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# BOOK OF ABSTRACTS 2024

5<sup>TH</sup> – 7<sup>TH</sup> June 2024 POZNAŃ – POLAND

> NanoBioMedical Centre



# BOOK OF ABSTRACTS 2024

5<sup>TH</sup> – 7<sup>TH</sup> JUNE 2024 POZNAŃ, POLAND



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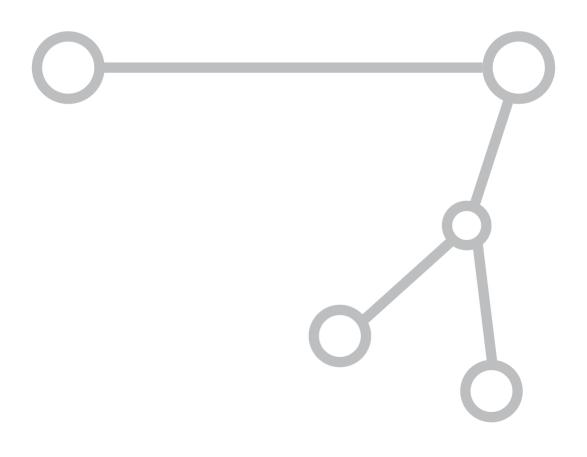
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# **PLENARY LECTURES**





#### Recent Advances and Emerging Applications of Atomic Layer Deposition (ALD) on High-Aspect Ratio Materials

#### Mikhael Bechelany

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Atomic Layer Deposition (ALD) is a cutting-edge technology that enables the fabrication of thin films using high-quality materials on substrates with high aspect ratios. This method offers precise control over thickness, uniformity, and excellent conformality, making it particularly suitable for modifying the structure and customizing the pores of highly porous materials like synthetic membranes. ALD coatings have been successfully applied across a wide range of membrane substrates, from inorganic templated supports to porous polymers.

This presentation aims to offer a comprehensive overview of the progress made in employing ALD on highly porous materials, particularly those utilized in membrane technology. By drawing upon a carefully selected collection of our research endeavors, we will showcase how ALD can effectively improve the operational efficiency of various membrane types, including inorganic, organic, hybrid, or composite membranes. Through examples, we will highlight the significant role of ALD in designing membranes with precisely adjustable geometries, facilitating systematic exploration of the relationship between physical-chemical properties and geometric parameters. This approach allows for thorough investigations into membrane performance across diverse applications such as renewable energy, including gas separation and osmotic energy harvesting, as well as environmental applications like water treatment and sensor technologies.

Moreover, we will address the challenges and opportunities associated with integrating ALD into membrane applications. This presentation aims to provide a comprehensive overview of the advantages of ALD and its applications across various aspects of membranes and related engineering processes. It seeks to illuminate the numerous opportunities within this emerging and rapidly advancing field.

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# DNA-engineered nanophotonics

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To sustain cellular functions, a cell needs to transport a variety of cargos within the complex intracellular milieu. This task is mainly carried out by molecular motors that move along filament tracks. Despite the grand challenges to fully understand how cells exactly manage to execute all their intelligent functions, construction of artificial nanosystems by taking inspiration from the working principles that cellular components follow, is undoubtedly an intellectually efficient approach.

In this talk, we will show several types of bio-inspired optical nanosystems, which can perform rotation, twisting, or swinging motions enabled by dynamic DNA nanotechnology. Our approach outlines a general scheme to build dynamic plasmonic nanoarchitectures, in which multiple optical elements can be readily reconfigured or transported to designated locations over long distances, resulting in programmed structural changes with high fidelity. Such plasmonic structures can find useful applications in different fields, ranging from optical sensing to data storage. In particular, the possibility to translocate optical elements in multiple configurations can be used to explore new approaches to encode information at high density.



FIGURE 1. DNA-assembled optical devices that exhibit multi-motions.



#### Sustainable nanobiosensors for diagnostics

#### Arben Merkoçi

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The development of sustainable point-of-care devices is one of the most important R&D in the area of health diagnostics in addition to environment monitoring and other fields. There is a high demand to develop innovative and cost-effective devices with interest for health care. The development of such sustainable devices is strongly related to new materials and technologies being nanomaterials and nanotechnology of special role. These devices should be REASSURED: Real-time connectivity, Ease of specimen collection, Affordable, Sensitive, Specific, User-friendly, Rapid, Robust, Equipment-free, Delivered to those who need it. How to design simple plastic/paper-based biosensor architectures including wearables through printing or stamping? How to tune their analytical performance upon demand? How one can couple nanomaterials with paper/plastics and what is the benefit? What are the perspectives to link these simple platforms and detection technologies with mobile communication? I will try to give responses to these questions through various interesting with extreme interest for clinical emergency applications that include detection of proteins, cancer cells, viruses and other important biomarkers. These devices and corresponding technologies are related to ubiquitous methods that would be quite important for democratising diagnosis and improving healthcare coverage.

#### Multifunctional materials for emerging technologies

#### Federico Rosei

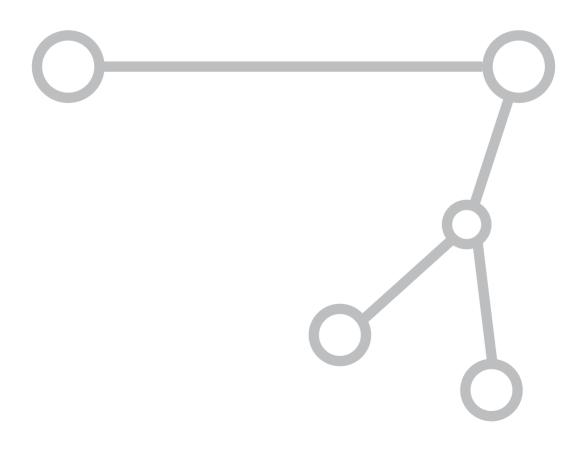
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This presentation focuses on structure-property/relationships in advanced materials, emphasizing multifunctional systems that exhibit multiple functionalities. Such systems are then used as building blocks for the fabrication of various emerging technologies. In particular, nanostructured materials synthesized via the bottom–up approach present an opportunity for future generation low-cost manufacturing of devices. We focus in particular on recent developments in solar technologies that aim to address the energy challenge, including third-generation photovoltaics, solar hydrogen production, luminescent solar concentrators, and other optoelectronic devices. [1-18].

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# **SPONSOR WORKSHOPS**



Sponsor workshops

#### Practical aspects of nanoparticle analysis using Muliquadrupole ICP-MS in single particle (SP-ICP-MS) Mode

#### Magdalena Muszyńska

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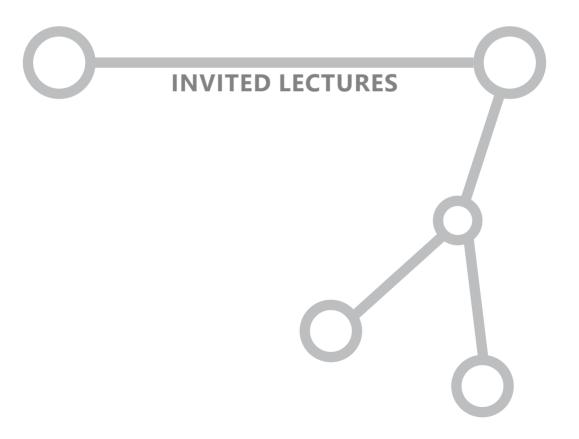
Nanoparticles (NPs) are, by definition, objects whose all three dimensions are in the range of 1 - 100 nm. Anthropogenic nanoparticles, intentionally produced by humans to obtain precisely defined properties, are called engineered nanoparticles (ENPs). Among them, nanoparticles of metals and their oxides occupy a special place.

The physical and chemical properties of nanoparticles make them materials that are becoming increasingly widely used, among others: in medicine, agriculture, transport, industry, electronics and cosmetics production, environmental protection, and chemical analysis.

Single nanoparticle inductively coupled plasma mass spectrometry (SP-ICP-MS) is a promising technique for nanoparticle analysis. It allows you to obtain quantitative information on the number, size, and size distribution of nanoparticles and the concentration of the ionic form of the tested element in the solution. The technique is distinguished by the ability to conduct analyses of nanoparticle concentrations corresponding to the concentration observed in the environment.

During the workshops, practical aspects of analyzing metal nanoparticles in the SP-ICP-MS mode using the NexION 5000 instrument with Syngistix Nano software will be presented.

# SECTION A ADVANCED NANOMATERIALS



#### Beyond the Bulk: Delving into Sub-Nanoscale Oxide Unicity

#### Alessandro Baraldi

#### Physics Department, University of Trieste, Italy

When we venture into the sub-nanoscale, we encounter a realm where novel physical and chemical properties emerge. Atomic nanoclusters serve as a compelling illustration of this phenomenon, as even the addition or removal of a single atom can induce remarkable modifications in their properties. Nanoclusters offer an unparalleled platform for exploring the uncharted territory of matter, with implications spanning diverse fields within materials science.

In our pursuit, we harness the power of the Exact Number of Atoms in each Cluster (ENAC) source, in tandem with the x-ray radiation generated by Elettra synchrotron. Supported by state-of-the-art density functional theory calculations, we delve into the intricacies of the oxidation process at the sub-nanoscale. What unfolds before us is a captivating panorama, revealing that the properties observed in bulk and surface oxides do not seamlessly translate to the nanoscale domain.

This exploration opens doors to a fascinating world, challenging conventional notions and paving the way for groundbreaking insights into nanoscale phenomena. By unraveling the unicity of oxidation processes at this scale, we aim to illuminate pathways for the design and development of tailored nanomaterials with enhanced functionalities.

#### Ferroelectric hafnia: an opportunity for next-gen memory devices

#### Ignasi Fina

#### Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus UAB, Bellaterra, Barcelona 08193, Spain

New paradigms in the development of new computing architectures require new devices based on different materials. During the last years there is a renaissance on the interest of the scientific community and industry on the use of ferroelectric materials for memory applications. The reason has been the discovery of ferroelectricity in a simple binary oxide fully CMOS compatible, i.e. doped HfO<sub>2</sub>. Most of the work related to ferroelectric hafnia is based on the characterization of polycrystalline samples, because these are not demanding in terms of growth. However, the understanding of the functional properties of polycrystalline films is challenged by the presence of multiple phases/orientations and blurry interfaces. In this regard, epitaxial films are an excellent platform for better understanding [1]. Epitaxial films present several interesting properties, as their atomically-flat surface, the absence of wake-up effect and the large polarization/endurance of ultrathin samples. I will show some interesting recent results related to the characterization of epitaxial ferroelectric hafnia films. These results are related to the obtention of record endurance values (up to  $10^{10}$  cycles) [2], and the proposal of novel HfO<sub>2</sub>-based light [3] and magnetic field [4] responsive memory devices. In brief, I will revise the multiple positive implications of the use of epitaxial ferroelectric hafnia films as a platform for the understating of different enhanced functionalities and for reimaging new electronic devices.

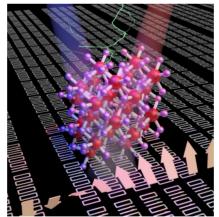


FIGURE 1. Schematics of light assited ferroelectric memory based on HfO2.

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#### **Tetrapods based Smart Materials for Advanced Technologies**

#### Elham Chamanehpour, F. Mirsafi, Sandeep Thouti, Mustafa Ismael, Yogendra Kumar Mishra

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Considering the size-dependent utilization complexities of nanoscopic dimensions tin real technologies, the focus of nanomaterials community is converging to three-dimensional (3D) nanomaterials which are built out of interconnected nanostructures building blocks. This talk will briefly introduce the importance of tetrapod nanostructures towards smart 3D nanostructuring via a simple and single step flame-based approach for synthesis of zinc oxide tetrapods. These tetrapods have already demonstrated their potential roles in many different technologies. These zinc oxide tetrapods can be used as solid backbone or sacrificial templates to design hybrid or new tetrapods as smart materials. These smart 3D nanomaterials offer many applications in engineering and advanced technologies. Application examples of 3D tetrapods in nanosensing, composite engineering, antiviral candidates, water purification, piezotronics, and in several other applications will be demonstrated [1-10]. The integration of tetrapods in electrospun fibers offer many advantages in biomedical engineering and few examples about nano-engineered electrospun fibers will be presented as recent developments.

Keywords: Smart Materials, Tetrapods, Hybrid Nanomaterials, Advanced Technologies

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#### Friction at the nanoscale: Experiments and simulations

#### Arkadiusz Ptak, Marek Weiss, Łukasz Majchrzycki and Dominik Florjan

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Understanding friction at various scales can lead to significant reductions in energy consumption and material degradation, benefiting industries ranging from automotive to micro-electromechanical systems (MEMS). At the nanoscale, tribological research becomes even more critical as devices continue to miniaturize, and new effects begin to dominate, where traditional macroscopic theories no longer apply. For example, numerous theoretical as well as experimental studies show different relationships of the kinetic friction force on the sliding velocity depending on the interacting materials, load, or velocity range.

In our work, we present a methodology for friction data analysis and interpretation to understand these complex and often unclear relationships [1]. The results of our measurements of the friction force versus the sliding velocity for different loads have been transformed into a dependence on a single comprehensive parameter (P), the core of which is the ratio of the sliding velocity to the load. This facilitated the analysis and ordering of the results of our and others authors, often seemingly contradictory, and made it possible to propose a uniform interpretative framework for a wide range of parameter P. As a result, we assigned to individual P ranges dominant friction mechanisms such as stick slip effect, mixed, sliding and adhesive friction (Figure 1).

To extend the range of sliding velocities beyond the limit of the atomic force microscopy experiments and to gain insight into the molecular details of the friction process, we performed molecular dynamics simulations for the model systems imitating the experimental ones.

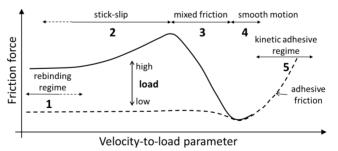


FIGURE 1. Schematic representation of the dependence of the friction force on the velocity-to-load parameter recorded in the experiments for high loads (solid curve) and near-zero loads (dashed curve) [1].

#### Acknowledgments

This work was supported by the National Science Centre in Poland under Project No. 2020/37/B/ST8/02023 (OPUS-19).

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#### Magnetic fluids in liquid-immersed transformers

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The growing demand for electric energy poses evolving challenges for energy transmission system. One of the key elements in the transmission system is a power transformer. Its reliability, efficiency and protection depend on effective cooling and insulating media. The cooling and insulating liquids like transformer oils play a significant role in maintaining the performance of transformers. To cope with the challenges in the energy transmission and to enhance both dielectric and thermal properties of liquids, various nanoparticles can be dispersed in the liquids resulting in effective nanofluids [1].

In this paper, a new generation transformer oil based on a gas-to-liquid technology has been used to prepare magnetic fluids with ferrite nanoparticles and a hybrid nanofluid with fullerene C<sub>60</sub> and ferrite nanoparticles, so-called C<sub>60</sub>-loaded ferrofluid. Magnetic, thermal and dielectric properties of the magnetic fluids have been investigated experimentally. Finally, the nanofluids were applied in a single-phase model transformer with a nominal power of 5 kVA, and temperature rise tests of the loaded transformer were conducted. We have demonstrated that a low-concentrated magnetic fluid significantly reduces the transformer temperature rise as compared with the cooling effect of pure transformer oil. The enhanced cooling performance is ascribed to the combination of effective thermomagnetic and natural convection and increased thermal conductivity. On the other hand, the application of a magnetic fluid with a high nanoparticle concentration resulted in a remarkable increase of the transformer temperature rise. The deteriorative cooling effect is attributed to the hindered natural and thermomagnetic convection due to the high ferrofluid magnetization and strong magnetic interactions of the ferrofluid with the magnetic field near the transformer core and winding. A significant decrease in the transformer temperature rise up to 5 K has been found for C<sub>60</sub>-loaded ferrofluid, as compared with the temperature rise achieved with the transformer oil. The mono-nanofluid with  $C_{60}$  nanoparticles provided even greater reduction of the temperature rise (up to 8 K).

#### Acknowledgments

This research was funded by Slovak Research and Development Agency under contract No. APVV-22-0115, APVV-18-0160 and Slovak Academy of Sciences and Ministry of Education in the framework of project VEGA 2/0011/20, 2/0029/24.

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#### Laser beam as a tool for the reshaping of nanomaterials

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Light is not only the source of renewable energy for electricity generation and essential source of warmth and energy for living organisms. An intense, coherent and monochromatic light commonly known as a laser can be used also as a powerful tool not only present in measuring equipment, for example Raman spectrometer, but also for the manipulation in the structure and morphology of nanomaterials.

Typically to change nanomaterials properties the most of undertaken efforts are based on the wet chemistry synthesis techniques, electrochemical deposition, chemical vapour or atomic layer deposition techniques. However, sometimes high precision requires advanced equipment or a lot of not environmentally friendly byproducts arise.

As an alternative, rapid and easily scalable method the direct laser interaction with the nanomaterial is proposed. The usage of pulsed Nd:YAG laser operating at different wavelengths: 266, 355 and 532 nm with optimized fluence and scanning speed brings a variety of options. The controlled movement of the sample enables modification within the selected area that is crucial for electrochemical/photoelectrochemical application when only part of the electrode material will have contact with the electrolyte or be exposed to the light source. Among others, laser can be used for the formation of the gold nanoparticles out of the gold thin layer, encapsulation of titania nanotubes with the initially open mouths [1] or titania phase transition from the amorphous to the crystalline one [2]. Apart from the treatment of nanomaterials in the form of layers on the stable, flat substrate, laser beam can interact with material suspended in the liquid medium or pellet of frozen compound. Due to the lightmatter interaction, light can be absorbed by the material and as an effect, one can observe its fragmentation or the reshaping. Even the layered structure of transition metal carbide (MXene) can be transformed into the spherical nanoparticles while dopamine can be graphitized [2]. It will be shown that without introduction of any foreign chemical compounds, the significant changes of electrochemical performance can be achieved in a very short time and a high degree of spatial ordering of formed nanostructures can be ensured that makes laser beam a very useful tool for the precise manipulation in the nanoscale.

#### Acknowledgement

Presented results were financially supported by the National Science Centre (Poland) via CEUS-UNISONO grant no.: 2020/02/Y/ST8/00030

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#### Controlling movement with light: new materials for soft robotics.

#### Anne Staubitz

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Organic photoswitches change their geometry upon switching. This change is extremely relevant when it comes to translating the photochemically induced movement into a movement that is observable on the macroscopic scale (photomechanical effect).[1]

In this presentation, photomechanical films based on switchable liquid crystalline elastomers will be presented.[2] A potential application in biomimetic adhesives[3] will be shown as well as considerations of how such films can be safely integrated into soft robotics: In the context of interactions with living organisms, UV radiation is dangerous and should be replaced by visible light. However, chemically, this presents its own challenges, which will be discussed.[4]

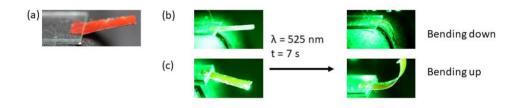


FIGURE 1. A photomechanical liquid crystalline elastomer.

#### Acknowledgments

This research was funded by the GERMAN RESEARCH FOUNDATION(DFG) within the priority program SPP 2100 "Soft Material Robotic Sys-tems", Subproject STA1195/5-1, "Insect feet inspired concepts soft touchgrippers with dynamically adjustable grip strength".

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# SECTION A ADVANCED NANOMATERIALS





#### Synthesis and characterization of functional silsesquioxanes

<u>Adrian Franczyk<sup>\*,a</sup></u>, Kinga Stefanowska-Kątna<sup>a</sup>, Joanna Wojtukiewicz<sup>a,b</sup>, Patrycja Kubiak<sup>a,b</sup>

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Silsesquioxanes are commercially available compounds that thanks to unique threedimensional, cubic, nanometric structure, physicochemical, and biological properties, and the possibility for their functionalization are of great interest to researchers from academia and industry. This is highlighted by the huge number of scientific and patent publications that describe them as reactive platforms for the synthesis of multifunctional, hybrid (inorganicorganic) molecules and macromolecules that have been applied in many different fields (coating materials, electrolytes, lithography, optoelectronic materials, Janus particles, anticancer drug carriers, dental materials, dyes, etc.).<sup>1</sup>

In this communication, we present our research on synthesizing mono-, tri-, and octafunctional silsesquioxanes *via* catalytic hydrosilylation of alkenes, alkynes, and 1,3-diynes. As a result, new compounds with various structures and functionalities were obtained. The physicochemical properties of molecular silsesquioxanes will be discussed and for selected examples, their application in the synthesis of hybrid polymers (linear and starshaped) by atom transfer radical polymerization (ATRP) and free radical polymerization (FRP) will be shown.<sup>2</sup>

#### Acknowledgments

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#### Effect of silver shell thickness on conductivity of coatings based on nickel-silver core-shell nanoparticles

<u>Anna Pajor-Świerzy</u>, Katarzyna Kozak, Dorota Duraczyńska, Agata Wiertel-Pochopień, Jan Zawała and Krzysztof Szczepanowicz

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In the last year, a growing interest in the fabrication of conductive coatings or patterns based on metallic nanoparticles (NPs) as promising pathways for the fabrication of printed electronic circuits and devices has been observed [1-2]. The crucial importance of this process is obtaining patterns containing metallic NPs with conductivity close to that of their bulk counterpart using low-cost technology. In this context, due to the low price, good mechanical and conductive properties of nickel its nanosize form can be applied for the formation of conductive structures. However, nickel tends to oxidation, which can lower the conductivity of Ni NPs-based materials. Therefore, to protect them from this process, the silver shell can be formed on their surface, which results in the formation of air-stable nickel-silver core-shell NPs. In addition, the possibility of controlling the thickness of the shell of such NPs can open up new opportunities for the fabrication of a broad range of attractive materials with tunable properties.

In our research, we focused on the synthesis of Ni-Ag NPs with various thickness of the silver shell and their application in the fabrication of conductive coatings by using the thermal sintering process. We analyzed the dependence of the formation process as well as the resistivity of such films on the thickness of the silver shell to obtain highly conductive metallic structures. We found out, that the temperature needed for the formation of conductive coatings by thermal sintering decreases; moreover, improvement of conductivity of metallic films can be achieved by using NPs with thicker Ag shells. We observed that the values of resistivities depend on the thickness of the silver shell as well as the sintering temperature. The highest decrease in its value from about 100  $\mu\Omega$  cm to 9  $\mu\Omega$  cm was observed when the thickness of the shell increased from 10 to 55 nm after sintering at 300 °C. At the lowest sintering temperature of 120 °C, the highest conductivity (about 50% of that for bulk nickel) was obtained for coatings based on Ni-Ag NPs with 45 and 55 nm of the Ag shell thickness. In this context, the selection of the optimal thickness of the silver shell depends on the final application of such conductive materials. For substrates sensitive to high temperature, a thicker silver shell will be optimal while for other applications where the higher sintering temperature could be applied thinner silver shell should be selected.

#### Acknowledgments

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#### Exfoliation and transfer of the Heusler alloys thin films grown on graphene

#### Karol Załęski

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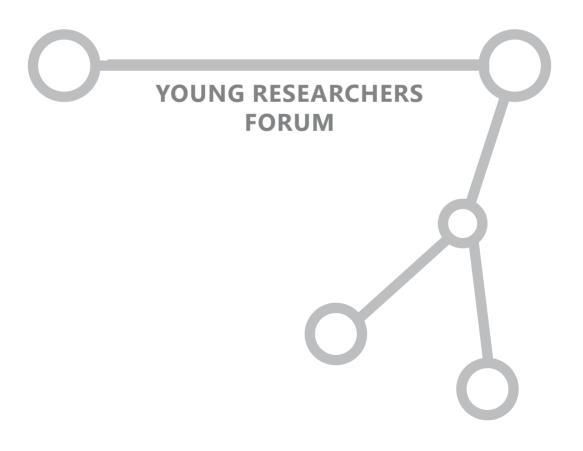
Spin transport in lateral spin valve (LSV) devices relies on the condition of their fundamental components: spin injectors/detectors (ferromagnetic electrodes) and a nonmagnetic spin transport channel. The core function in spintronic devices involves switching bistable nanomagnets—these ferromagnetic electrodes—used for injecting or detecting spin-polarized current. Thus, their spin polarization at the Fermi level is critical. Half-metallic ferromagnets, which show 100% spin polarization of conduction electrons, are ideal for spin injection and detection. Examples include certain Heusler alloys like NiMnSb, Co2FeSi, and Co2MnSi.

