



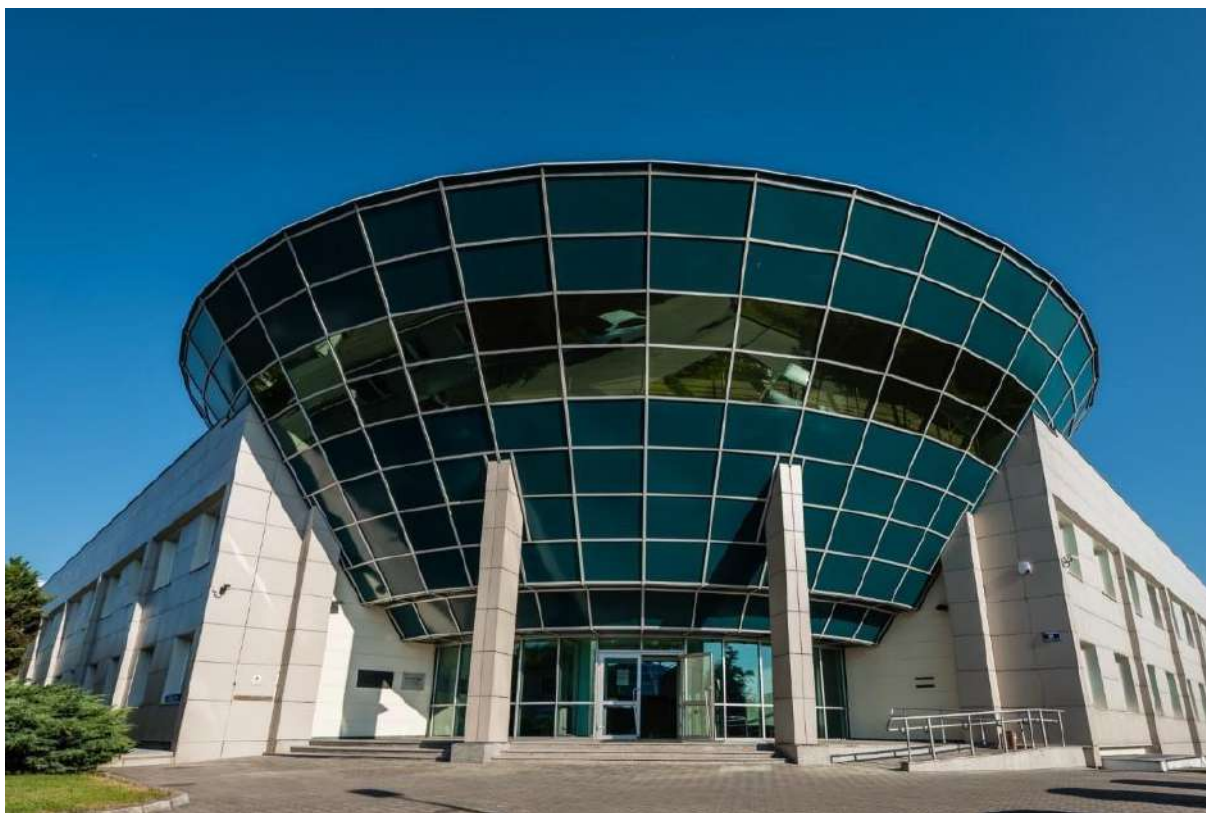
**JERZY HABER INSTITUTE OF CATALYSIS
AND SURFACE CHEMISTRY
POLISH ACADEMY OF SCIENCES**



HR EXCELLENCE IN RESEARCH

DETAILED RESEARCH REPORT

year 2020



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Statutory Research

Catalytic Materials and Processes for Sustainable Development

Effects of modifications of molybdenum trioxide on heat evolution accompanying the processes involving hydrogen bronze formation

(Professor Alicja Drelinkiewicz, Erwin Lalik PhD, Robert Kosydar PhD, Aleksandra Pacula DSc)

Aim of research. The research carried out in the systems Pd/H_xMoO₃ and Pd(Au)/(MoO₃/SiO₂) aimed to examine their activity and stability under exothermic cycles of hydrogenations and reoxidations in view of their use as an energy source.

