹ AgNPs-derived and five 100 mg·L⁻¹ AgNPs-derived 'Lilac Wonder' plants, and were manifested as the color change from pink to burgundy-gold. Stem height, number of leaves, and chlorophyll content in leaves varied depending on the AgNPs treatment and the cultivar analyzed. A significant influence of AgNPs on the genetic variation occurrence during adventitious organogenesis from leaf explants in chrysanthemum was proved.

Concluding, protocols using leaf explant treatment with AgNPs can be used as a novel breeding technique in chrysanthemum. However, the individual cultivars may differ in biochemical response, the efficiency of *in vitro* regeneration, genetic variation, and frequency of induced mutations in flowering plants.

Acknowledgments

This research was funded by The National Science Centre (NCN) in Poland, project "Studies on the use of silver nanoparticles in chrysanthemum breeding", founding MINIATURA 4, no. DEC-2020/04/X/NZ9/01667 (2020-12-12 – 2021-12-11).

Protein engineering using nanostructured solvents envisaging improved performance under oxidative stress and enhanced plant protection

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Considering the hydrotropism and probability of nano-structuring (Fig. 1a), we aim towards studying the effect of nanostructured hydrotropes (ATP and choline salicylate ionic liquid) towards activity and stability of cytochrome c in the habitual and oxidative stress condition to develop a novel and sustainable solvent manipulation strategy for robust protein packaging. The activity of bare Cyt c after the H_2O_2 induced oxidative stress found to be only $\sim 60\%$ of its original activity, whereas in presence of ATP $\sim 219\%$ activity was retained (Fig. 1b). This observation can be correlated with the earlier findings where ATP was found to prevent the oxidation of Cyt c from Cyt c oxidase enzyme in the mitochondria but by hampering the electron flow rate [1]. On the other hand, there was a severe drop in the activity of Cyt c from 6700% to just 80% in presence of IL. This results in not astonishing since salicylate counterpart is known to enhance the formation rate of reactive oxygen species (ROS) [2]. However, presence of ATP is found to prevent the oxidation and Cyt c from IL induced oxidative stress and showed 192% relative activity. These findings clearly demonstrate the stabilizing effect of nanostructured ATP against salicylate induced oxidative damage. This mechanism was further checked in vivo using tobacco BY2 cells and found that the plant cell death promoted by salicylate induced ROS production was significantly reduced by exogenous application of ATP as analyzed by cell viability assay and ROS estimation.

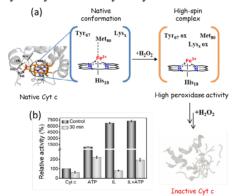


FIGURE 1. (a) Cytochrome c caged in ATP and ionic liquid-based nanostructured solvent. (b) Effect of nanostructured hydrotropes on the activity of cytochrome c under oxidation stress.

Acknowledgments

This work was supported by the NANOPLANT project, which received funding from the European Union's Horizon 2020 research and innovation program under grant agreement no. 856961.

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The application of Cu-MOF nanoparticles as immunomodulatory agent carriers for SARS-CoV-2 inhibition

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There is a growing demand for developing new antiviral therapies. Nowadays, many nanomaterial-based antiviral treatments are under investigation that can act directly on virus infection, increase the efficiency of antiviral drugs, and/or trigger the patient's immune response [1]. Due to special properties (porosity, modular structure, possibility of surface biofunctionalisation and biocompatibility) metal–organic frameworks (MOFs) has a great potential in antiviral therapies.

In this study, Cu-MOF nanoparticles were used as delivery systems for antiviral and immunomodulatory agent, hydroxychloroquine (HCQ). The molecular antiviral mechanism of HCQ is based on blocking the fusion between virus and host cells (virus entry is the first step of virus infection) [2]. In this work, we evaluated the effect of Cu-MOF and Cu-MOF/HCQ on SARS-CoV-2 infectivity. Moreover, we studied the effect of HCQ-loaded nanocarriers on the interaction between SARS-CoV-2 Spike (S) protein and ACE2 (human angiotensin converting enzyme 2) receptor.

Our findings demonstrate that Cu-MOF nanoparticles loaded with HCQ significantly reduced the infectivity of SARS-CoV-2, which can be attributed to the nanometric size of the carriers, the presence of copper in the MOF nodes, and the semi-controlled release of the drug (Fig.1). The proposed mechanism of antiviral action of Cu-MOF carriers loaded with HCQ is presented on scheme:

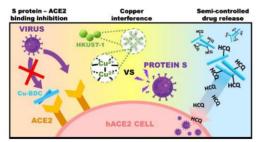


FIGURE 1. The proposed mechanism of antiviral action of Cu-MOF carriers loaded with HCQ

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