The spin transport channel should facilitate a long spin lifetime and allow for longdistance spin propagation. Due to its exceptional properties, experimental studies have identified graphene as the most favorable material for spin transport channels in spin-logic devices.

Spin polarization levels are generally intrinsic to the material. Some Heusler alloys exhibit such properties; however, achieving the desired electronic properties in these materials requires structural and chemical ordering. This is typically accomplished through specific thermal treatments, such as high-temperature deposition or post-annealing, which can be problematic for 2D devices using half-metallic materials. Such treatments can damage atomic-thin 2D material layers and degrade interface quality. Thus, developing a manufacturing method for devices based on 2D materials and high-quality electrode materials is essential to maintain interface quality and ensure thermal treatments do not impair device performance.

Herein, we present the potential for exfoliation and transfer of Heusler alloy thin films grown on various graphene substrates: epitaxial graphene on SiC, polycrystalline graphene on Si/SiO2, and highly oriented pyrolytic graphite, which has a surface similar to graphene. The weak interaction between the deposited material and the van der Waals layer allows for the exfoliation and transfer of the thin films to the target substrate. We also demonstrate the transfer of patterned samples prepared using the Focused Ion Beam method.

# SECTION A ADVANCED NANOMATERIALS



#### Materials with chiroptical properties - from chiral gold nanoparticles to organic chiral nanocomposites

<u>Filip Bandalewicz</u><sup>a</sup>, Natalia Kowalska<sup>a</sup>, Dorota Szepke<sup>a</sup>, Piotr Szustakiewicz<sup>a</sup>, Mateusz Pawlak<sup>a</sup>, Martyna Wasiluk<sup>a</sup>, Wiktor Lewandowski<sup>a</sup>

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In nature, chirality prevails, resulting in functional structures characterized by singlehandedness, hierarchy, and periodicity. The unique way natural materials are shaped, like the shells of beetles or the wings of butterflies, gives them unique optical properties. Lately, scientists have been copying these natural designs, and the knowledge in the field of chiral materials has increased significantly. As a main focus of our group, we present materials with chiral properties across different scales, from microscale solid-state systems with chiral patterning to nanoparticle helical assemblies on a single organic template and single chiral nanoparticles.

Efforts have been directed towards controlling the formation of chiral organic materials to create patterned solid-state systems. We propose a straightforward approach for fabricating films with chiroptically bipolar properties through photothermal laser patterning. Our method, termed DREAMCD, entails employing direct laser writing to selectively re-melt a liquid crystal (LC) film, allowing control over the nucleation points of chiral LC phases, facilitating the synchronization of chirality across designated regions [1]. Additionally, we propose an efficient technique to produce helical liquid crystals with tunable properties depending on plasmonic gold nanoparticles and disentangle optical effects present in such a complex 3D system using Mueller matrix polarimetry [2]. Finally, on the lowest level of chiral materials, we synthesize a broad range of gold nanoparticles, including examples of chiral gold nanoparticles. Such nanoparticles exhibit unique CD properties due to their morphology, which is easily controllable with a set of unique synthetic chiral inducers. The presented levels of complexity of chiral systems show great promise in applications such as optically secured information, circularly polarized light-emitting diodes (CP-LED), drug delivery systems with chiral nanoparticles exhibiting increased biological activity dependent on the chirality, and many more to find.

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#### **Optimization of obtaining nanocellulose**

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Cellulose, the most common natural polysaccharide that can be found on earth (its total content in plants is 33%), is a linear biopolymer consisting of D-glucose molecules linked by  $\beta$ -1,4-glycosidic bonds. It is insoluble in water and most organic solvents, but is biodegradable and can be charaterized with high mechanical strength, low density and high specific surface area [1]. Recently, a lot of attention is put to nanocellulose (at least one nanoscale dimension). Functional groups present in the cellulose chains allow for an easy modification, which allows the cellulose to be tailored for certain uses. It can be then used for example in catalysis, adsorption, food industry, pharmacy and textile industry [2].

The main aim of this work is to present the preparation process of nanocellulose-based functionalized materials which will be further used for water treatment purposes. We distinguish three routes of nanocellulose preparation: chemical, physical and combined methods. The focus of our work combined both chemical (with the use of sulfuric acid) and physical (with the use of BRANSON 550 ultrasonicator) methods. Time of chemical reaction, concentration of sulfuric acid as well as the time of ultrasonication have been optimized in order to obtain the best nanocellulose material. The resulting hydrogels were finally lyophilized, thus creating aerogels. In the next step, we focused on the quaternization of the prepared cellulose nanomaterials with glycylidyltrimethylammonium chloride. Once more the process was optimized to establish the highest percentage of quaternization. Those materials will further lead to the preparation of cellulose-based supported ionic liquids; an interesting class of adsorbents.

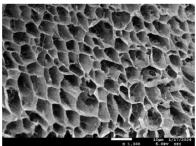


FIGURE 1. SEM image of the best nanocellulose in the form of aerogel.

#### Acknowledgments

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# Computational investigation of friction behavior at high sliding speeds for graphene oxide - silicon oxide materials pair

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Tribology, the branch of science dedicated to studying surfaces that move relative to each other, plays a crucial role in improving the efficiency and ensuring greater reliability of mechanical components. A thorough understanding of the interactions between two surfaces in contact allows for significant reductions in energy and material losses, as well as surface damage. It is estimated that on a global scale, friction-related losses account for approximately 23% of all energy produced [1]. With the continuous drive to increase the efficiency of mechanical devices and their miniaturization, this field of science is more important than ever.

The atomic force microscope (AFM) stands out as the predominant instrument for studying friction on the nanoscale. However, this tool has limitations in scanning speed and applied forces. As a result, computational methods, in particular steered molecular dynamics (SMD), complement physical experiments, providing a way to simulate the behavior of friction systems with great accuracy at atomic resolution. Using SMD, one can precisely control not only the temperature, pressure, or humidity of a friction system, but also the sliding speed and loading force, which is crucial for friction simulations.

Our research focuses on describing the mechanisms of dry friction observed for graphene and graphene oxide. The friction-reducing properties of both materials depend on numerous parameters, including sliding speed and loading force. The complex nature of friction still needs a thorough examination and, as demonstrated by experiments, requires additional investigation [2,3]. Special attention is paid to studying the relationship between friction force, sliding speed, and loading force [4]. We studied friction phenomena using SMD simulations across a range of cantilever tip sliding speeds, including values not achievable with an AFM. The tip sliding speed ranged from 0.1 m/s to 10 m/s, covering three orders of magnitude. We present the dependence of the friction force on the sliding speed for both investigated materials and discuss potential mechanisms underpinning this dependence, in particular for high sliding speeds.

#### Acknowledgments

The research was funded by the National Science Centre in Poland under the OPUS project No 2020/37/B/ST8/02023. The calculations reported in this work have been performed at the Interdisciplinary Centre of Mathematical and Computational Modelling of the University of Warsaw.

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YOUNG RESEARCHERS FORUM A

#### Towards Intrinsic Chirality: Gold Nanoparticles Synthesis via Multidentate Chiral Inducers

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Chiral nanomaterials attract special attention due to their specific, enantioselective interaction with light – they can exhibit differences in the absorption of right and left circularly polarized light. Currently, there is dynamic development of synthesis methodologies for intrinsically chiral nanoparticles. However, most of the developed protocols are based on the use of compounds of natural origin (amino acids, peptides, oligonucleotides) as chiral growth inducers [1-4]

In contrast to the current literature, in our work, we introduce multidentate, cysteinebased chirality inducers for the effective synthesis of intrinsically chiral gold nanoparticles. We find that the number and spatial arrangement of cysteine moieties are fundamental for the successful development of chiral morphology and chiroptical properties of the nanoparticles. Consequently, we enable the design of chirality inducers of beyond-natural origin, merging natural and synthetic chemical motifs.

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# 1D electrospun nanocomposite nanofibers for efficient photocatalytic applications

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Due to fossil energy depletion and environmental problems, water remediation and renewable, carbon-free energy are among the most important scientific challenges. Onedimensional (1D) nanostructures, such as nanofibers (NFs), nanorods, nanotubes, nanowhiskers, and nanowires, paving the way for a new generation of high-performance materials in fields of optics, mechanics, electricity, and catalysis resultant from the large specific surface area, nano-size effect, and interface effect, short ionic transport lengths, directional transmission. Compared to a hydrothermal method, template method, and self-assembly method, electrospinning synthesizing technology is characterized as a simple, easy control and low-price technique, which allows it to be easily scaled up to produce various nanomaterials at a large scale[1,2].

In the present issue, we report on the synthesis, characterization, and photocatalytic application of pristine polyimide nanofibers, polyimide nanofibers with TiO<sub>2</sub>, WO<sub>3</sub>, MXene additives, and ZnFe<sub>2</sub>O<sub>4</sub>/ZnO core-shell nanofibers, fabricated by co-axial electrospinning. The structure and morphology of the nanofibers have been confirmed using powder X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman spectroscopy, and transmission electron microscopy (TEM). The catalytic performance of electrospun materials was characterized by photocatalytic degradation tests with rhodamine 6G (R6G) selected as the model organic dye for polyimide-base composites, and by photoelectrochemical measurements in typical three-electrode cell for ZnFe<sub>2</sub>O<sub>4</sub>/ZnO core-shell nanofibers.

The nanofibers development offers promising prospects for the construction of highperformance photocatalysts for water purification and hydrogen production applications. These nanocomposites provide stable and repeatable photocatalytic materials with prominent efficiency, addressing the need for effective and sustainable solutions for posed scientific challenges.

#### Acknowledgments

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# Magnetic properties of disordered bulk FeCo alloys and FeCo-based ultrathin films

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Magnetic materials, especially permanent magnets, are vital components of modern technology. The use of rare earth elements such as samarium and neodymium has led to the development of the most efficient permanent magnets. However, with their limitations, such as a low Curie temperature ( $T_C$ ) and the fragility of the rare earth metal prices, there is a need to explore alternative materials. This challenge has prompted researchers to seek new magnetic materials to revolutionise the industry and pave the way for a brighter future [1].

One of the development directions of technology is electronic device miniaturisation, and modern science has broken through the barrier of a few monoatomic layers. This has opened up exciting possibilities for layered systems, which can be fine-tuned to improve material parameters like magnetocrystalline anisotropy energy (MAE). For example, magnetic tunnel junctions can now reach a thickness of just twenty atomic monolayers.

Among these, bulk and layered iron-based systems are especially intriguing. We are presenting our research on the bulk FeCo system. It was provided using density functional theory as implemented in FPLO18.00-52 [2], Perdew-Burke-Ernzernhoff exchange-correlation potential [3]. We looked at MAE,  $T_C$  and magnetic moments' dependence on the c/a ratio and cobalt concentration. Curie temperatures were obtained using the disordered local moment and Binder cumulant (as implemented in UppASD code) methods.

We also extended our research on 9-layered thin films of pure Fe, FeCo, FeCo-B, FeCo-C and FeCo-N containing 30% of Co [4], with the assumption of low Co concentration based on our previous work [5]. We concentrated here on changes in magnetic moments and MAE caused by the dopant.

#### Acknowledgments

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J.A. C-R acknowledges Olle Engkvist's Foundation and Knut and Alice Wallenberg Foundation for financial support. The simulations were enabled by resources provided by the National Academic Infrastructure for Supercomputing in Sweden (NAISS) at the NSC Centre, partially funded by the Swedish Research Council through grant agreement no. 2022-06725.

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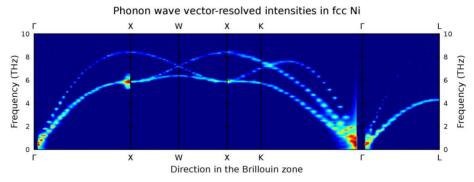
### Machine learning-based molecular dynamics for unveiling the ultrafast demagnetization of fcc Ni

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Since its discovery in 1996 [1], ultrafast modification of materials magnetization by femtosecond laser pulse attracted significant attention. This process involves the transfer of angular momentum between electrons, phonons, and magnons.

We study how phonons can contribute to re-establishing the equilibrium by carrying away the excess heat and angular momentum. Utilizing LAMMPS molecular modelling package 'as a library' feature, we evaluate the evolution of lattice vibrations from high temperatures of selected vibration modes towards an equilibrium using SNAP machinelearning interatomic potential (ML-IAP). Snapshots of the molecular dynamics trajectories allow us to follow recent suggestions [2] with a more detailed method, and predict changes in the electron diffraction patterns and energy loss spectra in a time-resolved way on a



picoseconds time-scale, suggested by previous modelling efforts [3].

FIGURE 1. Face-centred cubic Ni phonon dispersion after X transverse acoustic phonon branch modiffication by a tapered cosine-shaped pulse in atomistic model corresponding to 9.2 nm fcc Ni layer.

#### Acknowledgments

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#### Determination of magnetic properties of iron oxide nanowires on Cu(410) using magneto-optical Kerr effect (MOKE) measurements

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Islands of magnetic materials with well-defined geometry attract lots of interest due to their potential applications in spintronic and magnetic devices [1]. However, fabrication of such structures usually requires utilizing sophisticated technological processes, such as, e.g., electron lithography. We have developed a direct method for growing well-ordered magnetic iron oxide nanowires through the deposition of Fe under ultra-high vacuum (UHV) onto a vicinal copper surface faceted with molecular oxygen (Cu(410)-O)) and post-oxidation at elevated temperatures. The structure of the wires was investigated using scanning tunneling microscopy (STM), low energy electron diffraction (LEED) and X-ray photoelectron spectroscopy (XPS) [2]. The studies revealed that the wires grow along the step edges of the substrate, in the [111] direction and represent the ferrimagnetic  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> phase [2,3]. The magnetic properties of fabricated species were determined through magneto-optical Kerr effect (MOKE) measurements under UHV. The results confirmed ferri-/ferromagnetic ordering in the wires at room temperatures, as well as in-plane magnetic anisotropy expected for such nanowires based on micromagnetic simulations [3].

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YOUNG RESEARCHERS FORUM A

#### Computational Study of NO<sub>2</sub> Enhanced Adsorption Interaction on MoS<sub>2</sub>, MoSe<sub>2</sub>, and MoTe<sub>2</sub> monolayers

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The world's high levels of hazardous gas emissions necessitate the development of novel materials for monitoring them. Notable among the latter are transition metal dichalcogenide (TMD) monolayers such as MoS2, MoSe2, and MoTe2, which constitute excellent candidates for NO2 detection, enabling successful recognition at the ppb level. However, the mechanism of the gas adsorption on these is not yet fully understood. We present our attempt to illuminate the issue using methods of density functional theory (DFT). The results show that the adsorption interaction can be enhanced based on the nature of metal-chalcogen bonding, which affects the availability of electrons on the sheet surface. This correlation is graphically represented in Figure 1. In consequence, MoTe2 can be distinguished as the most sensitive of the examined TMD, albeit with a higher energetic cost for its recovery. We hope that the provided theoretical insight will be helpful in the design process of modern NO2 sensors, as it allows for a more informed and conscious design.

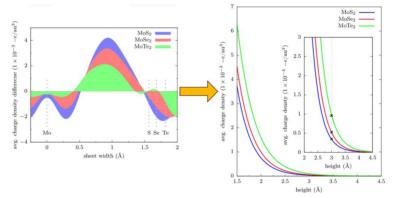


FIGURE 1. The graph on the left contains planar-averaged difference between sheet charge density and superposition of metal and dichalcogen densities whereas the one on the right presents resulting planar-averaged charge densities at heights relative to the TMDs surface.

#### Acknowledgments

This work was supported by the Ministry of Education and Science in Poland (Grant No. 0512/SBAD/2320) within the project realized at the Institute of Physics, Poznan University of Technology. Computations have been performed at Poznan Supercomputing and Networking Center (PSNC) under Grant No. 608.

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YOUNG RESEARCHERS FORUM A

### Ultrasound monitoring of emulsion-based magnetic colloidal capsules fabrication

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Magnetic nanoparticles offer plenty of applicational features. One advantage of those objects is their ability to act as a heat source when exposed to an external alternating magnetic field. This allows for more targeted, effective, and controlled heating. Here, we utilize magnetic nanoparticles' ability to generate heat in the process of colloidal capsules preparation. This involves raising the system's temperature, enabling particle fusion on the surface of the dispersed phase droplets.

Small capsules with shells made of microparticles emerged as promising delivery systems due to their potential for application in many fields, such as the food or pharmaceutical industry, where they can be used, for instance, as microscopic drug carriers. They can be fabricated from particle-stabilized emulsions (Pickering emulsions) by sintering together particles that cover Pickering droplets at high temperatures induced by magnetic heating of magnetic nanoparticles [1]. One of the challenges with this method is to accurately control the sintering process and the creation of a rigid shell of a capsule.

In our approach, we proposed a non-destructive ultrasound method that offers an effective evaluation of the encapsulation process in investigated systems. Ultrasound was employed to characterize how the structure of the multi-phase system evolves during capsules formation from oil-in-oil Pickering emulsion templates. The research showed that the ultrasound attenuation coefficient was sensitive to changes in oil droplet shell properties. The observed decrease in ultrasound wave amplitude after heating suggests effective sintering of the nanoparticles on the droplet surface, leading to the formation of the desired colloidal capsules [2].

Analysis of the attenuation coefficient offers a promising approach for monitoring the encapsulation process in Pickering emulsions, particularly when combined with optical imaging for a more comprehensive understanding of the system's behavior.

#### Acknowledgments

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YOUNG RESEARCHERS FORUM A

#### Recipe for a NanoHoneyCake: Organic/Inorganic Large-Scale Multilayer Nanocomposite Photocatalyst

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Heterogenous photocatalysis shows great promise in many emerging fields, e.g. water remediation, renewable energy conversion and storage. While striving to reduce production costs, hybrid organic/inorganic composites are one prominent solution. In particular, oxide/polymer nanocomposites combine the favorable optoelectronic properties of oxides and ample mechanical tunability of polymers. At the same time, TiO<sub>2</sub> nitrogen-doping increase its photocatalytic efficiency by reducing bandgap, broadening the light absorption, and raising the number of photogenerated charge carriers [1]. Moreover, we have previously shown that PDA free-standing films produced on a large scale at the air/water interface (a/w-PDA) can be *ex-situ* transferred to any desired substrate due to their extraordinary mechanical properties [2].

In this study, we introduce a straightforward and reproducible approach: the alternate layering of high-quality a/w-PDA nanometrically thin free-standing films, with precisely controlled atomic layer deposition of the TiO<sub>2</sub> layers, to achieve Honey-Cake-like multilayer nanostructure. Exceptionally sharp oxide/polymer interfaces in the large-scale were obtained, as indicated by FIB processing and HRTEM imaging. In turn, the XPS deep profiles combined with SIMS analysis confirmed the nitrogen-doping of the TiO<sub>2</sub> lattice in a gradient-like manner. This doping strategy relies on ALD with polymer nitrogen-sourcing at a relatively low temperature ( $200^{\circ}$ C). Described chemical and structural characteristics of the multilayer nanocomposites translate into a reduction of the band gap by over 0.63 eV as measured by UV-vis spectroscopy and an increase in the photogenerated current by over 60% compared to pure amorphous TiO<sub>2</sub>, which was revealed by photoelectrochemical tests. We presume that this novel doping strategy could be exploited in other N-accepting photoactive inorganic materials.

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### Electric and memristive properties of methacrylate-based polymer nanobrushes

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Today's world is dynamically developing technologies based on artificial intelligence. However, one of the limitations of progress in this field is the currently used von Neumann architectures. The main way to overcome memory and power walls, which are limiting current computing efficiency, is by applying the memristors. They feature fast reading and writing speeds and provide complementarity to standard metal semiconductor processes, which makes them ideal candidates for creating novel electronic components.

Memristors can be divided into two groups depending on material origination: inorganic, whose main representatives are binary oxides and perovskites, and organic which includes small molecules and polymers. Significant assets of the first of these groups are high switching speed and endurance. Despite considerable advancement in their properties, the power consumption and environmental stability should be corrected. Less-studied organic memristors allow to creation of flexible, large-scale systems with appropriate reproducibility.<sup>1</sup> The recent and promising member of this group became highly-organised surface-grafted polymer nanobrushes. They form the arrangement of macromolecular chains, covalently bonded to electrode material. The easiness of deposition and changing of electric properties by modification of polymeric structure are their undeniable advantages.

The aim of our studies was to obtain methacrylate-based nanobrushes on ITO surfaces by using 3-trimethylsilyl-2-propynyl methacrylate (TPM) as a monomer and changing the electrical behaviour by doping with Lewis acid. In the first stage, the brushes were synthesised on the electrode material by a photo-inferter polymerization reaction. During the next step, the side acetylene groups were conjugated by self-template polymerization with bicyclo [2,2,1]hepta-2,5-diene-rhodium (I) chloride dimer. Finally, the poly(TPM) brushes were doped by [FeCl<sub>4</sub>]<sup>-</sup> by immersing material in the concentrated FeCl<sub>3</sub> solution in nitromethane in inert gas conditions. The polymeric structure was characterized by FTIR spectroscopy and AFM to correlate structural modification with electrical and memristive properties. The adjustments in neuromorphic behaviour were studied by assessment of excitatory postsynaptic currents (EPSC) and potentiation-depression cycles measurement. The changes in material conductivity were investigated by cyclic voltammetry method.

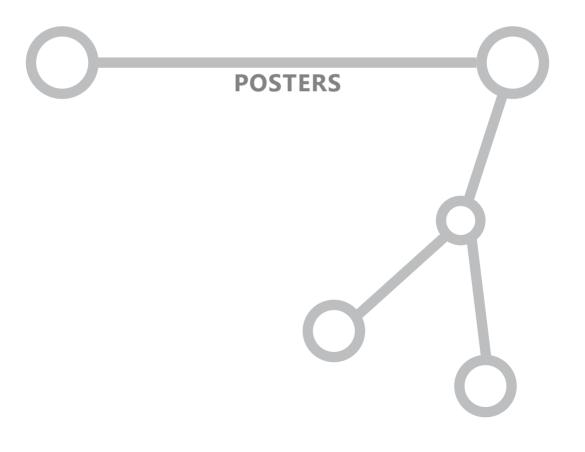
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## SECTION A ADVANCED NANOMATERIALS



#### Synthesis and Photocatalysis Study of ZnO/PDA Tetrapods

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Zinc oxide (ZnO) is a semiconductor with a high impact from the technological point of view, within nano and microscale, many different structures with several applications can be synthesized following different methods [1]. These structures show n-type conductivity, and a direct band gap of  $\approx 3.37$  eV which allows ZnO to absorb in the range of ultraviolet-visible (UV-Vis) making it a proper material for photocatalytic applications.[1] Here, ZnO tetrapods have been covered with polydopamine (PDA) to create hybrid composites. PDA is a biomimetic polymer that can be combined with semiconductors improving their photocatalytic behavior.[2] ZnO/PDA have been synthesized through the self-polymerization of dopamine at the ZnO surface achieving a smooth and homogeneous PDA cover. Its effect in photocatalysis was examined towards Rhodamine 6G (Rh6G) (5.0 µg mL<sup>-1</sup>) showing a total degradation of its initial concentration within 45 minutes of irradiation (1 sun) with a catalyst concentration of 2.5 mg  $mL^{-1}$ . Furthermore, stability was tested during 3 rounds of photocatalysis showing a negligible yield decrease indicating that our composite is stable and reusable. Moreover, additional concentrations of Rh6G have been tested (2.5  $\mu$ g mL<sup>-1</sup>, 7.0  $\mu$ g mL<sup>-1</sup>, and 10  $\mu$ g mL<sup>-1</sup>) and reaction kinetics have been studied through the Langmuir-Hinshelwood method. The proved efficient degradation of the organic dye along with the stability and reusability of the composite, shows an important upgrade in the photocatalytic behavior of bare ZnO tetrapods.

#### Acknowledgments

The author acknowledges the financial support from the National Science Centre of Poland (NCN) by the OPUS grant 2019/35/B/ST5/00248 and the French Government Scholarship for the financial support.

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#### Exploring nanostructured silica materials modified with aminosilane and copper ions as skin acyclovir carriers

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Emerging and recurrent cases of viral infections pose a public health challenge. One of the most prevalent viruses among humans is the *Herpes simplex virus*. Once infected, the virus remains in the body for a lifetime and can cause relapses [1]. Currently, there is no vaccine against *Herpes simplex virus*. Preparations containing acyclovir are used to treat the disease caused by this virus. Acyclovir can be given to patients in the form of intravenous infusions, orally, or as a topical ointment. Oral administration of the drug results in faster relief of local symptoms and lesions of genital herpes than semi-solid formulations such as creams, gels, hydrophilic and hydrophobic ointments [2]. Therefore, in recent years, intensive research has been conducted on increasing the efficacy and bioavailability of acyclovir administered through the skin. Mesoporous silica materials are valuable modifiers of the physicochemical properties of active antiviral substances. Their structural diversity, relatively easy synthesis, and high incorporation capacity are undoubted advantages that distinguish them from previously known carriers [3]. The possibility of modifying the release profiles of antiviral substances using ordered silica samples is a research direction intensively developed.

The research aimed to synthesize and use mesoporous silica materials such as WMS (Wrinkled Mesoporous Silica), KIT-6, SBA-15, and SBA-16 functionalized with amine groups and copper ions as acyclovir carriers. The materials were synthesized by a hydrothermal method and then modified with 3-aminopropyltrimethoxysilane and copper(II) chloride. They were characterized by low-temperature nitrogen adsorption/desorption, FT-IR spectroscopy, elemental analysis, and X-ray diffraction. The synthesized carriers were tested in the process of acyclovir adsorption and incorporated into a topical pharmaceutical formulation (oil-in-water emulsion). Release studies of the active ingredient from obtained materials and topical formulation were carried out at 32 °C in a phosphate buffer of pH 5.8.

Based on the XRD profiles in the small-angle range, it was observed that KIT-6, SBA-15, and SBA-16 materials are characterized by a highly ordered mesoporous structure. Their modification with aminosilane and copper(II) chloride led to a decrease in the BET surface area and pore volume. The FT-IR spectra of organic-inorganic hybrid systems confirm that acyclovir was efficiently adsorbed on the surface of the materials. The amount of drug adsorbed was dependent on the pH of its solution. Pristine and aminosilane-modified materials showed the highest sorption capacity toward acyclovir at pH 2. It was established that the carriers' functionalization significantly affects the release rate of acyclovir from their surface and the oil-in-water emulsion.

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### Obtaining of ZnO(ZnO:Ga) layers on BGO substrates for potential ultrafast γ-ray detection

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Positron emission tomography (PET) scanners are among the most efficient tools for the identification of tumors in the human body. However, the temporal resolution of Time-of-Flight (TOF-PET) is limited by both the metabolism of the tracer molecule in the patient's body, and delayed response of scintillation detectors to generated  $\gamma$ -quanta. Scintillation detectors with improved timing performance should enable both to increase TOF-PET sensitivity, and reduce radioactive doses injected into patients [1]. Heterostructures combining a heavy scintillator, which efficiently absorbs  $\gamma$ -quanta, with a light and fast scintillator, which converts recoil electrons from the heavy scintillator to fast light photons are considered among the approaches to enhance the TOF-PET timing [2].

In this work, BGO and ZnO(ZnO:Ga) were chosen as heavy and light components of the heterostructure, respectively. ZnO is a wide band gap semiconductor (Eg = 3.4 eV) with a large exciton binding energy (60 meV), strong exciton and defect luminescence at room temperature with a sub-nanosecond lifetime, and a low afterglow [3]. These important advantages make this material very promising for application in ultrafast scintillating detectors. Moreover, ZnO properties can be easily tuned by doping with n-type and p-type impurities, such Ga<sup>3+</sup> donor ions enhancing scintillation efficiency [4].

ZnO(ZnO:Ga) films were successfully obtained by the sol-gel technique on BGO substrates. ZnO/ZnO:Ga thickness was tuned to adjust luminescence and scintillation parameters. The proposed synthesis method enables obtaining highly crystalline ZnO/ZnO:Ga films with a thickness ranging from 10 to 100  $\mu$ m on BGO substrates. The surfaces are homogeneous and consist of ZnO seeds with sizes approximately 100 nm. Pristine ZnO films under 325 nm exhibit exciton and defect luminescence bands peaked in UV (353 nm) and visible green (657 nm) ranges, respectively. The variation of ZnO thickness as well as the presence of the impurities allows for tuning of luminescence spectra of ZnO.

#### Acknowledgments

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#### Hybrid gold nanoparticles with modulation of photophysical parameters as an effective platform for photodynamic therapy against bacteria

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Photodynamic therapy (PDT) is a safe form of treatment in which a photosensitising agent is activated by light of a specific wavelength. In the presence of oxygen, singlet oxygen and free radicals are generated. PDT is safe, it is non-mutagenic and can inhibit effect on the biofilm formation and reduce effect on the microbial load [1]. In recent years, numerous modifications of gold nanoparticles have been developed to enhance their antimicrobial potential. The gold nanoparticles have been linked to antibiotics, phospholipids, and polymers, among others [2,3].

In this work, we have presented the influence of functionalised gold nanoparticles and photosensitiser in physical mixtures to assess antimicrobial activity. The photodynamic effect can be controlled by modifying the size and the type of functionalisation coating. The potential additive effect between differently functionalized gold nanoparticles and the dye was also studied. The influence of the coatings on the singlet oxygen production process of hybrid systems based on gold nanoparticles was compared. The understanding of the effects of gold nanoparticles on living organisms has been continuously expanded by studying the interactions between gold nanoparticles and cellular membrane components. In order to be able to use the nanoparticles in therapies, the interaction with the cell membrane had to be understood. The results obtained predestine these systems to be excellent candidates for use in medical applications.

#### Acknowledgments

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#### Development of a new electrochemical sensor based on nanomaterials for testing active pharmaceutical ingredients

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Nanotechnology is a dynamically developing field, which has recently gained great importance in superior and more efficient sensing systems. The remarkable metal-organic frameworks (MOFs) applicability either as simpler detectors or advanced components in electrochemical sensors is of interest to many research groups from around the world. Each of their features can be refined for specific purposes. Broad pore tuning in terms of size, volume, and functionalization allows pairing with many molecules. The linker modification provides different optical and conductivity characteristics, whereas metal or metal clusters cannot only have an impact on crystallite morphology but also on magnetic properties [1]. All variations must be considered sensors/analyte enthalpies to maintain sensor reversibility and long-run use. Up to now, MOFs are more often considered to be a good receptor phase due to their selective confinement but also, thanks to dielectric abilities, they could take part in signal transducing systems. Although their commercial success is on the horizon, many efforts must be focused on easier and less expensive fabrication processes. Due to the evident demand for electrochemical sensors with improved sensitivity and selectivity, the study aimed to develop a modification approach of electrodes with copper-based MOF materials for dopamine sensors.

The synthesis of Cu-MOFs was carried out using the solvothermal method. To obtain Cu-BDC and Cu-BTC, copper(II) hydroxide with 1,4-benzenedicarboxylic acid and copper(II) acetate with 1,3,5-benzenetricarboxylic acid were mixed, respectively. The resulting mixtures were transferred to Teflon-lined steel autoclaves and placed in the oven at 120 °C for 24 h. After the solvothermal treatment, blue precipitates were collected by vacuum filtration, washed, and dried at 70 °C for 12 h. Then, another analogous series of materials was prepared with the addition of an HCOONa modulator. The materials were characterized by X-ray diffraction, FT-IR spectroscopy, scanning electron microscopy, and low-temperature nitrogen adsorption/desorption. To obtain new conductive nanomaterials, Cu-MOF systems were deposited on glassy carbon electrodes (GCE) and used as dopamine sensors.

Cu-MOFs are characterized by specific surface areas ranging from 9 to 441 m<sup>2</sup>/g. The use of a modulator in their synthesis has a significant impact on the textural parameters. SEM images showed that the resulting Cu-MOF nanoparticles differed in morphology and size. Among the modified materials tested, Cu-BDC proved to be the most promising for developing dopamine sensors in an aqueous environment, achieving detection levels in the order of nM. Such a system could serve as a medical diagnostic probe applied in *in vitro* studies to indicate potential health problems in patients suffering from neurochemically related diseases (Parkinson's, Alzheimer's, Tourette's).

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#### Determining The Flexoelectric/Photo-Flexoelectric Response of Strontium Titanate Cantilevers by Nanoindentation Instrumentation

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Flexoelectricity is a phenomenon where an electric polarization is induced in a material due to a non-uniform strain gradient. Unlike other phenomena like piezoelectricity and ferroelectricity, this effect is not limited by specific geometries or crystalline structures, which makes it significant in energy harvesting. Furthermore, it is possible to generate the so-called photo-flexoelectric effect in perovskite materials, both inorganic and organic, as the flexoelectric effect can be enhanced by the photocurrent generated in these materials.

Flexoelectricity is currently characterized by methods such as Dynamic Mechanical Analyzer or techniques based on Scanning Probe Microscopy. The main drawbacks of those methods are the limited achievable oscillation amplitude of a contact tip and the relatively large size of the sample. This work will show a novel, unique method using the Nanoindentation Instrumentation and free-standing cantilever beams. Using direct mechanical excitation, we will experimentally show the flexoelectric response of a single strontium titanate crystal (STO) obtained by sub-micrometre oscillations. See **Figure 1**. Furthermore, we will utilize LED light to investigate the photo-flexoelectric effect induced by the monochromatic light irradiation of different wavelengths. Contrary to the commonly used methods, the presented method allows access to a relatively small strain field and proves effective for investigating the responses of significantly smaller materials.

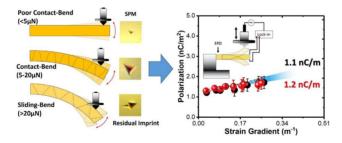


FIGURE 1: Schematic illustration of the contact bending at a different load and the corresponding residual imprint (left). Flexoelectric Polarization was measured from both sides of the cantilever, in agreement with the reported values for STO [1].

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Α7

#### Green Reinforcement of Plastic Packaging by Starch Addition: a Coupled Computational and Experimental Study

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Poly Lactic Acid (PLA) / Poly Butylene Adipate-co-Terephthalate (PBAT) blends are used as packaging green materials since they constitute hydrophilic and biodegradable plastic. With the aim of improving the mechanical characteristics of PLA/PBAT blends as biodegradable packaging materials for food products the addition of starch has been considered. In silico study performed by classical molecular dynamics (MD) highlighted that the addition of starch can reinforce the polymeric structure via starch-polymer interactions, suggesting that starch can be a suitable material to be added to the PLA/PBAT blend to obtain more resistant packaging materials. A snapshot of the MD simulation is reported in Fig. 1 left panel.

Experimental analysis of the mechanical properties of PLA/PBAT blends containing different amounts of starch confirmed what foreseen by MD, highlighting increases in Young modulus and glass transition as a function of added starch. Starch amount of 10 wt% turned out to be the optimum to maximize the elongation bearable under tensile stress before rupture (Fig. 1 right panel). The coupled theoretical/experimental approach constitutes added value of the present work, furnishing important data on the reinforcement of the packaging material performances and a molecule-based interpretation and comprehension of the observed phenomenon.

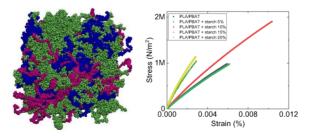


FIGURE 1. Fig. 1: left panel MD snapshot of PLA/PBAT/starch system (magenta starch, green PLA, blue PBAT); Right panel: stress- strain plot for PLA/PBAT/starch composites at various starch wt%.

### The comparison of perovskite oxides obtained by sol-gel method using organic and inorganic precursors

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Perovskites are materials with a cubic structure that can be described by the general formula ABO<sub>3</sub>. They are best known for their applications in photovoltaics due to their high absorption coefficient, high charge mobility, significant diffusion length, and suitable bandgap [1]. The interest in oxide perovskites stems from the search for non-toxic alternatives to lead-based perovskites, which currently lead in terms of solar cell efficiency [2]. Oxides are non-toxic and stable, and lanthanum has been chosen because it allows for the creation of oxide perovskites with higher conductivity compared to oxide perovskites based on other rare earth elements [3]. Additionally, both LaMnO<sub>3</sub> (LMO) and LaFeO<sub>3</sub> (LFO) can be classified as Mott insulators - materials with great potential for optoelectronic converters due to the phenomenon of generating multiple carriers with one photon [4].

Oxide perovskites are typically synthesized using inorganic precursors such as nitrides, which easily form powders. This well-known method has been utilized to create powders that became our point of reference for further research. Keeping in mind potential future thin-film applications of perovskite oxides, powders using alternative precursors acetylacetonates which are, in turn, organic, have also been carried out. To assess the temperature at which phase transitions take place, thermogravimetric measurements on dried gels were performed. The structural analysis including crystallographic phase and lattice parameters has been performed by Rietveld refinement methods using GSAS-II software. Raman spectroscopy studies allowed for the observation of distinct bands originating from the Pnma structure in LFO powders for both methods. LMO's Raman spectra, consistent with the conclusions from X-ray diffraction studies and due to Jahn-Teller effect, consists only of two broad bands originating from R-3c structure. The acetylacetonate route results in even weaker Raman bands compared to the nitrate one. For this reason FT-IR, a spectroscopic technique complementary to Raman, was included in the research. Scanning Electron Microscopy imaging revealed that all samples consist of nanoparticles - nitrates allowed for particles as small as 50 nm, acetylacetonates in turn created particles with 100-160 nm range in size.

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Α9

#### Polyaniline/TiO<sub>2</sub> nanocomposites as visible light-active photocatalysts

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Titanium dioxide (TiO<sub>2</sub>; titania) has been identified as the photocatalytic material with high application potential in the fields of water or air treatment and solar energy conversion into chemical energy to obtain valuable products such as hydrogen and hydrocarbons. Many strategies have been designed to improve the photocatalytic performance of titania to extend its activity into visible light region. In this relation, polyaniline(PANI)/TiO<sub>2</sub> nanocomposites are very promising photocatalytic materials. Their efficiency both under UV and visible light irradiations can be explained due to the synergistic effect of both components. This effect manifests in two aspects: (1) the presence of PANI as an effective visible light sensitizer of TiO<sub>2</sub> and (2) the formation of heterojunction (type II) between PANI and titanium dioxide which is decisive factor for lowering the charge carriers recombination effect increasing an efficiency of UV-induced reactions (Figure 1) [1, 2]. This study focuses on PANI/TiO<sub>2</sub> as visible light-active photocatalytic material. At first, different forms of PANI were subjected to the research to find its best form for the photocatalytic application, also as the part of the composite with titania. In this relation, the discussion about the influence of different preparation parameters on the resultant photocatalytic properties of PANI/TiO<sub>2</sub> materials was performed. Furthermore, the discussion on various titania materials considered in PANI/TiO<sub>2</sub> synthesis was also conducted. As the sources of visible light, different LED lamps were considered in the performed photocatalytic experiments

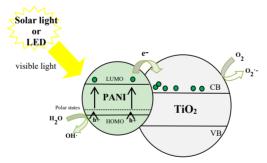


FIGURE 1. Mechanism of generation of reactive oxygen species under visible light by PANI-TiO<sub>2</sub> nanocomposite photocatalyst. [2].

#### Acknowledgments

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#### Ordered mesoporous silica@metal-organic framework composite as a dual-carrier drug release system for migraine treatment

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Non-steroidal anti-inflammatory drugs (NSAIDs) are applied for their analgesic, antiinflammatory, and antipyretic properties. The most commonly used NSAIDs include diclofenac sodium, naproxen sodium, and ketoprofen. Their effectiveness can be limited by poor bioavailability and solubility in water. As a result, there is a need for the development of innovative and safe delivery systems that ensure drugs reach the target site, enabling quick and effective treatment of migraines [1]. Metal–organic frameworks (MOFs), an interesting class of crystalline materials, are characterized by tunable structure, high specific surface area, pore volume, and biocompatibility, making them good active pharmaceutical ingredient carriers. However, they suffer from low stability and mechanical strength, which significantly hinders their potential applications. Therefore, combining MOFs with inorganic materials has emerged as a potential approach to address these limitations. The composites, consisting of MOFs and silica materials, typically have higher water stability and sorption capacity, as well as inhibit premature drug release [2].

The study aimed to synthesize the SBA-16@MIL-101 composite via the hydrothermal method. At first, SBA-16 was prepared using Pluronic F127 ( $EO_{106}PO_{70}EO_{106}$ ) template and tetraethyl orthosilicate (TEOS) as the silica source. Next, the silica was placed in a Teflon-lined autoclave with iron(III) chloride and terephthalic acid and heated for 24 h at 120 °C to obtain SBA-16@MIL-101 composite. For comparison, pure silica SBA-16 and MIL-101 materials were synthesized. All samples were characterized using X-ray diffraction, low-temperature nitrogen adsorption/desorption, thermogravimetric analysis, and scanning electron microscopy. They were tested in the adsorption of diclofenac sodium, ketoprofen, and naproxen sodium for 2 h at room temperature. The NSAID release process was conducted in phosphate buffer simulated rectal fluid (pH 7.7).

The SBA-16@MIL-101 composite obtained had an ordered mesoporous structure derived from SBA-16 silica. It was characterized by high specific surface area and pore volume. Adsorption of active pharmaceutical ingredients was more efficient in the case of the composite than pure mesoporous silica with sorption capacities towards ketoprofen of 91 mg/g, naproxen sodium of 490 mg/g, and diclofenac sodium of 589 mg/g. The drugs were adsorbed onto the samples following the Langmuir-type isotherm. The primary mechanism of drug adsorption on the composite surface was hydrogen bond formation, metal coordination, and electrostatic interactions. An in vitro drug release experiment conducted at pH 7.7 demonstrated that they diffused to phosphate buffer in a controlled manner. The percentage of the drug desorbed from the composite was 88, 89, and 94% for ketoprofen, diclofenac sodium, and naproxen sodium, respectively.

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#### Tailoring ZnO/MXene Interfaces for Improved Photoelectrochemical Water Splitting

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Hydrogen is gaining recognition as one of the cleanest, most sustainable, and renewable energy. Among the various methods to produce hydrogen, photoelectrochemical (PEC) water splitting stands out as a particularly promising technique for converting solar energy into hydrogen [1]. PEC water splitting has the potential to meet the growing demand for renewable energy and reduce our reliance on fossil fuels, thereby playing an important role in the transition to a sustainable energy future. The development of efficient and stable photoelectrodes for harnessing solar energy photoelectrochemical water splitting is crucial for sustainable production [2]. MXene ( $Ti_3C_2$ ) have been recently attracted as a potential cocatalyst candidates due to their unique properties, making them valuable in various energy conversion and storage applications [3]. The importance of MXenes lies in their combination of high electrical conductivity, chemical tunability, and large surface area, which can enhance the performance of metal oxide semiconductor-based photoelectrodes.

In this study, we introduce a novel fabrication approach for ZnO/MXene photoelectrodes, combining spray coating and atomic layer deposition (ALD) which enables precise control over material deposition, enhancing the performance stability of the photoelectrodes. The modified interface facilitated efficient charge separation and transfer, leading to improved photocurrent generation and stability. This study highlights the potential of ALD-modified ZnO/MXene photoelectrodes for efficient and stable PEC water splitting applications, paving the path for advanced materials in renewable energy applications. The synergistic effects between MXene and ALD modification offer valuable insights for the design and optimisation of photoelectrodes in renewable energy conversion systems. During the presentation, detailed information and performance of the ZnO/MXene photoelectrodes will be presented, including insights into new designs for improved charge separation and transfer. The presentation will also cover how novel materials, specifically MXene and ALD modified ZnO, contribute to these advancements.

#### Acknowledgements

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### Ultrasmall iron oxide colloidal gels with dopants: investigation of optical properties and confocal laser scanning microscopy study

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Colloidal gels are scientifically and technologically interesting materials that reveal phenomena of nanoparticle self-organisation and collective behaviour. They are a kind of soft matter in which particles are dispersed in a liquid phase forming a percolating network. Understanding their physicochemical and microstructural peculiarities is extremely important as they open the opportunity to manufacture macroscale materials keeping nano-scale advantages. Utilizing colloidal processing instead of individual nanoparticles (NPs) is a new level of nanotechnology on which collective behaviour of NPs under defined way and controlled conditions will be used to produce larger entities [1]. In this work, silver, copper and selenium were used as dopants to ultrasmall iron oxide colloidal gel. These elements, being in nanoscale range, exhibit improved optical and electronic properties compared to their bulk equivalent due to size quantization effects [2]. Optical properties of the USIO, and Ag-, Cu-, Se-doped USIO NPs were investigated by means of UV-Vis and fluorescence spectroscopies. The results reveal that Ag, Cu, and Se doping of USIO NPs significantly enhances their plasmon properties, causing an increase in fluorescence intensity. Among the dopants, Cu is the most effective doping element, Se occupies an intermediate position, and Ag provides lower fluorescence intensity. Confocal laser scanning microscopy measurements of the colloidal gels revealed some examples of their self-organisation and structuration. Thus, parallel stripes, unidirectional alignment and patterns were detected for all studied samples. Doped colloidal gels revealing plasmonic response are promising materials for catalysis and photocatalysis, sensing, electrocatalysis as well as for biomedical applications.

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#### Electric field driving assembly of nanoparticles in magnetic ferrofluids

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In the field of fundamental research on magnetic fluids, there are well-known magnetic and electric phenomena whose understanding and practical applications in engineering require deeper experimental study. We review the state of the art in the area of the impact of magnetic and electric field on the structure of magnetic fluids to highlight the significance of research on transformer-oil-based magnetic fluids vital in high voltage engineering.

Iron oxide nanoparticles were synthesized by chemical co-precipitation from aqueous solution of ferrous and ferric ions in the presence of NH<sub>4</sub>OH at 80–82°C, according to the wellestablished protocol after co-precipitation. The magnetite nanoparticles were sterically stabilized with a single oleic acid layer ( $C_{18}H_{34}O_2$ , Merk) chemisorbed on the particle surfaces. The transformer oil used as a carrier liquid in the studied ferrofluid was a commercial oil Mogul Trafo CZ-A. Samples with different particle volume fractions (1, 1.5, 2 %) were investigated.

Formation of magnetic nanoparticles layers was found to take place on a planar surface of copper electrode film on a single-crystal silicon substrate, under perpendicular homogeneous electric field, by small angle neutron scattering (SANSPOL) and neutron reflectometry. From the SANSPOL measurement in a combined electric and magnetic field, one can conclude that the electric field enhanced the magnetic anisotropy in the formed aggregates. The observed self-assembled layering could be used as an additional barrier at the inner surface of a transformer to increase dielectric breakdown voltage of working fluids.

# $-\alpha_{\rm o}^{\rm o}$

#### Fly ash-based zeolites and zeolite@carbon composites for the purification of water contaminated with 2,4-dichlorophenoxyacetic acid

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The global development has resulted in the production of extensive quantities of harmful pollutants, including pesticides. During the last few decades, a wide range of water treatment technologies have been developed. Due to the high cost, hazardous by-product formation, and less efficiency of conventional methods, applying a simple and inexpensive adsorption process in the elimination of dangerous organic compounds is a promising solution [1]. Even more significant cost reduction can be achieved by using adsorbents synthesized from waste materials such as fly ash, a solid residue obtained from the energetic combustion of coal in power plants and thermal power plants [2].

The purpose of the presented research was to investigate the potential of fly ash-based NaX zeolite and NaX@C zeolite-carbon composite in the removal of 2,4-dichlorophenoxyacetic acid (2,4-D) from water. The materials were synthesized via the hydrothermal method and were subjected to modifications with 0.05 mol L<sup>-1</sup> and 0.1 mol L<sup>-1</sup> cetyltrimethylammonium bromide (CTAB). All samples were characterized in detail and the impact of 2.4-D solution pH (2-10), the temperature of the adsorption process (RT, 35 °C, 45 °C), and contact time between adsorbent and adsorbate (0-240 min) on the sorption capacities of materials was determined.

XRD patterns showed that the structure of pure samples was not affected by modifications with CTAB. The decrease in specific surface area and the increase in pore size were observed as well, which can be explained by the blockage of zeolite and composite small pores by CTAB. The studies concerning the pH of pesticide solution and temperature of the adsorption process revealed that these parameters influence the effectiveness of 2.4-D removal from water. The sorption capacities of the samples were the highest at pH 4 and room temperature. The reason are electrostatic attractions between the positively charged surface of NaX<sub>CTAB-0.05</sub>, NaX<sub>CTAB-0.1</sub>, NaX<sub>@</sub>C<sub>CTAB-0.05</sub>, NaX<sub>@</sub>C<sub>CTAB-0.1</sub>, and the negatively charged molecules of pesticide. The functionalization with CTAB contributed to the substantial increase in the sorption capacities of adsorbents. Applying CTAB at the concentration of 0.05 mol L<sup>-1</sup> was more favorable for the removal of 2,4-D than 0.1 mol L<sup>-1</sup> CTAB solution. The Langmuir model turned out to best describe the experimental data in comparison with the Freundlich model since the values of the R<sup>2</sup> coefficient were closer to 1. Research proved that the use of fly ash-based adsorbents in wastewater treatment is beneficial in terms of waste materials recycling and makes adsorption processes a viable alternative for the purification of water.

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#### Tetrahedron clusters serving as a platform For foam-like structure design

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There are number of exceptional examples indicating the unique position of tetrahedral symmetry in the vast landscape of different spatial organization pathways which can be sampled by matter. This work shows that the design and analysis of relatively simple tetrahedra clusters can lead to the formulation of a new type of dendritic structures together with unique periodic frameworks resembling clathrates and foams. A simple sequential protocol leading from regular tetrahedra clusters to more complex structural motifs can be employed to determine interesting repetitive building units. Accordingly, four different hierarchical superstructures are introduced, in which the dominant population of nodes are based on tetrahedral symmetry. The introduced architectures could be of particular interest for the field of regenerative medicine and metamaterial engineering.

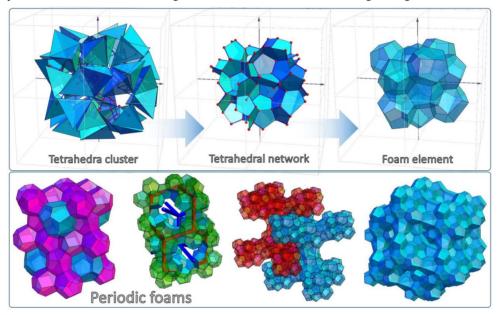


FIGURE 1. top) illustrates the sequence of foam-like unit formation from tetrahedron cluster, bottom) four different, periodic superstructures designed relying on tetrahedron clusters.

The simple algorithm employed here leads to remarkable dendritic objects, which alone would require separate and thorough studies. This work limits its analysis solely to the trivial  $G_5$  generation and hence there are number of additional questions to address, for instance i) what is the structural evolution of these dendritic objects for larger N? and ii) is there any repetitive structural motive observed for larger N?

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### Gold nanoparticles coated with a thin layer of polyaniline as a substrate in EC-SERS studies

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Surface-enhanced Raman scattering (SERS) involves a significant enhancement of the Raman signal when an analyte is placed on the surface of plasmonic nanostructures. Combining this technique with electrochemistry (EC-SERS) enables in-situ examination of differences in the spectrum under the influence of changing potential. Conductive polymers that can undergo reversible redox reactions have been used in EC-SERS studies [1], [2].

We synthesized gold nanoparticles surrounded by a thin layer of polyaniline (AuNPs@PANI) using a simple chemical method. The obtained composites were imaged using HR-TEM, and the EDS elemental map confirmed the presence of polyaniline on the gold surface. We examined the spectroelectrochemical properties of AuNPs@PANI on Screen-Printed Gold Electrode. Then we used them to detect hydrogen peroxide using EC-SERS and compared the effect of the addition of horseradish peroxidase on the detection limit.

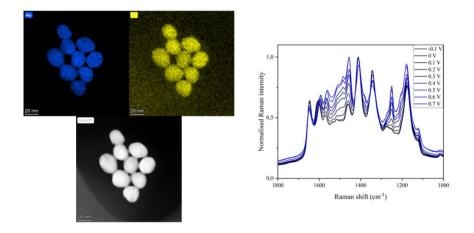


FIGURE 1. TEM images of gold nanoparticles covered with a PANI layer with EDS map of nitrogen distribution – yellow color and gold distribution – blue color (on the left). SERS spectra of AuNPs@PANI on gold working electrode as a function of the applied potential (on the right).

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#### Exploring the natural frequency effect of cantilevers in photo-flexo applications

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The flexoelectric effect is an intrinsic property of a material to create a current by the existence of a strain gradient in it (direct effect), or the existence of a strain gradient by applying an electric field (converse effect). The biggest advantage of this effect over the piezoelectric effect is not meeting a structural requirement - the flexoelectric effect is present in all crystalline materials. Moreover, this effect can be combined with photovoltaic (photo-flexo) or piezoelectric effect (flexopiezo) for much better performance. For instance, Z. Wang et al. proved that on a micro-scale, the applied local strain gradient enhanced the photovoltaic effect (open-circuit photovoltage increased) [1]. Another study has shown that lattice distortion, which assisted the strain gradient expansion in graphitic carbon nitride loaded with a single atom of Pt, enhanced the catalytic properties of about 23 times and increased the dye degradation reaction rate by about two times [2]. Doping of single crystals of semiconductors also increased their conductivity, which highly enhanced the flexoelectric coefficient [3]. In this work, we briefly report on the usage of flexoelectric materials' natural frequency mode that can induce the flexoelectric effect. Natural frequency is that one that occurs naturally when we disturb an object and cause its vibration - which causes the creation of a strain gradient in a material. Recent work reported that the thicker the sample, the smaller the flexoelectric response. Additionally, the frequency ratio is strictly dependent on the geometry of the sample (a/b), but independent of the thickness (a/h) [4]. The direct method of measuring the flexoelectric response has been recently established with great success [5]. Our idea is based on producing different length cantilevers, which will test the flexoelectric coefficient response. We expect to establish the optimal length and thickness of the single crystal samples for further application in flexophotovoltaic [6] or flexophotocatalysis [7].

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### 2K epoxy adhesives with electrochemically exfoliated graphite for joining magnesium fire protection boards

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The use of carbon nanomaterials as additives to polymers is a commonly used modification method. One of the interesting application areas of nanocarbons is the design of adhesives with their use [1,2]. Adhesives for joining magnesium fire protection boards used to protect reinforced concrete structures have been developed based on 2K epoxy resin. The composition of such adhesives, apart from almost 50 wt% of inorganic fillers, included 0.5, 1, or 1.5 wt% of electrochemically exfoliated graphite (EEG) synthesized from polycrystalline graphite in a process including oxidation, anion intercalation, and anodic exfoliation. The prepared adhesive compositions were characterized using selected methods of thermal analysis, such as differential scanning calorimetry, thermogravimetry, and cone calorimetry. The change in the value of the water contact angle (CA), surface free energy (SFE), and the color of the cross-linked adhesives (CIELab) were also assessed.

It has been shown that even the addition of 1.5 wt% of EEG does not contribute to a significant change in the analyzed properties of adhesive compositions. All tested variants were characterized by similar thermal stability. 5% weight loss occurred at 270-277°C for the reference sample and with 1.5 wt% EEG, respectively, and the glass transition temperature was approximately 130°C for all compositions. Interestingly, it was observed that the presence of EEG results in an increase in heat release rate. CA of 73-77° and SFE of approximately 44 mN/m were recorded. The color of the adhesives changed from L\* = 68.07,  $a^* = 0.43$ ,  $b^* = 6.50$  to L\* = 30.86,  $a^* = 0.02$ ,  $b^* = -0.30$ , which gives a color change of  $\Delta E = 37.83$ . Due to the above, it is planned to initiate further laboratory work on adhesive compositions obtained with the EEG content increased to 2.5, 5, and 10 wt%, repeating the tests performed and extending them with strength tests.

#### Acknowledgments

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### Carbon nanomaterials as components of anticorrosive epoxy-zinc primers

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Coating systems used for anti-corrosion protection usually consist of a primer, intermediate layers, and topcoats, i.e. primers. Zinc primers are commonly used in such systems, which not only serve as cathodic and barrier protection but also ensure good adhesion of such a system to the substrate. Due to the fact that the functioning of the abovementioned coatings is related to the conduction of galvanic current, these types of coatings are highly pigmented with zinc (up to 80 wt% in the dry coating). This may result not only in a deterioration of the performance of the coating system but also has a negative impact on the environment. Taking into account the above, anticorrosive primers with zinc content reduced to approximately 50%, containing graphene and carbon nanotubes, have been developed. The properties of the primers. The anti-corrosion properties of the composition were assessed using accelerated methods (salt spray tests and electrochemical impedance spectroscopy) and in the real marine environment, off the coast of the island of Heligoland (54°10′57″N 7°53′07″E) in the sea water splash zone. The key functional properties of the primers were also tested, such as adhesion to the substrate, flexibility, and hardness of the coatings.

It was confirmed that the developed compositions showed higher effectiveness in protection against corrosion compared to products available for commercial sale, and at the same time had a favorable system of functional properties. Primers with chemically treated zinc pigment had very good anti-corrosion properties both in laboratory conditions and in the natural marine environment, most likely due to its slower dissolution (which extends the period of cathodic protection) and improved compatibility of the pigment with the binder, which improves the barrier properties of the coating. Equally good properties were obtained for primers pigmented with zinc dust and carbon nanotubes. Coatings of this type provided cathodic protection to the substrates throughout the entire testing period.

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#### Large-scale photo-activated PDA/rGO nanofilms for electronics

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Polydopamine (PDA) free-standing films form on the air/water interface through the self-assembly of dopamine's oxidation products, creating a easily-transferable, large-scale films of nanometrical thickness [1]. This experiment aimed to use the synergy of properties within both PDA and reduced Graphene Oxide (rGO) to produce a nanocomposite freely transferable to virtually any surface. Our studies show unexpected electronic and photonic effects demonstrated by these films, opening new opportunities for advanced photoelectronics.

The one-pot synthesis method uses boric acid as both an essential part of rGO's reduction process [2] and an antioxidation agent improving PDA's mechanical properties [3]. After the synthesis, the PDA/rGO film's morphology was analyzed through XRD, SEM, AFM and its' chemistry through XPS, IR and Raman Spectroscopy.

The conductivity of the PDA/rGO films was examined through highly sensitive 4-Point Probe Measurements. The results revealed that the nanocomposite's conductivity decreases in a quantified and reversible manner under irradiation (8 mW/cm2) with UV and white LED light. Such behavior is attributed to the morphological and structural changes within the films driven by light actuation. Time-resolved reflectivity was used to examine the film's contraction and relaxation under on/off cycles of illumination. Unlike PDA alone [4], the PDA/rGO nanocomposite actuates mainly by thermal expansion, not by water adsorption/desorption. The film's response is much faster compared to PDA, which is essential for practical applications. Lastly, conductive AFM measurements revealed a complex electronic phase nanostructure with higher-conductivity domains adjacent to domains of lower, yet significant conductivity.

#### Acknowledgments

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### Investigating water effects on electroconductive carbon composites incorporating sodium carboxymethylcellulose

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Organic electronics is a rapidly evolving field that is characterised by continuous development. Conductive coatings, especially those containing carbon nanotubes (CNTs), are widely used in flexible electronic devices such as displays, heating surfaces, and sensors [1]. The literature [2,3] extensively discusses materials with excellent parameters that affect the dispersion of CNT, but many of them have drawbacks such as high costs, unnatural occurrence, or solubility in toxic solvents. Compliance with industrial and ecological standards is crucial in the search for environmentally friendly, biodegradable, water-soluble, and cost-effective composite CNT coatings produced by proven/scalable production techniques. The testing of coatings containing CNTs and sodium carboxymethylcellulose (NaCMC) meets these criteria. NaCMC effectively increases the dispersion of carbon nanomaterials in water due to the hydrophobic and hydrophilic groups it contains [4]. NaCMC glucose rings interact with CNTs through hydrophobic interactions, forming conjugates that limit CNT agglomeration due to van der Waals and/or electrostatic interactions [5]. The potential of the NaCMC/CNT suspension to create conductive layers was noticed, especially on cellulose substrates. The appropriate combination of NaCMC/CNT in aqueous suspensions is crucial to achieve optimal viscosity, structural stability, substrate compatibility, flexibility, and conductivity relevant for potential applications. Determining the influence of environmental factors, such as high air humidity and the presence of water, on the properties of the composite coatings produced is necessary to understand their behaviour in practical applications. Because of the high thermal stability and hydrophobicity of nanotubes, the selection of the appropriate concentration of NaCMC in the composite layer will be a key parameter that influences the physicochemical properties of NaCMC/CNT coatings in the presence of water, especially when used as very sensitive water sensors.

#### Acknowledgments

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#### **Optical properties of anisotropic subwavelength metal nanostructures**

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Structural modulations in metal surface reorders the collective oscillation of surface charges, resulting in the excitation of different types of plasmon resonance modes, as in a roughened metal surface the EM near field is focused on its rough tips, due to the localization of surface plasmon resonance in its sharp lateral cross-sections. Substrates decorated with metal nanoparticles(MNps) of different size, shape and arrangements exhibit tuneable (LSPR)localized surface plasmon resonance modes<sup>[1]</sup> and are most commonly used in surface enhanced spectroscopies specifically due to its high order of near field enhancement  $(10^{-15})$ . Percolated metal films with semi-continuous networks exhibit unique plasmonic properties with enhanced scattering cross-section. Percolation theory and its recent experimental studies of optical, electrical and morphological properties provided evidence of both localized and delocalized plasmon modes coexisting in near-percolated metal films<sup>[2]</sup>. In this poster we discuss the optical properties of non-percolated Au films deposited by electron beam evaporation in ultrahigh vacuum conditions onto uniaxial and biaxial transparent sapphire dielectric<sup>[3]</sup>. This causes the nucleation of Au clusters forming to self-assemble based on the template surface topography as anisotropic subwavelength metal arrays. We study the topographical and optical properties of these samples, and specifically analysis its dependence on light attributes such as polarization and wavelength. We understand and present the anisotropic plasmonic response of these samples. Further, these substrates with tuneable (LSPR throughout the visible -NIR region are highly beneficial in various applications such as meta-surfaces, optical filters, SERS sensing and on-chip communications.

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#### Bifunctional upconverting luminescent-magnetic FeS<sub>2</sub>@NaYF<sub>4</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> core@shell nanocomposites for temperature sensing

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In last years a significant development in optically acitve materials, especially in the field of bifunctional materials combining light-emitting properties with magnetic capabilities, has been made. This fusion of functionalities has greatly expanded the range of potential applications, *i.e.*, storage and transmission of data, bioimaging, sensing, and optical thermometry, which is crucial for cutting-edge technology [1-4].

Our research have focused on optimizing the synthesis of nano-sized FeS<sub>2</sub> as the magnetic core and NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> nanoparticles as the luminescent, temperature-sensitive shell. This core@shell nanocomposite material exhibits a bimodal, unique features of both core and shell components. Under 975 nm laser excitation, the synthesized materials *i.e.* NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> and FeS<sub>2</sub>@NaYF<sub>4</sub>:Yb<sup>3+</sup>,Er<sup>3+</sup> show characteristic Er<sup>3+</sup> emission bands as a result of up-conversion luminescence. Differences in the absorption properties of nanoparticles and nanocomposites influenced the luminescence properties e.g., the visible luminescence color. Furthermore, comparison of the magnetic properties between FeS<sub>2</sub> core nanoparticles and the synthesized core@shell nanocomposites confirms the potential application as a novel bifunctional luminescent-magnetic material.

Additionally, we compared the optical sensing properties of temperature for both, NaYF4:Yb<sup>3+</sup>,Er<sup>3+</sup> and FeS<sub>2</sub>@NaYF4:Yb<sup>3+</sup>,Er<sup>3+</sup>, nanoparticles and nanocomposites, revealing a very high relative temperature sensitivity of approximately 2.0%/K for both materials. The luminescence of both materials changes with increasing laser power density, and temperature conditions, providing laser-power and temperature-dependent color-tunable upconversion luminescence.

#### Acknowledgments

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#### Comparative Efficacy of Alternating and Rotating Magnetic Fields in Néel and Brownian Regimes for Hyperthermia Treatment

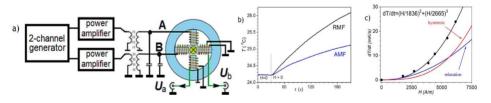
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This study evaluates the efficacy of rotating magnetic fields (RMF) compared to alternating magnetic fields (AMF) in the application of magnetic hyperthermia for cancer therapy, using magnetite nanoparticles sized at 10 nm and 20 nm. These sizes were specifically chosen to assess their heating responses under Neel and Brownian relaxation mechanisms, respectively based on the Raikher model [1].

Utilizing a patented, in-house built RMF system operating at 1-6 kA/m and 50-400 kHz, the findings reveal that RMFs provide twice the heating efficiency of AMFs across both relaxation mechanisms [2]. This consistent performance highlights RMF's potential for broader clinical applications, particularly in environments where environmental viscosity varies, making it a preferable option in clinical settings where uniform and effective heating is crucial. For this reason both ferroluid and ferrogels at the maximim stable concetration were tested, where dipol-dipol interactions can be minimised [3].

Additionally, the data from this study will help build simulations models aimed at improving the application of RMF in hyperthermia, making treatments more precise and effective. The research supports using RMF to potentially enhance the effectiveness and safety of hyperthermia treatments in medical practice.



(a) RMF generator featuring a dual-phase system powered by sinusoidal signals.

(b) Graphical comparison of the heating efficiencies between RMF and AMF

(c) Analysis of how relaxation and hysteresis contribute to the release of thermal energy under varying magnetic field conditions.

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#### Poly(methacrylate)s with nanometric polyhedral oligosilsesquioxane (POSS) units obtained by ATRP

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Polyhedral oligosilsesquioxanes (POSS) [1] with the empirical formula RSiO<sub>1.5</sub> are one of the most intriguing examples of well-defined, nanostructured moieties for the construction of high-performance, hybrid polymers. The first POSS-based polymers described in the literature were poly(methacrylate)s obtained by the conventional free radical polymerization (FRP) of (c-C<sub>5</sub>H<sub>9</sub>)<sub>7</sub>POSS-(CH<sub>2</sub>)<sub>3</sub>-MA and (c-C<sub>6</sub>H<sub>1</sub>)<sub>7</sub>POSS-(CH<sub>2</sub>)<sub>3</sub>-MA. The molecular weights of resulting poly((c-C<sub>5</sub>H<sub>9</sub>)<sub>7</sub>POSS-(CH<sub>2</sub>)<sub>3</sub>-MA) and copolymer reached Mn,GPC=117,000 (Mw/Mn=1.9), indicating that POSS-MA monomers can be readily polymerized. Due to their unique structures and high thermal stability (up to ca. 400 °C), the interest in such systems has arisen instantly. However, all further works employing FRP (in bulk or solution) or controlled polymerization methods provided only low MW macromolecules. Since high MW polymers with different types of POSS moieties could strongly enhance their mechanical and thermal properties, or facilitate the self-assembly of block copolymers, we decided to use POSS-methacrylates with various linkers and inert substituents bonded to silicon-oxygen cubes and investigate the possibility of the formation of poly(R7POSS-(Y)-MA)s with high polymerization degree obtained by atom transfer radical polymerization (ATRP) [2] - the method that gives a unique opportunity for the synthesis of systems with complex architecture and composition as well as different functionalization. Therefore, in this communication, we present the results of our studies which concern both synthesis and characterization of linear as well as star-like polymers with POSS moieties [3].

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### GO-AgNWs free-standing composite films for microwave electromagnetic interference shielding

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The ongoing progress in communications, broadcasting systems, and the electronic industry results in increased exposure to electromagnetic interference (EMI). The proliferation of electromagnetic waves pollution is attributed to the extensive use of electronic devices like mobile phones, Wi-Fi, and microwave ovens in everyday activities [1, 2]. The risk of EMI is especially highlighted for individuals with implanted active medical devices or profesionals working in close contact to this type of irradiation. EMI shielding materials with 30 dB shielding efficiency are deemed appropriate for commercial applications based on references. Therefore, there is a strong need for lightweight, elastic, stretchy, transparent, robust, and highly efficient shielding materials that are appropriate for textile manufacturing and equipment covering.

Presented work investigated composite materials made of graphene oxides (GO) [3] and silver nanowires (AgNWs) and their effectivenes as EMI shielding materials. Composites were generated from GO with sheet sizes ranging from 150 to 2000 nm and flake thicknesses between 2 and 5 nm. The average thickness of the free-standing films was approximately 14.8  $\mu$ m. The ratio of these nanomaterials was analysed to adjust the shielding effectiveness throughout a wide microwave frequency range up to 18 GHz. A shielding effectiveness of around 6.5 dB was recorded for the r-GO free-standing film.

#### Acknowledgments

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### The influence of the morphology of spherical-fibrous carbon composites on their functionalization and catalytic activity in glycerol etherification

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The global biodiesel market is expected to expand at a notable CAGR (compound annual growth rate) of 8.1% from 2023 to 2032, generating huge amounts of co-produced glycerol (Gly) that need to be managed. The demand for glycerol in traditional uses is, however, quite low, therefore finding new methods for its conversion is strongly justified for economic and environmental reasons [1].

Tert-butyl glycerol ethers (TBGEs), especially di- and tri-substituted ones (DTBGEs and TTBGE, respectively), are one of the most important glycerol derivatives that can act as promising "green" fuel additives. Importantly, these compounds are an excellent alternative to currently used methyl tert-butyl ether (MTBE) with questionable environmental neutrality.

Novel TBGEs production processes are usually performed in the presence of heterogeneous acid catalysts, preferably using tert-butyl alcohol (TBA) as an etherifying agent [2]. In the current work, a series of new acidic carbon-carbon composites (C-C) was prepared. In the first step, a glucose solution was hydrothermally treated at 180 °C for 8 h, washed, and dried. Next, the obtained product was carbonized at 500 °C yielding the carbon sphere (CS) sample which was further impregnated with Ni(NO<sub>3</sub>)<sub>2</sub> and calcined. The asprepared materials (1%, 5%, or 10%Ni/CS) were used in the CCVD (catalytic chemical vapor deposition) process applying isobutane (IB) as a carbon source, yielding C-C composites. Finally, the C-C samples were functionalized with sulfuric acid or generated in situ diazonium salt (BDS) and applied as catalysts for glycerol etherification with TBA. The process was performed at 110 °C under autogenous pressure, and the reaction mixtures were analyzed by means of a gas chromatography method.

Using x%Ni/CS samples for CCVD of IB resulted in the growth of carbon fibers (CF), finally producing CS-CF composites with different contributions of CF (higher for a higher Ni loading). The applied methods of CS-CF functionalization introduced sulfur or sulfur and oxygen groups into the structure of samples, generating also their acidity. The obtained materials showed different susceptibility to functionalization depending on the modifying agent used. The BDS-method had an advantage over the treatment with acid, introducing 2.45% of S into 10%Ni/CS-CF, while the modification with  $H_2SO_4$  introduced max. ~1.25% of S, significantly increasing, however, the sample total acidity.

All the prepared samples catalyzed the etherification of glycerol with TBA, and the samples' activity depended on their functionalization degree, specifically on the number of sulfonic groups introduced. The best results were obtained using the 5%Ni/CS-CF\_BDS catalyst, i.e., ~57% glycerol conversion, ~48.5% MTBGEs yield, and ~8.5% DTBGEs+TTBGE yield within 4 h. A selected BDS-modified sample was also found to be reusable without significant loss of activity.

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#### The influence of conditioning graphene oxide and its composites in solutions of different pH on their spectroscopic properties and the generated SERS enhancement

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In the 21st century, theoretical predictions about a two-dimensional graphene sheet have come true. This discovery earned the authors a Nobel Prize. Despite the researched properties, single-layer graphene is limited in its application due to the difficulty of creating specially organized structures.

Graphene oxide (GO) is an oxidized analogue of graphene that has been the subject of scientific research in the last decade. It has also been observed that it influences the enhancement of the Raman signal [1]. The combination of graphene oxide with noble metal nanoparticles additionally enhances the SERS signal, the magnitude of which is the result of the synergistic effect of two mechanisms: electromagnetic and chemical. Work in our research group has shown that conditioning graphene oxide in an ammonia solution affects the generated SERS enhancement [2].

Graphene oxide modified in solutions with different pH (equal to 1, 5.6 and 13) was used to create the substrates, as well as gold nanoparticles in the shape of nanobowls, which in previous studies showed a large impact on SERS enhancement [3]. The tested compounds were rhodamine 6G and folic acid with concentrations ranging from  $10^{-6}$  M to  $10^{-12}$  M.

Based on the conducted research, it was shown that conditioning affects the spectroscopic properties of graphene oxide. A composite consisting of graphene oxide modified at an acidic pH and gold nanoparticles enhances the spectra of rhodamine 6G and folic acid better than composites with graphene oxide conditioned at a higher pH. It was also shown that folic acid adsorbs on the composite surface differently - depending on the graphene oxide modification used.

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#### Phase transitions of water confined in nanoporous carbon

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This study presents a analysis of nanocarbon structures, focusing on activated carbon fibers (ACF). Our research delves into the behavior of water in both bulk and confined states within carbon nanopores.

We synthesize several mesoporous carbon samples basing on polymerization processes in different mixtures of resorcinol, formaldehyde and melamine. During the work we are studying crystalic structure, crystalic size pore size distribution of synthesized materials, then investigate the structure and dynamic of the confined liguid nanophases in this porous materials. For the characterization we used these technique: X-ray diffraction (XRD) SAXS, N2 adsorbtion measurement (BET), Raman spectroscopy and AFM

To achieve our objectives, we conducted experiments utilizing both dielectric and tensiometric methods. Dielectric tests enabled the examination of liquid behavior during the melting process and facilitated the determination of phase transition temperatures for both bulk and confined liquids within nanoporous matrices. Tensiometric analyses provided insights into the contact angle within the porous structure and facilitated the determination of the energy of interaction between pores walls and adsorbed water within the pores.

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#### The influence of purification and ion intercalation processes of MXenes onto their efficiency in photocatalytic hydrogen production

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Transition metal carbides and carbonitrides called MXenes, are well establisted family of two-dimensional (2D) materials, featured by unique combination of properties, namely electrical conductivity with hydrophilic surface. For this reason, the MXenes are widely investigated toward advanced application, ranging from energy storage systems to anti-cancer therapies, drug delivery systems, tissue scaffolds and many more. One of the scientific direction undertaken by our group is application of MXenes as a support for photocatalytic hydrogen generation system. In this system we deposited  $Co^{2+}$  cations on a model  $Ti_3C_2T_x$ MXene monolayers with the presence of Eosine Y and investigated the hydrogen evolution rate. Interestingly, the obtained values differed among various Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> samples. As we found, the critical issue was dispersion of the monolayers in obtained colloidal solution, which varied between the samples obtained by different purification routes or used intercalant agents. Therefore, we investigated obtained MXene samples by powder X-ray diffraction, scanning electron microscopy and Raman spectroscopy to find out, that the MXene's surface accessability for Co<sup>2+</sup> catalyst cations is a key factor to obtain efficient photocatalytical system. In this work we present the results of optimization of the purification and ion intercalation processes toward high quality MXene colloidal dispersion.

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#### Synthesis of platinum group metal nanoparticles in bioorganic systems

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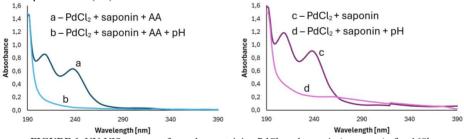
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Platinum group metals (PGMs), such as Pt, Pd and Rh, are considered critical raw materials due to their limited natural resources and high demand, making them the most expensive metals in the world. PGMs play a key role in automotive catalytic converters, neutralizing volatile organic compounds and nitrogen oxides ( $NO_x$ ). For this reason, the automotive industry is the main secondary resource of these elements. In a circular economy, the recovery and reuse of PGMs play an important role, which is why new, more environmentally friendly methods of producing catalytically active PGM nanoparticles (NPs) are being sought. Use of PGMs in the form of new catalytically active nanomaterials aligns with the European Commission's planned activities to enhance wastewater treatment efficiency of pharmaceuticals in the forthcoming years [1, 2].

The aim of the research was to study the influence of conditions (type of saponins, presence of an ascorbic acid (AA), pH) on the precipitation efficiency of PGM-NPs. For this purpose, four test systems were created with the following parameters:

- group I: PGMs precursor + saponin + AA,
- group II: PGMs precursor + saponin,
- group III: PGMs precursor + saponin + AA + pH regulation,
- group IV: PGMs precursor + saponin + pH regulation.

After precipitation, the samples were analyzed using atomic absorption spectrometry (AAS) and UV-VIS spectroscopy (after 1, 24, 48, 168 h). Using Na<sub>2</sub>CO<sub>3</sub> as a pH-controlling agent (~7) allowed to obtain much higher PGM precipitation efficiency compared to systems without pH control (~2).





#### Acknowledgments

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### Effect of functionalized gold nanoparticles on biological membranes in biomimetic systems

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Gold nanoparticles (Au-NPs) are extensively utilized throughout scientific research. Due to their biocompatibility, low cytotoxicity, and antibacterial effect, they possess medicinal and pharmaceutical applications [1,2]. Exploration into new and unique applications of Au-NPs requires a comprehensive examination of their effects on living organisms. Therefore, our studies were conducted on a molecular level to determine the impact of Au-NPs on the properties of lipid monolayers constituting model biological membranes. This was achieved using the Langmuir technique, which is widely accepted as a typical two-dimensional surface chemistry method for studying the structures and properties of lipids, proteins, and surfactants. This approach is considered an alternative to experiments on living cells, as it generates analogs of biological membranes. Moreover, it provides qualitative information regarding the influence of substances on the phase state, fluidity, and morphology of the model biomembranes [3].

Our research involved the production of monolayers consisting of lipids and Au-NPs covered with polyethylene glycol at the air-water interface. During monolayer formation, the dependence of the surface pressure ( $\pi$ ) on the surface area per single molecule (A) was recorded. Additionally, Brewster angle microscopy (BAM) imaging was performed during compression. The influence of Au-NPs on the stability of lipid monolayers was also examined via relaxation studies, where the mixtures consisting of Au-NPs and lipids were applied to the surface of the aqueous subphase. Then, the monolayer was compressed to a surface pressure of 30 mN·m<sup>-1</sup> and changes in the relative surface area per molecule in the monolayer were recorded at a constant pressure value.

The obtained results showed that the presence of Au-NPs affected the properties of model biological membranes. Furthermore, the components of individual monolayers mixed at the air-water interface and monolayers containing Au-NPs were less stable than lipid monolayers.

#### Acknowledgments

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#### Semitransparent heterojunction based on the hydrogenated nanotubes decorated with bissulfides – relation between synthesis conditions and the electrochemical performance

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Nowadays, growing environmental awareness and the need to reduce greenhouse gas emissions impose an urgent need to use renewable energy sources. In this context, solar energy is becoming an increasingly attractive alternative, but the key challenge remains the efficiency of converting sunlight into electricity. This is why focusing on the search for materials with the highest possible light absorption becomes crucial for the future of photovoltaic development. Research on titanium nanotubes, modified with different metal sulfides, like bismuth sulfide, is aimed at formation of heterostructures able to efficient sunlight absorption and separation of photogenerated charge increasing the overall conversion efficency. In order to obtain uniform distribution of sulfides over the hierarchical nanostructure, successive ionic layer adsorption and reaction method known as SILAR can be adopted. This route is considered as facile, does not require any sophisticated equipment, and enables to verify the impact of different processing conditions like, concentration of precursors, amount of the sulfide or the post-treatment onto the heterojunction performance.

Herein, titanium nanotubes (NTs) formed on ITO glass substrates that ensures semitransparency act as a hierarchical platform for sulfide deposition while bismuth sulfide were used as a decorating compounds. On the contrary to typical calcination in air, as-anodized titania was treated in hydrogen atmosphere ensuring oxygen vacancies affecting its conductivity and optical properties. The deposition of sulfides was realized via SILAR when ITO with nanotubes were immersed step by step in solutions providing metal and sulfur ions. To investigate the influence of processing parameters, the number of SILAR cycles, solution concentration and the solvent (water, ethanol, methanol, 2-methoxyethanol) were studied. Finally, the heterostructure was annealed in argon atmosphere at 250°C.

Characterization including UV-vis and Raman spectroscopy confirmed the presence of titanium nanotubes as well as embedded sulfides. Morphology studies using SEM show the organized arrangement of titania and further changes after SILAR treatment. The electrochemical results revealed that in consequence of sulfide deposition from various concentration of precursors, the material's activity both in dark and under irradiation can be controlled. This is particularly evident in the sample of a 70 mM solution of bismuth sulfide using 30 cycles, which exhibited the highest electrochemical capacity. The collected results suggest the importance of selecting not only the number of cycles but also the concentration of the solution for the SILAR process.

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# SECTION B NANOBIOMEDICINE



#### Nanoparticle cell uptake and distribution: From the single particle to the cell population level

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How nanoparticles interact with human cells is important for many applications, ranging from drug delivery using nano-sized carriers, to controlling the risk posed by inclusion of nanoparticles in consumer products. It is of particular importance to understand the uptake and subsequent intracellular distribution, as the local dose will determine most effects, whether they be beneficial or hazardous. Here we will discuss quantitative measurements of the uptake and intracellular distribution of model polystyrene nanoparticles at three different levels: At the single particle level [1], we observe adsorption of nanoparticles to the cell membrane, with most nanoparticles rapidly desorbing again (~within seconds). A minority of nanoparticles, however, are internalised by cells and they are internalised surprisingly rapidly (~seconds), something we interpret to stem from non-specific internalisation. At the single cell level, subsequent distribution within the cell occurs much slower (~hours) and mainly along the endo-lysosomal pathway [2]. At the cell population level, the accumulation of nanoparticles by cells becomes coupled to the cell-division-cycle at longer timescales (~day), something that can be well understood using kinetic models [3]. In general, there is a large cell-to-cell variability, even for cells within the same population, stemming from variability in cell size, genetics and other effects [4]. Overall, our results demonstrate the uptake and intracellular distribution of nanoparticles at different length scales (single particle to cell population) and time scales (seconds to days).

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### Bioconjugates of photon-upconversion nanoparticles for single-molecule assays and imaging

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Photon-upconversion nanoparticles (UCNPs) are lanthanide-doped nanocrystals that exhibit anti-Stokes luminescence, enabling their detection without optical background interferences. Therefore, conjugates of UCNPs with biorecognition molecules are well-suited as labels in immunochemical assays and imaging. Our work explores different ways of modifying the surface of UCNPs and employs their conjugates to develop immunoassays for a wide range of analytes, from small molecules to bacteria. As part of our research on cancer biomarker detection, we developed a single-molecule immunoassay for prostate-specific antigen based on counting individual immunocomplexes under a wide-field epiluminescence microscope (Figure 1a) [1]. This work was followed by transferring the assay from the surface of a microtiter plate to magnetic microparticles for sample preconcentration [2], and we are currently studying different approaches for high-throughput single-molecule counting in microfluidics. Furthemoore, we have employed the UCNP bioconjugates for high-contrast labeling of HER2 biomarkers on breast cancer cells (Figure 1b). Due to the insignificant optical background and low non-specific interactions, the upconversion readout provided a superior signal-to-background ratio compared to the fluorescence-based detection [1].

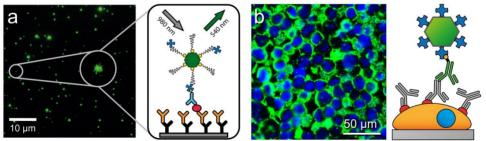


FIGURE 1. Upconversion microscopy images and schemes of immunocomplexes corresponding to (a) microtiter plate after binding of prostate-specific antigen and (b) section of a BT-474 cell pellet with labeled HER2 biomarker (green – upconversion, blue – DAPI).

#### Acknowledgments

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#### Remodeling and Sensing of Lipid Membranes using DNA Origami

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Biological lipid membranes play an important role in cells, as they define the boundary between the interior and exterior of organelles and the cell itself, and serve as support for many proteins involved in key biological functions. Understanding the biophysics of membrane remodeling and how to recognize membrane properties, such as phase separation or curvature, is therefore crucial, as this knowledge can be used to develop even more active molecules that can better target lipid bilayers. Using nanotechnology approaches, we aim to decipher and artificially recreate minimal features of membrane-active systems and develop novel devices and tools to identify intrinsic membrane properties as potential targets for biomedical applications. To this end, we utilize DNA origami, an emerging technique that explores nucleic acids and their intrinsic properties for the development of customized devices and materials with sub-nm precision and improved functionality. Here, we have successfully combined DNA origami with lipid membranes [1], pioneering the development of biomimetic membranebinding and triggerable membrane-active origami devices.

For example, we are exploring ways to manipulate the localization of lipid anchorfunctionalized DNA origami in different membrane environments, to gain more insight into phase-separated lipid domains and mimic membrane trafficking in a controlled manner. To elucidate the minimal physicochemical requirements for membrane bending, we also constructed curvature-inducing DNA origami nanostructures that follow the putative design features of scaffold proteins and filaments for membrane remodeling. In particular, we constructed curved BAR protein-like DNA origami structures [2] and filament-forming cytoskeleton-like origami structures [3] and investigated their ability for membrane binding and remodeling. Overall, we showed that DNA scaffoldings can indeed reproduce the activity of membrane shaping proteins, depending on curvature, oligomerization state, membrane affinity and surface density. Finally, we have also developed a series of DNA origami structures [4] that can sense different membrane curvatures using fluorescence resonance energy transfer as a transduction mechanism at the single molecule level.

Overall, the various biomimetic and nanotechnological strategies here developed open new avenues for mapping membrane properties and deciphering common principles underlying membrane remodelling; highlighting the unique advantages of DNA origami in the field of lipid membrane biochemistry and biophysics.

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#### Atomic scale structural and physical properties of nanoparticles

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The first stage of the presentation consists of reviewing the main questions relating to the structural and magnetic properties of nanoparticles in correlation, on one the hand, with their size, the morphology, and chemical composition and, on the other hand, with their applications, particularly in biomedicine. The second step is to study the structural nature of the surfaces to understand their role in magnetic properties.

To illustrate this strategy, we discuss a few examples based on results established on different types of "full" nanoparticles and hollow nanoparticles. Thus, we report experimental results obtained particularly using <sup>57</sup>Fe Mössbauer spectrometry, a local probe technique well suited to the study Fe-containing nanostructures, in addition to usual techniques (X-ray diffraction, transmission electron microscopy, magnetic measurements, ...), and computer modelling data, the combination of which makes it possible to describe the structural surface at the atomic scale.

#### Self-assembled Nanoparticles in Clam Soup: Secret behind Traditional Chinese Medicine and Mediterranean Cuisine

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The naturally occuring food nanoparticles (FNPs) were identified from soup made from the freshwater clam (*Corbicula fluminea Muller*), a renowned remedy for fatty liver and hepatitis in China and East Asia. Their hydrodynamic diameters and  $\zeta$ -potentials were from 50 to 70 nm and from -10 to -28.0 mV. The clam soup nanoparticles (CFNPs) contained  $\alpha$ type heteropolysaccharides, proteoglycans and phytosterols, and are resistant to pH and enzymatic hydrolysis but responsive to temperature.<sup>[1]</sup> They effectively inhibited cellular cholesterol uptake *in vitro*<sup>[1]</sup> and hyperlipidemia *in vivo*.<sup>[2]</sup>

Resveratrol (Res) from grape/wine is renowned for its their antioxidant and health promoting functions. However, low bioavailability of Res makes its health claims questionable. Steamed clam with wine, a popular Mediterranean delicacy, may facilitate the Res to be encapsulated in the FNPs of clam soup and subsequently gain better stability and bioavailability. Aiming to shed lights on this, this study demonstrated that CFNPs can effectively encapsulate Res (efficiency>70%) and enable desirable controlled-release of Res, which fits both first and Higuchi order kinetics. CFNPs-Res exhibited an improved oxidant stability, retaining over 90% of antioxidant capacity after 3-d storage at ambient temperature. CFNPs-Res showed a significantly higher bioaccessibility and antioxidant retention in the simulated gastrointestinal digestion than the wine Res and free Res. The discovery and use of food derived nanoparticles to carry micronutrients and antioxidants could lead to a paradigm shift in functional food design and nutritional advice, advocating the transformation of therapeutic-centric model of disease prevention towards a Food-First Strategy.

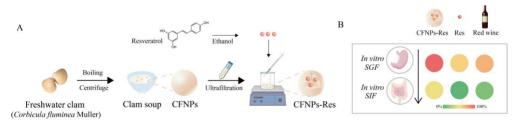


FIGURE 1. Graphic abstract. (A) Preparation of the freshwater clam soup nanoparticles (CFNPs) and CFNPs-Res. (B) Retention of antioxidation capacity of Res, CFNPs-Res and wines during *in vitro* simulated digestion.

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#### A Paradigm Shift: The Role of AI and Morphological Profiling in Shaping Early Drug Discovery

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The Traditional Drug Discovery process is time-consuming and costly. It typically takes from 12 to 15 years and costs around 2.5 billion dollars to bring a new drug to the market. This high cost is primarily due to a significant rate of failure, with only  $\sim$ 10% of early drug discovery projects progressing to the clinical phase. Furthermore,  $\sim$ 90% of potential drugs are subsequently rejected at later stages of development due to issues such as lack of efficacy, off-target activity, or toxicity [1].

In this context, artificial intelligence (AI) appears as a transformative force, offering opportunities to revolutionize every stage of the drug discovery pipeline with a promise to develop new treatments faster and cheaper. For over a decade, machine learning and other AI methods have been employed for target identification and validation, design of small molecules or antibodies, virtual screening, as well as lead optimization, activity, and toxicity prediction [2]. The field continues to evolve, enabling researchers to analyze vast datasets, uncover hidden patterns, and generate actionable insights at an unprecedented scale and speed.

AI-driven approaches are particularly well-suited for leveraging information encoded in High Content Screening (HCS) images, providing a means for morphological profiling. Specifically, the phenomics method based on the Cell Painting imaging assay, developed by the Anne Carpenter Lab at the Broad Institute, is gaining increasing attention in academia and the pharmaceutical industry. The assay utilizes six fluorescent dyes to stain eight cellular compartments, enabling visualization of cell morphology in a target-agnostic manner [3]. Subsequently, thousands of morphological measurements per cell are extracted through automated image analysis pipelines and used to generate phenotypic signatures, enabling detection of even subtle alterations in cell phenotype that are often not visible to the human eye. During the presentation, we will explore how morphological profiling can be applied to predicting the mode of action, on-target and off-target small molecule activity, as well as for image-based virtual screening and hit identification and triage. Additionally, we will discuss the impact of this technology on the early stages of drug discovery.

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# Bioinspired and green approaches based on nanozyme 2D materials beyond graphene to address new challenges in health and environment.

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Bioinspired nanomaterials with intrinsic enzyme-like properties are referred to as nanozymes. The exploitation of the properties of graphene-based nanozymes, which exhibit excellent optical, mechanical, and biological properties, can open new routes in the fields of tissue engineering, e.g., to study and guide neural growth and differentiation, as well as in nanomedicine applications, e.g., wound healing and antitumour therapy, and sustainable environmental management.

Here two case studies will be illustrated. The first one is about scrutinizing the nano-bio interface between the cell membrane and hybrids made of graphene oxide (GO) nanosheets functionalized with neurotrophin-mimicking peptides, to exploit their potential for targeting neurodegenerative diseases as well as angiogenesis [1]. The hybrid peptide-GO systems were assembled by spontaneous physisorption onto GO nanosheets of peptide sequences mimicking the Brain-Derived Neurotrophic Factor, the NeuroTrophin 3 and the Nerve Growth Factor, respectively. The interaction of peptide-GO nanoplatforms with artificial cell membranes was analyzed both in 3D and in 2D, by utilizing model phospholipids self-assembled as small unilamellar vesicles or planar-supported lipid bilayers, respectively. The experimental physicochemical characterizazion, by UV-visible, FTIR and Raman spectroscopies, TEM, AFM, zeta potential and DLS was paralleled by MD computational analyses. Proof-of-work *in vitro* cellular experiments with undifferentiated neuroblastoma, differentiated (neuron-like) neuroblastoma, and human umbilical vein endothelial cells were carried out to shed light on the capability of the peptide-GO nanoplatforms to stimulate the neurite outgrowth as well as tubulogenesis and cell migration.

The second case study concerns hybrid nanocomposites of 2D GO/palladium nanoparticles (PdNP) for application in anticancer tumor and [2]. Various spectroscopic and microscopic analyses as well as theoretical DFT calculations were carried out for the physicochemical characterization of the samples. The functional properties of the GO/Pd hybrids were tested in terms of photocatalysis experiments of  $H_2$  evolution and photothermal response.

The assessment of nanozyme features for the GO/Pd nanoplatforms unveiled a strong enhancement of hydrogen evolution and broad antioxidant activities, as revealed by photocatalysis experiments of glycerol photoreforming, MitoSOX and SOD-like activity, respectively.

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#### Multifunctional nanoparticles enhanced hydrogels for wound healing

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In recent years, various types of nanoparticles (NPs) and polymers have been employed to build nanocomposite hydrogels. The resulted nanocomposite hydrogels have exhibited mechanically tough [1], stimuli response [2], micro fabricated structure [3, 4], and adhesive properties [4]. Those hydrogels have been used in regenerative medicine, drug and gene delivery, biodevices and biosensors, wound healing, and so on. In the past several years, we have developed a library of multifunctional NPs that are encapsulated in the hydrogel or knotted in the hydrogel to form versatile biopatches for wound healing. The resulted hydrogels possess several distinct advantages:

1) The precise regulation of gelation time and mechanical strength within a wide window.

2) The swelling and degradation of IHs can be regulated by the chemical structure of polymers and NPs.

3) The sensitive hydrogels can be convenient upgraded through the optimization of NPs.

4) The electrical, optical, and biological properties of the resulted hydrogels can be endowed by the changes of NPs. In this report, I will introduce the recent research progress in my lab based on NPs enhanced hydrogels, and exhibit the various applications of those NPs enhanced hydrogels in biomedicine.

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# SECTION B NANOBIOMEDICINE





# Novel virus-like particle arrays for biosensing applications based on surface lattice resonance

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Severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2) that causes COVID-19 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. Nowadays, there are two widely used methods: molecular diagnostics and serologic test. The first one is considered to be a very sensitive, but time-consuming, whereas the second is fast and simple but cannot be applied for early COVID-19 diagnosis. Thus, there is a need for developing new methods that would provide fast and reliable detection of viruses [1,2].

Surface-enhanced Raman scattering (SERS) is a powerful analytical technique used in chemistry, pharmacology, and biomedicine for studying biological systems, e.g. proteins, tissue, bacteria, and viruses. This method, based on the appearance of the so-called localized surface plasmon resonance (LSPR) in noble metal nanostructures that amplies vibrational signals from the analyte deposited onto them, deserves consideration when it comes to biodetection due sensitivity towards even nanomolar concentrations of biomolecules, such as viral particles or biomarkers, with the measurements being performed in a lable-free way [3].

With the use of the capillary-assisted particle assembly (CAPA) [4], we have prepared an innovative matrix composed of SARS-CoV-2 virus-like particles (VLPs) characterized by the presence of the LSPR in the gold cores and the surface lattice resonances (SLR) related to the periodic arrangements of particles. The SLR further amplifies the SERS signals originating from molecules specifically binding to VLPs, making the fabricated system suitable for applications in ultrasensitive biodetection [5-6].

#### Acknowledgments

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#### Micro/nanopatterning of conductive polymers for advanced biointerfaces

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Conductive polymers (CPs) and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) in particular have emerged as promising materials for biomedical applications, including neurotechnological ones, due to their unique properties, namely mixed ion-electronic conduction, high processability in water and biocompatibility, and low impedance [1]. In this talk, I will show the possibility of exploiting both the conductivity and micro/nanopatterning of PEDOT:PSS to promote neuronal development in vitro and to fabricate highly flexible functional neural interfaces for brain recording. In particular, I will describe the design of PEDOT:PSS substrates that exhibit nanomodulated surface topography that can promote neuronal proliferation and differentiation and guide neurite elongation, especially under electrical stimulation (Figure 1a) [2]. These features are highly desired to promote neural tissue repair in cases of trauma and diseases of central and peripheral nerve tissue. Then, I will report on the fabrication of ultra-flexible PDMS-based µEcoG multielectrode arrays (MEAs), where the integration of 3D micrometric pillars of PEDOT:PSS [3] allows for the achievement of ultra-low impedance and high softness of the electodes. These micropatterned MEAs have been shown to correctly record somatosensory evoked potentials (SEPs) in rat model with a high signal-to-noise ratio (SNR), confirming the advantages of CP micropatterning in the field of neural recording (Figure 1b).

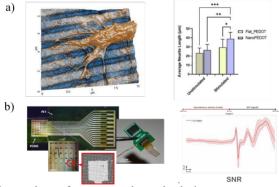


FIGURE 1. Detail of a growth cone from a neuronal axon developing on nanopatterned PEDOT:PSS (a, left) and neurite length upon cell electrical stimulation (a, right). "Neuropillar" device for electrocortical recording featuring micropillar-based microelectrodes (b, left) and a typical SEP trace recorded in rat model.

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# Effects of lipid liquid nanocrystalline nanoparticles on murine macrophage cell line

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Macrophages are believed to be plastic immune cells that respond to microenvironmental stimuli by changing their phenotype. Classically activated (M1) cells express markers such as CD11b, CD11c, iNOS, Gpr18, Fpr2 [1] and play an essential role in the process of inflammation. Alternatively activated (M2) express CD206, c-myc, or Arg1 markers and participate in pathogen clearance, tissue repair, and regeneration Earlier studies have shown that a variety of nanoparticles can induce a particular phenotype or lead to a repolarization of the existing one [2]. In this study, we intended to investigate the effects of LLCNPs on the murine macrophage cell line on viability, phenotype induction, and repolarization.

Lipid liquid nanocrystalline nanoparticles were synthesized with glycerol monooleate (GMO) as a structure-forming lipid, modified with cationic lipid DODMA, 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.

RAW 264.7 cells were incubated with increasing concentrations of LLCNPs for 24 and 48 hours to assess their impact on viability by the WST-1 test. The ability of LLCNPs to polarize and repolarize cells was investigated on M0, IFN- $\gamma$ , and LPS-induced M1 as well as IL-4 and IL-10-induced M2 macrophages. The expression of respective markers was confirmed by real-time PCR.

The obtained results will give us a novel insight into the therapeutic potential of LLCNPs.

#### Acknowledgments

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## The antibacterial and antifouling properties of nano-enhanced membranes for hemodialysis

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Integrating metallic nanoparticles into polymer matrices represents an emerging trend in membrane modification [1]. This approach offers a multitude of potential advantages, including the enhancement of thermal, chemical, and mechanical stability of modified polymers. This enhancement contributes to the durability and longevity of the membrane, ensuring sustained performance over extended periods. Moreover, one of the most compelling advantages of incorporating metallic nanoparticles is their antibacterial properties and biocompatibility [2-3].

The objective of this study is to evaluate the antifouling, antibacterial, and mechanical properties of cellulose acetate membranes after modification with silver oxide nanoparticles synthesised in situ within the polymer matrix. The novelty of this work lies in the fabrication of membranes that exhibit excellent biocompatibility and stability while also possessing bacteriostatic properties against *S. aureus*.

#### Acknowledgments

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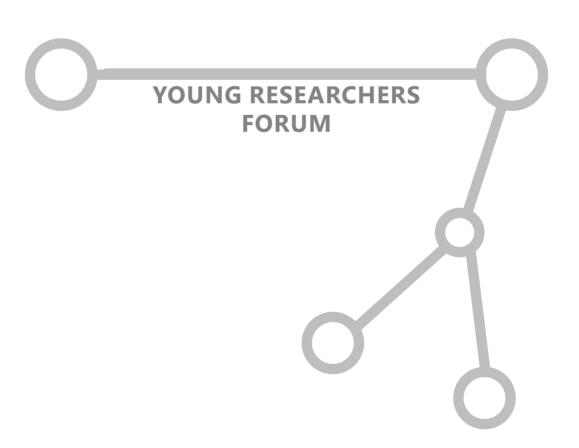
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# SECTION B NANOBIOMEDICINE



### Nano-armor against pathogens: exploring the antibacterial potential of bismuth selenide nanoparticles

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Bismuth selenide nanoparticles have emerged as promising candidates for various biomedical applications due to their unique physicochemical properties. In this study, we explore the antibacterial potential of bismuth selenide nanoparticles against pathogenic bacteria [1][2]. The primary objective of this research is to evaluate the antibacterial efficacy of bismuth selenide nanoparticles and understand the underlying mechanisms of their antibacterial activity. Bismuth selenide nanoparticles were synthesized using sol-gel and hydrothermal methods and characterized using techniques such as scattering electron microscopy (SEM), Xray diffraction (XRD), ultraviolet visible spectroscopy (UV-vis), and Fourier transform infrared spectroscopy (FTIR). The antibacterial activity of nanoparticles was assessed against bacterial strains, including Gram-positive and Gram-negative bacteria, using the disk diffusion method [3]. Our results demonstrate that bismuth selenide nanoparticles exhibit potent antibacterial activity against both Gram-positive (e.g., Staphylococcus aureus) and Gramnegative (e.g., Escherichia coli) bacteria. The antibacterial efficacy was found to be sizedependent on nanoparticles. This study highlights the significant antibacterial activity of bismuth selenide nanoparticles and underscores their potential as novel antimicrobial agents. Further investigations into the mechanisms of action and in vivo efficacy of bismuth selenide nanoparticles are warranted to fully elucidate their therapeutic utility in combating bacterial infections.

#### Acknowledgments

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#### Simultaneous detection of serotonin and sertraline with surface-enhanced Raman spectroscopy (SERS) for potential clinical application

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One of the most challenging aspects of the treatment of clinical depression is the slower onset and variability in the efficiency of the prescribed drugs.[1] An important tool on the path toward personalized medicine in psychiatry is the development of a robust, reliable, and fast method capable of clinical monitoring of relevant biomarkers such as neurotransmitters and antidepressants.

In this work, we employed a novel plasmonic gold-nanocone-based substrate for SERS detection of the neurotransmitter serotonin and antidepressant sertraline from artificial cerebrospinal fluid. The achieved limit of detection for sertraline, 90 ng/mL, is one order lower than its clinically relevant levels. The limit of detection for serotonin is 30 ng/mL, which is relevant to whole-body levels of serotonin. An example of the analyzed results describing a multiplex detection of serotonin and sertraline can be seen in Figure 1. These results support the potential of our approach for clinical SERS monitoring of neurotransmitter and antidepressant levels.

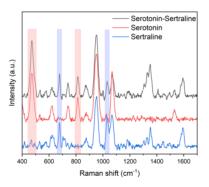


FIGURE 1. SERS spectra of serotonin, sertraline, and an equimolar mixture of serotonin-sertraline from artificial cerebrospinal fluid.

#### Acknowledgments

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#### GMO@DTPA-BSA-Gd lipid nanoparticles as new class of gadoliniumbased contrast agents for Magnetic Resonance Imaging

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Contrast agents are used in magnetic resonance imaging (MRI) to improve the visibility of the details of the organ structures. Gadolinium-based contrast agents (GBCAs) have been utilized in MRI since 1988. However, there are concerns regarding their safety due to releasing toxic  $Gd^{3+}$  ions. To date, no substitute for MRI imaging has been found that provides the same benefits as GBCAs due to the paramagnetism of gadolinium [1]. The challenge, however, involves developing GBCAs that possess improved relaxivity, do not release toxic  $Gd^{3+}$  ions, exhibit targeted and/or activated effects, have high intracellular uptake, and have favorable pharmacokinetics and pharmacodynamics. One promising direction is the use of Gd-chelating lipids to create matrix lipid nanocarriers to enhance the relaxivity properties of Gd-chelate which also allows for to reduction of the  $Gd^{3+}$  amount in medical imaging [2].

The primary objective of the study was to prepare lipid nanoparticles utilizing glycerol monooleate (GMO) as the structure-forming lipid and gadolinium chelating lipid (DTPA-BSA-Gd) as the contrasting providing molecules, at various concentrations. Further, the effect of DTPA-BSA-Gd on the physicochemical properties of the formed lipid nanoparticles, such as particle size, long-term colloidal stability, and morphology, was investigated and followed with the biocompatibility tests. Additionally, the Gd loading efficiency and total Gd ion concentration in the samples were determined. Finally, the effectiveness of the prepared lipid nanoparticles as a contrast agent in magnetic resonance imaging was studied using relaxometry measurements and MR imaging.

The results demonstrated that prepared lipid nanoparticles exhibited a highly ordered structure for low (5 wt.% to GMO) DTPA-BSA-Gd content. However, despite the self-assembly process having been strongly interrupted in the samples with high DTPA-BSA-Gd content (30, 40, 50 wt. %), their relaxometry performance was satisfying. The advantages of the prepared GMO@DTPA-BSA-Gd nanoparticles allow us to conclude that they may be considered as a new type of MRI CAs with further potential for the development of multifunctional systems combining diagnostics and therapy in a single system.

#### Acknowledgements

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#### Application of Silica Nanoparticles for Cellular Senescence Detection

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Cellular senescence is implicated in the pathogenesis of various age-related diseases, such as cancer, as well as in normal tissue development and regeneration. A commonly used method to detect cellular senescence is the senescence-associated beta-galactosidase assay technique (SA- $\beta$ -gal). Beta-galactosidase activity is higher in senescent cells compared to non-senescent cells, as this enzyme is predominantly found in the lysosome where it catalyzes the breakdown of galactose-containing carbohydrates [1].

Based on our previous work where we found out that senescent cells accumulate silica nanoparticles (SiNPs) unlike proliferative cells that can dilute with each division [2], we tested the hypothesis that the detection of senescent cells can be improved by using fluorescent Silica Nanoparticles (SiNPs) that can simultaneously detect the growth arrest and SA- $\beta$ -Gal +.

We used SiNPs with a rhodamine dye permanently embedded into their core structure and a fluorogenic substrate called fluorescein Di- $\beta$ -D-galactopyranoside (FDG) on their surface. FDG acts as a substrate for  $\beta$ -gal and is activated in cells with high levels of this enzyme, producing a green fluorescence with green spectral properties [3].

In our approach, we employed a click chemistry method, leveraging the presence of free amino groups on the silica nanoparticles' surface. For the conjugation process, we utilized a linker called PFB-FDG, which is FDG linked to a polyfluorobenzoyl (PFB) group. Additionally, we activated the modified SiNPs with  $\beta$ -galactosidase and the obtained activation serves as a starting point for further in vitro and in vivo studies.

#### Acknowledgments

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### Nanoscale structural response of biomimetic cell membranes to controlled dehydration

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The genesis of phase separation and the dimensions of the resulting ordered phase domains are influenced by a dynamic interplay of molecular interactions between membrane constituents, among them we can distinguish lipid-lipid, and lipid-protein interactions. Moreover, membrane segregation into phases is affected by external-environmental factors such as temperature, pH, or hydration. Here, we focused on the last factor, which is the presence of water - molecules indispensable for sustaining life in all organisms.

In this research, we undertook the challenge of unraveling the nanoscale structural response of the phase-separated SLBs to a wide range of hydration conditions. Fluorescence microscopy imaging revealed significant change in the shape of the  $L_0$  domains, which with lowering the hydration were characterized by a more jagged perimeter and decreased circularity. The analysis of the intensity of  $L_d$ -labeling fluorescent probe DOPE-Atto 633 within  $L_0$  phase regions, pointed out towards increased migration of lipids forming  $L_d$  phase inside membrane domains. To overcome the diffraction limit of the fluorescence microscope and investigate the nanoscale structural reorganization of the membrane, we performed AFM measurements. The decreasing of the membrane hydration state led to an enhanced mixing of lipids forming the  $L_d$  phase with those composing the  $L_0$  phase, which was 2-fold lower for completely desiccated membrane than for fully hydrated. This was associated with a 3-fold decrease in the line tension. Importantly, this process was entirely reversible, and upon subsequent rehydration, the height mismatch returned to its initial value.

It should be noted that this research is novel in two areas: science and engineering. First of all, it broadens our understanding of processes that require transient, local dehydration of the cell membranes, such as endo- and exocytosis, viral entry, fertilization, and various cell fusion events. Secondly, it highlights a new methodology of AFM measurements under varying hydration conditions, which can successfully be applied to study other model cell systems.

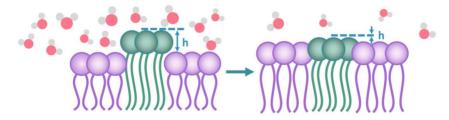


FIGURE 1. The decrease in the membrane hydration state leads to the reduction of the hydrophobic mismatch between  $L_d$  and  $L_o$  phase.

#### Synthesis and characterization of gadolinium oxide hollow spheres as a drug carrier for doxorubicin

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The gadolinium oxide nanospheres are a promising material for biomedical applications. Their paramagnetic behaviour and surface modification properties make them potential candidates for use as multifunctional drug or biomolecule carriers [1]. Doxorubicin is a drug widely used in cancer therapy. Although, it is a hydrophobic compound with non-specific *in vivo* distribution. Consequently, researchers seek protective and target-specific drug delivery systems with high drug loading capacity, criteria that nanocarriers meet [2]. Achieving a predetermined porosity level is crucial for materials intended for further drug loading and enhancing their effectiveness as drug delivery systems [3].

In this study, gadolinium oxide spheres and hollow spheres ( $Gd_2O_3$  S and  $Gd_2O_3$  HS) served as carriers for the chemotherapeutic agent doxorubicin. The nanospheres were synthesized via soft chemistry co-precipitation and template-directed methods. Physicochemical characterization, including morphology, structural and surface properties, was conducted using TEM/SEM, XRD, and FT-IR analysis. Doxorubicin loading efficiency on the Gd<sub>2</sub>O<sub>3</sub> spheres was assessed using UV-Vis spectroscopy. The obtained pristine nanospheres based on measurements of the electron microscopes had a diameter of approximately 150 nm. In comparison, composites with doxorubicin presented slightly larger sizes. SEM and TEM measurements also confirmed the porosity structure of hollow spheres. UV-Vis and FT-IR spectroscopic analyses revealed that the adsorption efficiency indicated the presence of the drug on the surface of  $Gd_2O_3$ , with the extent of adsorption being contingent upon surface properties. The higher surface area of Gd<sub>2</sub>O<sub>3</sub> HS facilitated a greater loading of chemotherapeutic compared to Gd<sub>2</sub>O<sub>3</sub> S, reaching approximately 27% after 15 minutes, and increasing to about 52% after 24 hours. In cytotoxicity studies, the effect of doxorubicin on cancer cell lines (HeLa cells) depended on their concentration. The suggested synthesis methods produced Gd<sub>2</sub>O<sub>3</sub> nanospheres with adjustable surface characteristics, presenting a potential nanoplatform for a doxorubicin delivery system in cancer therapy.

#### Acknowledgments

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#### Double functionalization of silk material- spheres for controlled delivery of oligonucleotherapeutics into HER2-overexpressing cancer cells

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Currently, drugs based on nucleic acids are being widely developed to treat diseases, including cancer. However, their use is associated with limitations, which can be eliminated by the application of a drug delivery system (DDS). We constructed a drug delivery system based on spheres made of MS1-type spider silk functionalized with the KN peptide, which binds nucleic acids, and the H2.1 peptide, which recognizes the HER2 receptor. The simultaneous functionalization of silk with two peptides can increase the efficiency of oligonucleotherapeutics delivery to HER2-overexpressing cancer cells.

This study aims to develop a double-functionalized silk sphere to deliver nucleic acidbased therapeutics into HER2-positive cells.

The sequences encoded bioengineered silks, such as MS1, H2.1MS1, and MS2KN were constructed previously. A new construct, H2.1MS1KN, was developed, which encodes the double-functionalized silk. All constructs were introduced into a bacterial expression system, and then proteins were produced at a semi-large scale in a bioreactor and purified by the thermal method. The ability of MS1, H2.1MS1KN, and the blend of H2.1MS1 and MS2KN proteins (80:20) to bind oligonucleotidetherapeutics was tested on agarose gel and spectrofluorometrically. To form spheres, the silk proteins were intensively mixed with 2M potassium phosphate buffer. The morphology and size of spheres were analyzed using a SEM. The Zeta Potential (ZP) of spheres was measured on ZetaSizer. The cell-binding of spheres was analyzed using flow cytometry and scanning confocal microscopy.

All silk protein variants were successfully produced and purified. However, the yields for recombinant silk proteins differed depending on the protein. The yield (expressed as the amount of purified protein per gram of bacterial pelet) of H2.1MS1KN silk was approximately four times lower than other silks. Both H2.1MSKN and the blend of H2.1MS1:MS2KN proteins efficiently bound nucleic acid in a 1:10 nucleic acid: protein ratio. However, H2.1MSKN shows a higher binding strength than the H2.1MS1:MS2KN blend. Both H2.1MSKN and the blend of H2.1MS1:MS2KN silks formed nanospheres with similar sizes (approximately 140 nm) and ZP (approximately 25 mV). Spheres made of these proteins were successfully loaded with oligonucleotidetherapeutics. Spheres with the H2.1 peptide more effectively bound and entered into HER2-positive cells than the control spheres.

The results indicate that nucleic acid-based therapeutics can be delivered to HER2positive cells using silk-based DDS. The strategy to develop a double-functionalized silk sphere will be chosen based on the completed study. In future studies, we plan to use this drug-delivery system to silence STAT3 in chemoresistant breast cancer cells with HER2 overexpression.

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### Indomethacin-Loaded Nanostructured Lipid Carriers - new approach for repurpose old drug towards antitumoral therapy

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Indomethain (IND) is non-steroidal anti-inflammotry drug exerts a wide range of theraputic activities. Since 1960s, it is clinically use and available over the counter. Its anticancer activity has been studied for four decades, and it was confirmed that its mechanism of action goes beyond cyclooxygenase inhibition [1]. However anticancer aplication of IND is limied due to its poor bioavailability and many side effects observed in the gastrointestinal tract [1]. To overcome this obstracles, we propose an innovative approach applying nanostructured lipid carriers (NLC) as a carrier to passive targeting of IND to tumor cells.

IND loaded NLC (IND-NLC) were prepared using hot high-pressure homogenization technique (HPH). Physicochemical parameters of produced nanocariers were analysed using a Zetasizer Nano ZS whereas the morphology was confirmed by Transmission Electron Microscopy (TEM). The rate of release of drug from the lipid nanoparticles was studied using direct dialysis technique. Antiproliferative activity of IND formulation (IND-NLC) was evaluated towards two selected cancer cell lines: PC-3 (prostate cancer) and MDA-MD-468 (breast cancer) using SRB assay. Resulted IND-NLC particle size, polydispersity index and zeta potentials were as follow: 168.1 nm, 0.14 and -30.1 mV, respectively. TEM imaging confirms no particle aggregation and sphereical shape of produced nanoparticles (Fig 1a). As it is shown in Fig 1b, free IND reached equilibrium after 10 h whereas release od IND from the formulation was slower, only on the level of 25% at the same time. The results of biological stude confirmed that IND after encapsulation in the lipid nanoparticles inhibits the proliferation of cancer cells PC-3 and MDA-MD-468 at low dosage 14.4 and 17.3  $\mu$ M, respectively.

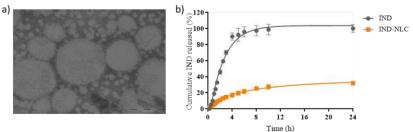
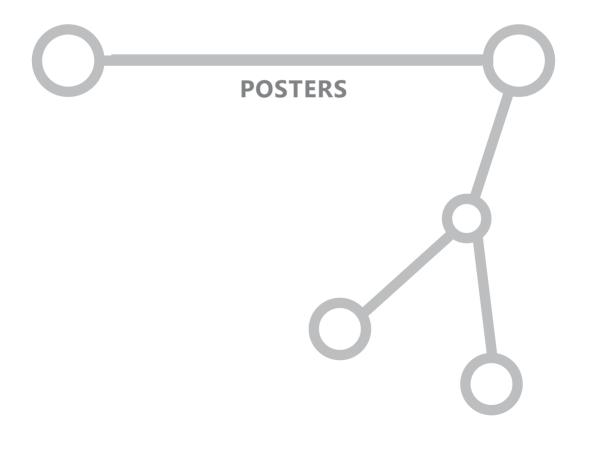


FIGURE 1. TEM image (a), and In vitro release profile of indomethacin from IND (free) and IND-NLC (b).

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# SECTION B NANOBIOMEDICINE



# $\mathcal{C}_{\mathcal{O}}$

# Photothermal treatment of therapy-induced senescent cells using AuNRs/PDA

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The Senescence Associated Secretory Phenotype (SASP) is a well-known hallmark of senescence, containing various components such as proinflammatory cytokines and growth factors. This creates an inflammatory environment in the tissue, potentially leading to increased tumor resistance and higher probability of cancer recurrence and spread [1].

The study focuses on senescent cancer A549 cells treated with photothermal therapy using polydopamine coated gold nanorods (AuNRs/PDA). Gold nanoparticles have the ability to absorb light at specific wavelengths, leading to photoacoustic and photothermal properties. This makes them potentially useful in cancer therapy through hyperthermia and in medical imaging [2]. Senescence in A549 cancer cells was induced by doxorubicin and the senescence hallmarks were investigated. Next, senescent A549 cells were incubated with AuNRs and AuNRs PDA at various concentrations (1  $\mu$ g/ml, 5  $\mu$ g/ml, 10  $\mu$ g/ml, 25  $\mu$ g/ml), followed by treatment with photothermal therapy (laser power 3W/cm<sup>2</sup>). The viability of the cells was subsequently examined. The results suggest that AuNRs/PDA exhibit sufficient photothermal properties to be used in photothermal therapy of senescent cells.

#### Acknowledgments

The research was financed by The National Science Centre (NCN), Poland under project number 2019/33/B/ST5/01495

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# Real-time monitoring of pulmonary chronic disease with a non-invasive sputum assessment technique

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Chronic obstructive pulmonary disease (COPD) is marked by narrowed airways and longterm respiratory symptoms. The lack of an effective cure for COPD makes prevention and symptom management pivotal.

COPD and sputum composition are correlated [1] and the different values of solid concentrations in sputum samples are associated within the three typical sputum categories traditionally attributed by physicians [2]: purulent samples display solid concentrations ranging from 6-10%, while mucoid samples fall within the 2-5% range. This suggests that sputum with higher purulence tends to contain a higher concentration of solid materials, augmenting critical stress and viscoelastic modulus [3]. Mechanics and fluorescence are commonly used techniques to measure fluid viscosity, which is not always possible when analyzing biological samples. This work focuses on the implementation of a technique for measure microfluidic viscosity based on Molecular Rotors (MRs). The fluorescence of MRs depends on the viscosity of the fluid they are in. When a photon is absorbed, the molecule gets excited to a locally excited state. The excited electrons move from donor to acceptor, causing the molecule to twist along bond axes. If the fluid is viscous enough, the molecule will relax back to its ground state by emitting fluorescence. The more viscous the fluid is, the more the molecule's rotation is inhibited, leading to more energy emitted by fluorescence.

The first step of our project involves synthesizing the molecular rotor FCVJ (2-carboxy-2-cyanovinyl)-julolidine farnesyl ester) [4]. To a solution of ethylene glycol:glycerol (2:8), a 40  $\mu$ L of FCVJ in methanol was added. This solution was excited by a 405nm laser source at 40mW, which resulted in an emission peak at 500nm.

While this research is at its initial phases, it introduces the potential of Molecular Rotors to measure viscosity in small sputum samples. This opens the door for further exploration in non-invasive techniques for COPD monitoring and treatment.

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#### Modification of membranes used in hemodialysis with silver nanoparticles

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The kidneys are an essential component in the functioning of the body, playing a crucial role in eliminating toxins from the blood, regulating blood pressure, and carrying out other important physiological processes. In the case of patients affected by chronic kidney disease, characterized by a gradual loss of kidney function, disturbances in significant processes are observed, such as the retention of toxins and excess water, as well as the development of bone and cardiovascular diseases [1]. There are two treatment options for such conditions: dialysis or kidney transplant. Due to a shortage of organs for transplantation, patients require long-term renal replacement therapy. Hemodialysis (HD) is one of the membrane techniques used to remove metabolic waste products and excess water from the body. Unfortunately, it can have side effects. Complications resulting from subjecting the body to hemodialysis can lead to various problems, ranging from electrolyte disturbances in the serum, anemia, bacterial infections, neurological complications, peripheral neuropathy, parathyroid gland adenoma, to cardiovascular diseases [2]. The main reason for the occurrence of the aforementioned problems is membrane fouling, which involves the adsorption of blood components such as proteins and blood platelets on the membrane surface. Numerous scientific studies show that fouling depends on the hydrophilic properties of membranes - the more hydrophilic the membrane surface, the lower its degree of fouling [3]. In addition, bacterial infections are also a threat to patients undergoing HD [4].

These problems can be addressed by modifying HD membranes with silver nanoparticles. They have proven antibacterial properties, which will protect the patient from infections, and they are also highly hydrophilic. As a result, a membrane modified with silver nanoparticles will exhibit greater hydrophilicity, and therefore less fouling.

The aim of the presented research was to obtain HD membranes based on cellulose acetate modified with silver nanoparticles and to determine their potential for use in the HD process. The conducted experiments also allowed for determining the optimal conditions for membrane synthesis. Properties such as membrane hydrophilicity and the adsorption of model proteins were also investigated. The conducted research allowed for the verification of the assumptions underlying the obtaining of the proposed materials.

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# Study on the behavior of model lipid monolayers for the optimization of pharmaceutical liposomal formulations

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In recent years Langmuir monoalayer technique has been shown as a useful tool to support a a rational design and optizimation of lipid-based drug delivery systems [1-2]. In this work lipid monolayers were formed at the air/water interface and used as model systems to study the behavior of liposomal drug carriers. Langmuir monolayer technique served as a convenient approach to investigate the interactions between the potential drug and the lipid core of the carrier at molecular scale. Moreover, that approach was applied to find the best combinations of a soluble surfactant and a lipid layer which could be utilized to produce transferosomes. These ultra-deformable vesicles for transdermal drug delivery are promising carriers that may encapsulate wide range of hydrophilic and hydrophobic molecules and transport them across the skin with higher permeability than typical liposomes.

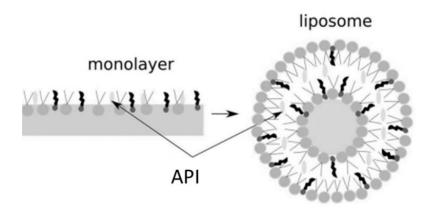


FIGURE 1. A model molayer used to investigate the interactions between lipids in liposomal drug carrier and active pharmaceuticakl ingredient (API)[2]

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# Determination of Gd<sup>3+</sup> ion content in GMO@DTPA-BSA-Gd lipid nanoparticles and their cell uptake by novel single-cell ICP-MS method

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Lipid-based nanoparticles offer attractive benefits for the development of a new generation of magnetic resonance imaging (MRI) contrast agents (CAs) exhibiting positive contrast ability [1]. This is mainly attributed to their loading ability of different cargos, but also physicochemical stability and high biocompatibility. Gadolinium chelates are the leading so far type of MRI CAs, and despite great scientific and research efforts, it seems that Gd cannot be entirely excluded from that research [2]. The promising direction is the design of high molecular weight Gd ion-containing CAs, potentially satisfying the characteristics mentioned above.

Investigated nanoparticles are lipid nanoparticles composed of matrix glycerol monooleate (GMO) with embedded Gd-chelating lipids (DTPA-BSA-Gd, (diethylenetriaminepentaacetic acid)-bis(stearylamide) (gadolinium salt)), possessing high molecular weight in comparison to Gd-chelates (Gd-DTPA, gadopentetic acid). These nanoparticles were investigated towards the metallic ion content and their cell uptake using single-cell inductively coupled plasma mass spectrometry (ICP-MS) as a novel approach. The loading of DTPA-BSA-Gd into GMO was done in two weight ratio regimes, low (5 wt. %) and high (30, 40, 50 wt. %). Formed supramolecular structures of GMO@DTPA-BSA-Gd differ significantly in terms of structure and morphology but preserve similar nanoparticle size and surface charge. Increasing the amount of DTPA-BSA-Gd in the systems affects the self-assembly process, and the nanoparticles with a highly disordered interior, in shell resembling lipid bilayer vesicles are becoming predominant in the system. Increasing the number of  $Gd^{3+}$  per CA molecules and eventually its presence in the imaged tissue on a cellular level is a critical factor in improving its performance in MRI. Single-cell ICP-MS results show that the loading efficiency (LE%) is strongly limited in the system, as it remained below 10%, and reached around 56000 - 71000 $Gd^{3+}$  ion/NPs. However, the prepared nanoparticles are effectively uptaken by cells, where they remain at the concentration level within the range of 800 - 1800 ag of Gd /cell, depending on the nanoparticle type. Moreover, regarding the Gd<sup>3+</sup> ions leakage, the study did not reveal the presence of free  $Gd^{3+}$  ions in the nanoparticle dispersions, which indicates their strong entrapment within the formed lipid-based nanoassemblies. The ionic background was revealed upon cell uptake at the nanomolar level. Finally, this study also provides evidence of the biocompatibility of prepared nanoassemblies in vitro.

#### Acknowledgements

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#### **Combating Cellular Senescence: Nanoparticle-Delivered Fisetin**

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Cancer treatments have evolved dramatically, improving survival rates and quality of life. However, the risk of cancer recurrence remains a significant concern. Numerous factors influence the recurrence of cancer; one of them is therapy-induced senescence. Senescent cells can influence their microenvironment through the Senescence-Associated Secretory Phenotype, where they release inflammatory cytokines, growth factors, and proteases. Although SASP can promote tissue repair and regeneration, it can also create a proinflammatory tissue microenvironment which may lead to the emergence of a more aggressive, therapy-resistant tumor phenotype, thus increasing the risk of cancer recurrence and metastasis [1]. Nanotechnology offers promising avenues for targeting and eliminating senescent cells. By using nanocarriers, we can deliver senotherapeutic drugs more effectively throughout the body. This targeted approach could potentially reduce the harmful effects of TIS while maintaining the initial benefits of cancer therapy. In conclusion, while effective cancer treatment remains a dynamic and evolving field, post-cancer treatments to lower the risk of cancer recurrence are still at a very low level of study. The strategic use of nanotechnology in the delivery of senotherapeutics might address these concerns, thereby reducing the likelihood of recurrence and leading to better long-term outcomes for cancer patients.

This study was performed on cancerous cell line A549 and healthy fibroblasts WI38 to analyze the senescence induction and its impact on both cell types. Furthermore, the liposomes with Fisetin were created and administered to the cells to investigate the influence of the senolytic drug on senescent cells.

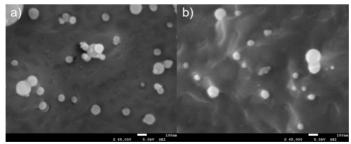


FIGURE 1. CryoSEM images of a) empty liposomes and b) liposomes with encapsulated fisetin.

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#### Antibacterial properties of new lipid liquid crystalline nanoparticles with glycerol monolaurate additives

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Increasing antibiotic resistance in bacteria, as highlighted by the World Health Organization, poses a serious global health threat [1, 2]. The misuse and overuse of antibiotics have led to previously nonresistant microbes developing multidrug resistance, creating significant challenges in treating bacterial infections and necessitating the exploration of alternative approaches [3, 4]. While antibiotics have been the mainstay of antimicrobial therapy for many years, the rise of resistant bacteria calls for innovative strategies. Non-antibiotic antimicrobial agents like antimicrobial lipids offer a potential solution by targeting different mechanisms that bacteria struggle to develop resistance against.

One promising candidate is glyceryl monolaurate (GML). GML interacts with bacterial membranes, causing strain and disruption [5, 6]. By destabilizing bacterial membranes, GML prevents the active expulsion of antibiotics, thereby enhancing their effectiveness. By incorporation the lipid into previously studied glyceryl monooleate (GMO) lipid liquid crystalline nanoparticles (LLCNPs), a new nanosystem with antibacterial properties and enhanced bioretention could be obtained.

The objective of this study was to design and assess the physicochemical properties and antibacterial activity of lipid liquid crystalline nanoparticles composed of glyceryl monooleate and the antibacterial lipid glyceryl monolaurate.

#### Acknowledgments

The research was finance by the National Science Centre, Poland, grant SONATA-BIS 6: 2016/22/E/ST3/00458 and from Research University – Excellence Initiative: 017/02/SNP/0034.

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# Calcium and strontium phytate nanoparticles as carriers in controlled release of risedronate

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Bisphosphonates (BPs) are drugs mainly used in the treatment of bone-related diseases such as osteoporosis. BPs are analogs of natural pyrophosphate (P-O-P), containing a carbon atom (P-C-P) instead of an oxygen atom between phosphorus atoms. Due to the presence of such a bond, they are resistant to many factors such as enzymatic hydrolysis [1]. BPs can effectively bind divalent metal ions including  $Ca^{2+}$ , which are the main building blocks of bones, and induce osteoclast apoptosis, leading to inhibition of bone resorption [2]. These drugs have two main routes of administration, both of which are associated with side effects. Side effects after oral administration of the drug are mainly related to the digestive system, including esophagitis or nausea. On the other hand, intravenous administration of the drug may cause fever, muscle pain, or vomiting. Other side effects during BP therapy include acute or chronic renal failure and electrolyte disturbances. Another problem during therapy with this group of drugs is their low bioavailability. This is due to very poor absorption from the gastrointestinal tract (<5%) after oral administration. However, during intravenous therapy, approximately 50% of the drug reaches the bone tissue [3,4].

A potential solution to the problems associated with bisphosphonate administration may be their controlled release using a carrier. The prepared carrier should be non-toxic and release the drug in a controlled manner in body fluids. Nanoparticles (NPs) of calcium and strontium phytate may serve as potential carriers for bisphosphonates. Their main component is phytic acid, which is a natural plant compound. Bisphosphonates have a high affinity for divalent ions, making it possible to retain them on the proposed carrier. Additionally, due to ion-drug interactions, the drug will be released gradually in a controlled manner.

The aim of the presented work was to synthesize NPs of calcium and strontium phytate and determine the potential of the obtained nanoparticles in the controlled delivery of Risedronate (RSD), which was selected as a model drug from the bisphosphonate group. It has been demonstrated that the prepared materials are capable of sorption and controlled release of BPs. Studies using various research techniques confirmed the effective sorption of RSD. The influence of the applied ion on the sorption and release of RSD was also demonstrated.

#### Acknowledgments

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Β9

#### Exploring the impact of natural products on viral infection – for nanotechnology-based drug carrier system

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Naturally derived compounds have been extensively studied for years, and numerous molecules with therapeutic potential have been identified. Nowadays, most natural products are well-known as anticancer and antimicrobial constituents. Unfortunately, the main problem associated with the use of naturally derived products and secondary metabolites is the limited bioavailability and drug efficiency. Therefore, investigating natural products as multitasking drug nanocarriers for anticancer and antiviral therapies is necessary and opens novel, exciting opportunities for phytomedicine [1].

The aim of this study was to determine the antiviral effect and immunomodulation potential of different naturally derived compounds and develop a specialized drug delivery system with the release of drugs. Our research focused on protoberberine plant alkaloids, honeybee venom and its selected peptides (apamin, tertiapin).

Our preliminary results showed that studied plant phytochemicals exhibited antiviral activity, reducing HPV (*human papillomavirus*) and coronavirus SARS-CoV-2 infectivity on HaCaT and hACE2 cells, respectively. Similarly, it was found that peptides extracted from bee venom can potentially reduce the infectivity of SARS-CoV-2. The study demonstrated differences in protein-peptide profiles between SARS-CoV-2 infected and uninfected hACE2 cells following treatment with selected concentrations of bee venom peptides, specifically apamin and tertiapin, and whole venom.

Additionally, we assume that the antiviral activity of naturally-derived compounds can be an effect of destabilizing the structure of viral particles, blocking viral entry and replication in host cells. We believe that combining bioactive compounds with biocompatible nanomaterials can significantly increase their antiviral properties and efficiency [2].

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#### Hyaluronic acid-based hydrogels as a potential therapeutic agent for postmyocardial infarction cardiac muscle therapy.

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Ischemic heart disease is the most prevalent cardiovascular disease. Despite tremendous advancements in medicine in recent years, the number of incidents related to hypoxia of cardiac cells leading to structural and functional abnormalities of the heart is on the rise [1]. A promising approach to heart repair in regenerative medicine involves the use of hyaluronic acid-based hydrogels. Hyaluronic acid is a natural anionic polysaccharide with a broad range of physicochemical and functional properties, making it highly useful as a drug delivery platform [2]. It is characterized by biodegradability, non-toxicity, and the ability to modify its properties through the chemical conjugation of functional groups [3].

The main aim of the study was to design and develop innovative functional nanomaterials based on hyaluronic acid using dendrimers modified with the Apelin-13 polypeptide, as drug delivery systems for the cardiac muscle after a heart attack. To achieve this, potential therapeutic systems based on hyaluronate were prepared: pure sodium hyaluronate and hyaluronates modified with lithocholic acid (HA-LCA) and  $\beta$ -cyclodextrin (HA- $\beta$ CD). The hydrogel platforms were then functionalized with hyperbranched Bis-MPA PEG 6k dendrimers (4th generation) with hydroxyl groups and the Apelin-13 polypeptide.

During the research, a detailed characterization of the nanomaterials was conducted, including the assessment of their morphology, size, surface charge, and chemical structure using physicochemical methods such as SEM, DLS, FTIR, and UV-VIS. Cytotoxicity tests were also performed on the AC16 cell lines, which demonstrated therapeutic concentrations and the non-toxicity of the hyaluronic acid-based complexes under hypoxic conditions, which is promising in the context of their further clinical applications.

#### Acknowledgments

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# Is magnetic separation good method to isolate liposomes with biomolecular corona-?

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Size exclusion chromatography and ultracentrifugation are well-known methods for nanostructure isolation based on their size and density. Although these techniques may be effective for separating larger or denser nanoparticles, they are unsuitable for efficiently distinguishing lipid-based nanoplatforms below 100 nm from other lipoproteins or nanocomponents occurring in biological medium. Magnetic separation is a rapid method to isolate magnetic nanocarriers from other components in a solution, regardless of their size and surface properties. Recently, this technique has been used to separate lipid-based nanocarriers with magnetic cores from complex biological solutions [1].

We evaluated the suitability of the magnetic separation method for the isolation of liposomes encapsulating iron oxide nanoparticles (IONP) with biomolecular corona (BMC). The liposomes were produced using a microfluidic technique by mixing lipids (DSPC, cholesterol, DSPE-PEG2000) and IONP. After preparation, dialysis was used to remove non-entrapped molecules. Liposomes were incubated with 20% FBS solution at 37 °C for 15 min to perform molecular corona formation. Bare IONP-liposomes and IONP-liposomes with BMC were separated on MACS® Cell Separation system. The magnetic columns were rinsed and washed with PBS solution. Nanostructures were examined in terms of size and zeta potential after preparation, separation, incubation with the 20% FBS, and separation after the formation of BMC. Also, the purity of the eluted rinsing buffer in terms of the presence of any nanostructured materials was evaluated.

The obtained IONP-liposomes had a size of 84 nm and, were characterized by high homogeneity (PdI  $\approx 0.07$ ) and were stable during storage at 2-8 °C. The separation column used for magnetic separation was a source of nano-sized materials by itself since the eluted rinsing buffer contained several fractions of particles with a high particle spread. Magnetic separation of bare IONP-liposomes led to an increase in size and size distribution (d=176.8 nm and PDI=0.5), resulting possibly from liposome aggregation. IONP-liposomes with BMC, obtained during incubation with 20% FBS, contained two fractions of particles with mean diameter of 18.6 nm and 73.6 nm, corresponding to the sizes of unbound proteins and IONP-liposomes with BMC, respectively. Magnetic separation of IONP-liposomes with BMC led again to the *ca.* two-fold increase in diameter size (d=131.7 nm, PDI=0.6). Particle size analysis in the collected flow-through buffers used to wash out unbound material from bare IONP-liposomes and IONP-liposomes with BMC pointed out the efficient removal of unbound material.

When applied to liposomes, the magnetic separation method affects the size of particles in the eluted sample. The technique allows for the purification of the sample from unbound material but leads to higher diameters and polydispersity.

#### Acknowledgments

The authors gratefully acknowledge the financial support by the National Science Centre of Poland from the SONATA BIS project 2021/42/E/NZ7/00287.

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# Poly(GMA) brushes with 4-phenylobenzyloamine functional groups as advanced scaffolds for the differentiation of stem cells into chondrocytes

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The great attention of regenerative medicine is dedicated to materials that can imitate the properties or even obtain cartilage tissue, which is very desirable due to its difficulty in regeneration and human susceptibility to injuries. This study aimed to fabricate systems based on surface-grafted polymer brushes as a support for the differentiation of stem cells into chondrocytes. The polymer brushes built of poly(methacrylate) glycidyl (poly(GMA)) were obtained using the controlled atom transfer radical polymerization (ATRP) method and were functionalized with 4-phenylbenzylamine working as a functional analog of kartogenin molecule [1]. The physicochemical properties, like height, roughness, chemical composition and wettability of the obtained surfaces were characterized by atomic force microscopy (AFM), infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and contact angle measurements. The structure and biological response of functionalized brushes were compared with the native poly(GMA) brushes. The cellular response of human umbilical cord mesenchymal stem cells (HucMSCs) on the obtained substrates was carried out. The rate of proliferation and viability were checked by the Trypan Blue test, and cytotoxicity by MTT assay. The expression of genes characteristic for chondrogenesis (COL2, SOX9, ACAN) was investigated by the RT qPCR method. The obtained results indicate that used molecule working as an analog of kartogenin may support the chondrogenesis of stem cells.

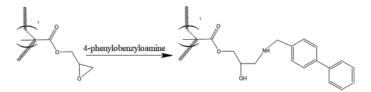


FIGURE 1. Scheme of the attachment process of 4-phenylobenzyloamine to the side groups of poly(GMA) brushes chains.

#### Acknowledgments

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#### Delivery of therapeutic oligonucleotides into tumor microenvironment using a system based on functionalized silk nanospheres

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Small interfering RNA (siRNA) is highly effective in silencing target gene expression and minimizes the risk of side effects of conventional cancer therapies. Yet its delivery to the target cells still needs to be expanded and requires the employment of an efficient delivery system. Bioengineered silk is a promising biocompatible and biodegradable material for drug delivery. Functionalization with specific recognizing peptides or nucleotide-binding domains can effectively target specific cells and facilitate the delivery of nucleic acids. Angiogenesis, the formation of new blood vessels from pre-existing vessels, is one of the main hallmarks of cancer progression. Hypoxia-inducible factor 1-alpha (HIF-1 $\alpha$ ) plays a central role in regulating angiogenesis. Thus, delivering HIF-1 $\alpha$ -siRNA using silk spheres targeting VEGF receptors, which are overexpressed in cancer and endothelial cells, offers a potential avenue for cancer treatment.

The study aimed to determine potential of loading silk nanospheres with therapeutic oligonucleotides, delivering them to target cells, and evaluating gene silencing efficiency.

Previously, we constructed five bioengineered silk proteins recognizing receptors overexpressed on the surface of endothelial and cancer cells: VE1MS1, VE1bMS1, VE1cMS1, as well as VE2bMS1, and VE2cMS1 (targeting VEGFR1 and VEGFR2, respectively). The MS2KN silk, incorporating the nucleic acid binding domain KN, was used to form blends with VEGFR-targeting silks. These bioengineered silk variants were mixed with siRNA at a 1:1 molar ratio. Agarose gel electrophoresis was then performed to determine oligonucleotides binding to the blended silk proteins. Next, nanospheres were formulated by mixing protein/siRNA solution with a high-concentration potassium phosphate buffer. Cell viability in plain and blended spheres was assessed with an MTT assay. Subsequently, fluorescently labeled oligonucleotides were incorporated into nanospheres, and the loading efficiency was measured using spectrofluorometry. Prepared spheres were characterized in terms of morphology (SEM), size (Nanosight), and zeta potential. The effectiveness of delivering siRNA-loaded spheres to the VEGFR-positive endothelial (HUVEC) and lung cancer (H1975, HCC4006) cells was evaluated with flow cytometry and confocal microscopy. Finally, qRT-PCR was performed to determine the silencing effect of sphere-mediated siRNA delivery on the *HIF-1* $\alpha$  mRNA level.

MTT assay displayed no toxicity of VEGFR-targeting spheres to the cells. Agarose gel electrophoresis revealed the high efficacy of oligonucleotide binding to the blends of VEGFR-functionalized silks with MS2KN. Moreover, therapeutic oligonucleotides were successfully and efficiently incorporated into spheres, allowing effective delivery of the drug to the VEGFR-positive cells. HIF-1 $\alpha$ -siRNA delivered via silk nanospheres reduced the expression of the target gene, compared to scrambled-siRNA.

Our results indicate VEGFR-targeting silk spheres as a promising tool for the effective delivery of oligotherapeutics to the VEGFR-overexpressing cells.

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#### Engineering biocompatible iron-based metal-organic frameworks for controlled delivery of dapagliflozin antihyperglycemic drug

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Diabetes is a metabolic disease characterized by raised blood glucose levels, which leads to serious damage to the heart, blood vessels, eyes, kidneys, and nerves [1]. The most common form of the disease is type 2, which occurs when the pancreas does not produce enough insulin, or the body cells become unresponsive to the hormone's effects. Dapagliflozin is a selective sodium-glucose co-transporter 2 (SGLT2) inhibitor with antihyperglycemic activity. Despite its many advantages, dapagliflozin may cause some side effects, such as polyuria, dysuria, dizziness, abnormal triglyceride and cholesterol levels in the blood, increased hematocrit, back pain, and rash. One way to reduce them is to introduce the drug into appropriately designed carriers which will release dapagliflozin in a precisely defined place in the body, increasing the bioavailability. This has a key impact on the functioning and further recovery of the patient. In recent years, much attention has been paid to the use of metal-organic frameworks (MOFs) as drug carriers due to their low toxicity, biocompatibility, wide range of pore sizes, and high specific surface area. MIL (*Material Institute Lavoisier*) nanoparticles containing iron cations linked to various organic ligands via coordination bonds are good platforms for controlled dapagliflozin delivery [2].

The main goal of the study was the synthesis of stable and biocompatible MIL nanomaterials with defined morphology and porous structure, and their use as carriers for dapagliflozin. MOFs containing iron were synthesized using the solvothermal method – MIL-101 at 120 °C (iron source: FeCl<sub>3</sub>·6H<sub>2</sub>O, linker precursor: terephthalic acid, modulators: acetic acid, sodium acetate) and MIL-88A at 80 °C (iron source: FeCl<sub>3</sub>·6H<sub>2</sub>O, linker precursor: fumaric acid, modulators: acetic acid, sodium acetate). All materials were subjected to physicochemical characterization using various methods such as low-temperature nitrogen sorption, X-ray diffraction, scanning electron microscopy, and infrared spectroscopy. Dapagliflozin was adsorbed on the surface of the synthesized MIL samples at room temperature for 2 h. The adsorption mechanism was determined using Langmuir and Freundlich models. Next, the drug was released from nanocarriers in a phosphate buffer of pH 7.2 at 37 °C.

MIL-101 materials are characterized by higher specific surface areas than MIL-88A. They have pore sizes in the range of 2.3–2.7 nm and 8–11 nm, respectively. Depending on the synthesis conditions, the particles of MIL-101 and MIL-88A samples indicate hexa- or octagonal morphologies. The lowest sorption capacity towards dapagliflozin exhibits MIL-88A obtained in water with acetic acid (26 mg/g). A higher amount of the drug was adsorbed on MIL-101 material (345 mg/g), which is in agreement with the results obtained by FT-IR analysis. Dapagliflozin molecules are gradually released within 48 h to almost 100%. It should be mentioned that the release process is not only related to the structure of materials but also to their morphology and textural parameters.

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#### Biocompatible liquid marbles with additional magnetic properties enhanced by magnetosomes

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Liquid marbles (LMs) are tiny non-stick droplets coated with (nano)particles that repel liquids, maintaining a spherical shape. They are recognized for their promising biomedical applications due to their versatility and simple preparation. LMs can be used for carrying and protecting sensitive materials or drugs, as well as for developing novel smart materials. The current trend is to modify LMs to acquire new specific properties, such as magnetism. The magnetic modification of droplets allows for guided movement or the possibility of being heated up by applied oscillating fields. Our goal was to create innovative LMs using magnetic nanoparticles isolated from the magnetotactic bacteria Magnetospirillum magneticum, which synthesizes chain-like magnetite nanoparticles known as magnetosomes within its body. The advantages of magnetosomes lie in their significant response to magnetic fields, as well as in their organic envelope on the surface of particles. In the frame our research, we made LMs with different cores including water, agar-based hydrogels, magnetic fluids, and non-aqueous substances. We coated these marbles with biocompatible particles of plant origin like turmeric grains and Lycopodium pollen. We also introduced magnetic properties by adding magnetosomes or iron oxide nanoparticles, resulting in stable structures that could be manipulated by external magnetic fields. In Figure 1, we can see a sample of variously stabilized LMs with magnetosomes, which interact with the applied alternating field, resulting in an increase in their temperature. We also observed that hydrogel LMs functionalized with magnetic materials, exhibited enhanced responsiveness to external magnetic fields, thereby facilitating their transportation. The inherent elasticity of the hydrogel cores contributed to the overall stability of the LMs while still enabling extensive functionalization [1].

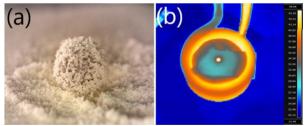


FIGURE 1. Optical microscopy images depict liquid marbles with magnetosomes stabilized by lycopodium pollen, showing a thermal response to an alternating magnetic field, IR camera (b); 16.2 kA/m, 356 kHz.

#### Acknowledgments

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#### Photonics for the Point-of-Care Diagnosis of Bacterial Urinary Tract Infections

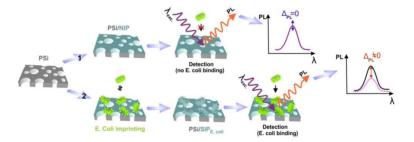
<u>Valerii Myndrul</u><sup>a</sup>, Rocio Arreguin Campos<sup>a</sup>, Igor Iatsunskyi<sup>b</sup>, Kasper Eersels<sup>a</sup> and Bart van Grinsven<sup>a</sup>

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Bacteria, as integral components of our ecosystem, play critical roles in maintaining human health and well-being. Among them, Escherichia coli (E. coli) stands out for its dual nature: while essential in our gastrointestinal tract for food digestion, it poses significant risks when found in other organs, particularly causing urinary tract infections (UTIs) [1]. Current diagnostic methods for UTIs often rely on empirical treatment, contributing to antibiotic resistance and posing challenges for effective management [2].

This research proposes the development of a user-friendly biosensor utilizing Surface Imprinting of Polymers (SIP) technique for UPEC detection [3]. SIP enables the creation of artificial recognition layers on photonic transducers, ensuring scalability, reliability, and minimal pre-detection steps. The biosensor employs porous silicon (PSi) substrates as photonic transducers, leveraging their superior sensitivity and compatibility with SIP recognition layers [4].



**FIGURE 1.** Sketch-diagram of the proposed PSi/SIP biosensor for E. coli detection. Pathway  $(1\rightarrow)$  outlines the fabrication process of PSi/NIP, where NIP refers to a non-imprinted polymer. The PSi/NIP chip lacks recognition ability towards E. coli, preventing bacterial binding and resulting in no change in PL intensity. In contrast, pathway  $(2\rightarrow)$  depicts the fabrication of PSi/SIP, where after imprinting, cavities with high affinity to bacteria remain, rendering the chip sensitive and selective to E. coli upon detection. Consequently, a noticeable change in PL intensity can be observed, facilitating correlation analysis of PL change with E. coli concentration.

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#### Silk Nanospheres for Targeted Delivery of Photosensitizers to CD133-Expressing Cancer Stem Cells

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**Introduction**: Cancer stem cells (CSCs) play crucial roles in tumor initiation, metastasis, and treatment resistance. Conventional cancer therapies target proliferating tumor cells, leaving CSCs relatively unaffected due to their slower division rates. Effective anticancer therapy should aim to eliminate both differentiated tumor cells and CSCs, which express specific stemness markers such as CD133. Silk-based drug carriers offer a promising strategy for targeted drug delivery to CSCs, leveraging silk proteins' biodegradable and biocompatible nature. Photodynamic therapy (PDT) is an emerging approach in cancer treatment, and targeting photosensitizers (PSs) to CSCs via bioengineered silk spheres may enhance its efficacy in PDT.

**Objective**: The construction of a targeted porphyrin photosensitizer delivery system based on bioengineered silk spheres functionalized with CD133-binding peptide.

**Methods:** The pETNX-CD133-MS1, pETNX-CD133(2x)-MS1, pETNX-CD133b-MS1 constructs were obtained by cloning oligonucleotide sequences encoding corresponding peptides into the *Nhe*I restriction site for 5'-terminal functionalization of the MS1 silk. The sequences of the obtained artificial genes were confirmed by sequencing. Functionalized spider silk proteins were produced in *E. coli* strain BLR and purified by thermal denaturation. Spheres were formed by mixing 0.5 mg/mL of silk with 2 M potassium phosphate buffer (pH 8) using a pipette. The morphology of spheres was examined by SEM. The 20,000 cells/well of ovarian cancer cell line (OVCAR3) was seeded on a 96-well plate, cultured for 48 h, and then treated with 10, 20, 50, 100, 200, and 500 nM of PS3. After 24 h, the cells were irradiated with 2, 5, or 10 J/cm<sup>2</sup> or not-irradiated (control) using a lamp emitting light at 425 nm. After 24 h, the cell metabolic activity was measured using an MTT assay.

**Results**: The CD133MS1, CD133(2x)MS1, and CD133bMS1 genetic constructs were cloned, and then the corresponding proteins were successfully produced and purified. The yield of CD133MS1, CD133(2x)MS1, and CD133bMS1 proteins was 2.37, 1.23 and 5.66 mg per 1 g of bacterial pelet, respectively. All silk variants formed spheres indicating that functionalization did not impede the sphere assembly process. The spheres exhibited a spherical morphology. PS3 demonstrated dose-dependent cytotoxicity upon irradiation ranging from 2 to 10 J/cm<sup>2</sup> in the OVCAR3 cells. Importantly, non-photoactivated PS3 did not show cytotoxicity.

**Conclusion** The CD133-targeting drug delivery system based on spider silk was constructed, and new variants of spheres were successfully obtained. Moreover, new PS (PS3) indicated properties usefull for PDT. However, further research is needed to determine the binding affinity of the spheres to CD133-expressing cells and the potential for incorporating PS3 into the spheres.

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# $\sim^{\circ}$

# Survivin based biosensors: promising tools for early detection of cancer diseases

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Cancer is a major public health problem worldwide. According to the World Health Organization (WHO), 20 milion new cases and neraly 10 million deaths were reported globally in 2022. However, following to the WHO predictions, in 2050 the number of new cancer cases will increase by approximately 77 percent and deaths by 90 percent. The most common type of cancers are breast, lung and colorectal [1]. Early diagnosis of cancer generally enabling more effective treatment and better recovery outcomes. Therefore methods for early cancer diagnosis and innovative cancer treatment strategies are highly sought.

Over the past decades, extensive research have shown that biomarkers are promising and valuable tools in the diagnosis, prognosis and treatment of diseases. The variety biomolecules are used as biomarkers, including proteins, DNA, mRNA, and enzymes. They often occur in very low concentrations, mixed with various other proteins, making their identification difficult. In many cases, detection of biomarkers at very low concentrations is difficult and time consuming. Moreover, early-stage diseases are usually treated with the highest probability of success. Therefore, early detection of biomarkers is very important in cancer and other pathological conditions [2]. In recent years, investigations have revealed, that biosensors become an effective and attractive analytical tool for cancer biomarkers detection. It was indicated that biosensors can provide an alternative diagnosis methods over other analytical methods due to their high sensitivity, selectivity, stability, low cost, and easy application. Currently, research studies efforts are focused on development biosensors for detection of the inhibitor of apoptosis proteins (IAP) family, protein survivin. Moreover, this protein is overexpressed in various type of cancers, but its expression is negligible in normal adult cells. Survivin overexpression is highly correlated with cancer progression, chemoresistance, cancer recurrence, poor prognosis, and reduced survival rate of patients. These features make this protein as a potential biomarker of cancer diseases. Furthermore, recent studies indicate that small-molecule survivin inhibitors seems to be a favorable factor in the treatment and therapy of cancer diseases [3-7].

#### Acknowledgments

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#### Development and optimization of stable w/o/w nanoemulsion system loaded with cinnamoyl/3-methoxycynnamoyl lysophosphatidylcholine with improved antileukemia activity

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Naturally occurring aromatic acids – cinnamic acid (CA) and it's O-methoxy- and hydroxy derivatives are of great interest in the functional foods, nutraceutical, and pharmaceutical industries. They are integral part of human diet and possess a high spectrum of pro-health activities proven in the *in vitro* studies. However, they are characterized by low bioavailability which is due to their low solubility in water (CA approx. 0.29 g/L), partition coefficient (CA P<sub>octane/water</sub> approx. 2.41), poor stability, passive diffusion and active efflux in the gastrointestinal tract which make them unsuitable for use as therapeutic compounds in the free form. In last five years the strategies for synthesis of aromatic acids conjugated with phospholipids were successfully applied and it was proved that they exhibit higher anticancer potential in the *in vitro* studies against many types of cancers. The results showed that conjugation with phospholipids contributed to an increase in the activity while gaining high selectivity of action and being non-toxic towards normal cells (Balb/3T3). Especially active conjugates in the synthesized series turned out to be lysophosphatidylcholines against human leukemia cells (MV4-11) which were 11 times more active than in the case of native acids [1].

The aim of this work was to develop a double emulsion for two hydrophilic, biologically active lysophosphatidylcholine conjugates containing covalently bound cinnamic (CA) and 3-methoxycinnamic acid (3MCA) and check their effectiveness against leukemia cells line MV4-11. In the first stage the attention was focused on the development and optimization of the process of formation of a stable nanoemulsion characterized by an appropriate nanoparticle size (Z-Ave), Z-potential (ZP) and polydispersity (PI). Evaluation of cytotoxic activity against the leukemic cell line MV4-11 showed that the 50% inhibitory concentration of the nanoemulsion was two times lower than that observed for free conjugates. These studies are a response to the need to look for preparations based on natural compounds that could be used in chemoprevention or as preparations with a complementary effect in relation to classic cancer therapy methods. Considering the high biological potential, low toxicity towards normal cells and the composition based on "GRAS" ingredients, the developed preparation seems to have potential in this area.

#### Acknowledgments

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#### Zinc-doped nanohydroxyapatite as a pH responsive drug delivery system

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Due to the formidable challenges of developing new drugs researchers worldwide are focusing on enhancing the delivery mechanisms of existing medications. These modifications aim to refine the properties of pharmaceutically active compounds, such as improving their bioavailability or targeting specific areas within the body. In this research, we prepared nanohydroxyapatite doped with zinc ions, and used it as a carrier for 6-Mercaptopurine (6MP). 6MP serves as a pivotal component in the maintenance therapy for Acute Lymphoblastic Leukemia and exhibits promising anticancer properties [1]. Despite its therapeutic significance, 6MP encounters certain limitations during treatment. One of the major problems is its low bioavailability, ranging from 10% to 50%, with an average value of 16% [3]. This is due to the poor solubility. Another issue is the drug's short half-life in plasma, ranging from about 1 to 3 hours. This is because the renal system eliminates 6MP rapidly. Furthermore, the drug has some adverse effects, such as bone marrow suppression and hepatotoxicity. We hypothesized that nanohydroxyapatite doping with  $Zn^{2+}$  ions could enhance 6MP retention through coordination bonds. In the present research, zinc-doped nanohydroxyapatite was successfully synthesized and used in the controlled release of 6mercaptopurine. Crucially, the carrier maintains stability in conditions mimicking human body fluids, with particle sizes averaging 130 nm, facilitating potential use in intravenous drug administration. The release of the drug varies depending on pH levels, exhibiting slow release at neutral pH resembling healthy tissues, thereby counteracting the drug's short halflife. Conversely, at acidic pH levels resembling those of cancer cells, the drug is promptly released. This underscores the carrier's potential to effectively deliver 6MP for cancer treatment.

#### Acknowledgments

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#### Natural, bionic and chemically synthesized Fe<sub>3</sub>O<sub>4</sub>-based particles: evaluation and comparison of biological antioxidant and antiamyloid activity

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In a biological context, reactive oxygen species (ROS) are formed as a natural byproduct of cellular aerobic metabolism. 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. Because of their highly reactive nature, ROS can modify other oxygen species, proteins, nucleic acids, lipids, and other molecules. Their ability to be scavenged is important in combating serious oxidative stressrelated diseases, such as aging, cancer, diabetes mellitus, or neurodegenerative diseases, including Alzheimer's. However, despite decades of intensive study, highly successful treatment of both oxidative stress and protein misfolding in neurodegenerative diseases is still missing. This opens the door for nanomaterials with unique physicochemical properties, tenability, and multifunctionality to improve the understanding and treatment of diseases. Additionally, composite nanomaterials are being developed improve to therapeutic/theranostic techniques, that appear to be forging a path toward a multifaceted approach to the pathologies of age-related diseases [1,2]. In turn, Fe<sub>3</sub>O<sub>4</sub>-based particles/composites have drawn increased attention thanks to their remarkable properties arising from magnetism, such as the heat generation under oscillating magnetic fields or the possibility to be guided by external magnetic fields. Among such materials, magnetosomes (MTS) undoubtedly belong. MTS are magnetic nano-sized particles (in our case of Fe<sub>3</sub>O<sub>4</sub> nature) created by magnetotactic bacteria. These particles form unique chain-like structures linked by a natural organic envelope. The combination of MTS' biocharacter and magnetic properties could potentially improve treatment for oxidative stress-related diseases and advance nanomedicine therapies.

Obtained results demonstrated that  $Fe_3O_4$ -based particles exhibit the anti-amyloid activity expressed as the ability to inhibit fibril formation and disassemble pre-formed amyloid fibrils as well. The extent of anti-amyloid activity exhibits a size-dependent efficacy to alter protein amyloidogenesis and points the importance of the presence of magnetic (Fe<sub>3</sub>O<sub>4</sub>) core and the interplay between particle size and surface chemistry. Moreover, our results demonstrate well-defined valence- and size-dependent catalase- and SOD-like activity.

#### Acknowledgments

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#### Highly sensitive electrochemical immunosensor for CD5 detection in human blood serum based on laser-processed Ti/Au electrodes

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Biomarkers have become indispensable for transforming disease diagnosis, treatment, and management in modern medicine. Cluster of differentiation 5 (CD5), a cell surface glycoprotein predominantly found on immune cells such as T cells and B-1a lymphocytes, plays a pivotal role in immune regulation and is closely linked to autoimmune diseases. CD5 has emerged as a crucial biomarker with vast diagnostic and therapeutic potential. However, its detection remains underexplored, creating a significant knowledge gap.

In this study, we present an innovative electrochemical biosensor based on laserprocessed Au-Ti electrodes meticulously designed for the highly sensitive detection of CD5 protein in human blood serum. The developed biosensor outperforms commercial ELISA kits, boasting an exceptional limit of detection (LOD). Rigorous biofunctionalization and thorough testing in phosphate-buffered saline (PBS) and human serum (HS) yielded compelling results.

We demonstrated remarkable analytical performance using differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS). In PBS, our biosensor achieved an LOD of  $1.1 \pm 0.2$  fg/mL with DPV and  $3.9 \pm 0.5$  fg/mL with EIS. The sensitivity range covers a wide span of concentrations, from very low (fg/ml) to relatively high (ng/ml) concentrations. Serum optimization efforts in HS revealed an LOD of  $6.6 \pm 3.1$  fg/mL with EIS at a 0.1% HS concentration.

These findings fill a crucial void in CD5 biomarker detection, offering a potent tool for disease diagnosis and research while optimizing serum conditions for enhanced clinical utility.

#### Acknowledgments

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#### Cell membrane coated gadolinium modified polydopamine nanoparticles for photothermal therapy of liver cancer

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Polydopamine (PDA) nanoparticles are nature-inspired material that have been extensively studied for their therapeutic features, making them promising candidates for cancer treatment. During the synthesis of PDA nanoparticles, metal ions can be incorporated into the polymer matrix through coordination bonds with the functional groups of dopamine. The addition of metal ions may affect the physicochemical characteristics of PDA nanoparticles, including their photothermal properties. However, these types of nanoparticles have not yet been fully explored, which limits their application as therapeutic agent that can be used in photothermal therapy (PTT). Additionally, low delivery efficiency negatively affects the translation of nanotechnology to clinical applications. Therefore, an tumor-specific theraputic system needs to be designed with particular targeting towards cancer cells.

In this study, we aimed to assess the influence of gadolinium (Gd) dopant on the photothermal properties of mesoporous PDA nanoparticles. In addition, biomimetic coating of the PDA nanoparticles with the HepG2 tumor cell-derived membranes was used to increase their targeting abilities and therapeutic efficiency. The cell membrane coated Gd modified PDA nanoparticles were characterized using various techniques, including HR-TEM, DLS and Western blot. These nanoformulations exhibited robust photothermal properties under near infrared (NIR) irradiation. The photothermal effect evaluation demonstrated enhanced cytotoxicity of HepG2 cancer cells upon laser irradiation highlighting the synergistic effects of the nanomaterials and photothermal therapy. Our findings provide insights into the potential application of metal-doped PDA nanoparticles for cancer treatment.

#### Acknowledgements

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# Optimization of the loading method of a new PEG-functionalized porphyrin photosensitizer into silk spheres

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**Introduction:** A bioengineered spider silk functionalized with a human epidermal growth factor receptor 2 (HER2) binding peptide is employed to produce a nanosphere, namely H2.1MS1. H2.1MS1 sphere is biocompatible and biodegradable, which can further target HER2-overexpressing cancer cells. Photodynamic therapy (PDT) is a clinically approved cancer treatment with minimal systemic adverse effects using a light-activated substance, photosensitizer (PS). To improve selectivity, the new synthetic porphyrins PS functionalized with polyethylene glycol (PEG) is incorporated into H2.1MS1 spheres for targeted delivery to HER2-overexpressing cancer cells. Nevertheless, due to the hydrophobic property, PS is immiscible in a hydrophilic environmental condition of the H2.1MS1 sphere.

**Objective:** To develop a loading method for a new PS, 5,10,15,20-tetra [4-methoxy-3-(1,4,7,10-tetraoxoundecyl)phenyl]porphyrin (PS-1) into H2.1MS1 spheres.

**Methods:** The functionalized silk protein was produced in *E. coli* strain BLR and purified using the thermal method following precipitation with 20% ammonium sulfate. The H2.1MS1 spheres were formed using 0.5 mg/mL silk protein and 2 M potassium phosphate buffer in a micromixing device. The characteristics of H2.1MS1 sphere were analyzed by Zetasizer, Dynamic Light Scattering (DLS) and scanning electron microscopy (SEM). The miscibility of PS-1 under the DMSO, water, and acetone environment was examined by spectrophotometry using excitation ( $\lambda_{ex}$ ) and emission ( $\lambda_{em}$ ) wavelengths at 428 and 665 nm, respectively. PS-1 at various concentrations was incorporated into 100 to 300 µg of H2.1MS1 spheres at room temperature for 24 hours under the acetone environment. The concentration of PS-1 in H2.1MS1 was spectrofluorometrically measured and calculated using a standard curve.

**Results:** H2.1MS1 sphere was biotechnologically produced and showed a spherical shape under SEM analysis with a diameter, polydispersity index (PdI), and zeta potential of 312 nm, 0.37, and +2.52 mV, respectively. The fluorescence signal of PS-1 was detectable under the DMSO and acetone environments, while remaining undetected in water. In the acetone environment, 10 and 100  $\mu$ M PS-1 were incubated with 100  $\mu$ g of H2.1MS1 spheres, and the drug-loading concentration was 1.34 and 15.68  $\mu$ M, respectively. On the other hand, under the loading conditions, i.e. 100  $\mu$ M PS-1 and 100, 200, and 300  $\mu$ g H2.1MS1 spheres, the final drug-loading concentration was 15.68, 4.5, and 5.0  $\mu$ M, respectively.

**Conclusion:** The functionalized silk sphere, H2.1MS1, was successfully produced and incorporated with new synthetic photosensitizers, PS-1. The highest concentration of PS-1 in H2.1MS1 spheres was obtained by incubation of 100  $\mu$ M PS-1 with 100  $\mu$ g H2.1MS1 spheres under the acetone environment. In further experiments, the PS-1 incorporated H2.1MS1 spheres will be tested for their binding and cytotoxicity towards HER2-overexpressing and control cancer cell lines.

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