Synthesis and characterization of samples. The typical Pd/MoO₃, as well as a composite Pd/(MoO₃/SiO₂) with various contents of MoO₃ (17 i 24 % wgt. MoO₃, XRF) have been used. The support MoO₃/SiO₂ was obtained by coprecipitation of TEOS and (NH₄)₆Mo₇O₂₄·4H₂O, followed by thermal decomposition (500 or 600 °C), leading to microcrystalline MoO₃ (XRD). The SEM images showed that so prepared material contained spherical grains of amorphous SiO₂ and the scattered MoO₃ microcrystals of typical platelet morphology (XRD). The XPS revealed an extent of surface reduction of molybdenum (Mo⁺⁶, Mo⁺⁵). For the depositions of nanoparticles of Pd (1 % wgt) and PdAu, three methods have been applied: 1) the reversed microemulsion, 2) impregnation from the Pd(Ac)₂ solution in acetone followed by reduction in H₂ (250 °C, 2 h), 3) deposition of pre-obtained Pd nanoparticles (6 nm); confirmed with XPS.

Thermal effects. The measurements using gas flow-through microcalorimeter involved cycles of hydrogenations (5% vol.H₂ in N₂) and subsequent reoxidations (synthetic air) of the samples at temperatures between 25 and 116 °C. The former sees the formations of H_xMoO₃ bronze (x = 0.4 - 1.7). The molar heats of the bronze formation and that of the reoxidation, as well as the H/MoO₃ ratio were measured. **Fig. 1 a** and **b** represent the molar heats of hydrogenation (in red), reoxidation (in blue) and their sum (in green). **Fig. 1a** shows that the heats of bronze formations in the 3%Pd/MoO₃ are constantly in agreement with the literature value (around 100 kJ/mol H₂), thus attesting to the apparent stability of the system. The analogous results for the 1%Pd(24%MoO₃/SiO₂) are shown in **Fig. 1b**. This catalysts were reduced in situ, rather than being pre-reduced at 250 °C, as the latter was found to cause an amorphization of MoO₃. Moreover, the higher of the two temperatures (600 °C) used in the MoO₃/SiO₂ synthesis turned out to be favorable. The H/MoO₃ ratios obtained for Pd/(MoO₃/SiO₂) depended on the synthesis methods and ranged from x = 0.3 to 1.7, also the heats of the bronze formation and reoxidation varied accordingly.

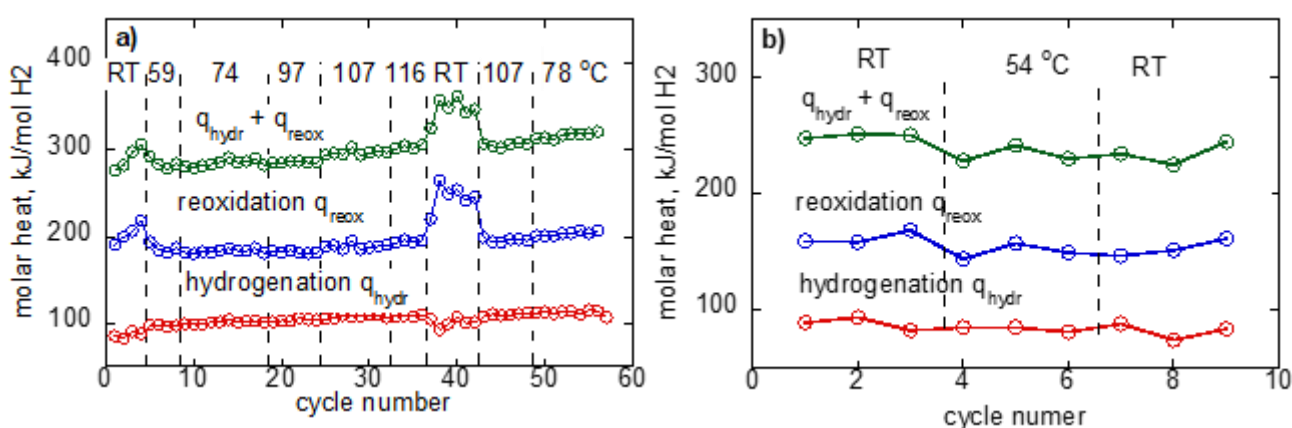


Fig.1 The hydrogenation/reoxidation for: **a)** 3%Pd/MoO₃ i **b)** 1%Pd(MoO₃/SiO₂) (dashed lines delimiting temperature ranges).

Summary. The obtained composite materials that contain microcrystalline MoO₃ in SiO₂ matrix is able to form the hydrogen bronzes and works persistently in the hydrogenation/reoxidation cycles. The Pd/MoO₃ system exhibits satisfactory durability against prolonged hydrogenation/reoxidation cycling.

Studies on the properties and application of enzymes with application potential

(Professor Tomasz Borowski, Maciej Guzik PhD, Anna Milaczewska PhD, Mateusz Tataruch PhD Eng., Professor Maciej Szaleniec, Justyna Andrys MSc, Anna Kluza MSc, Beata Mrugała MSc, Justyna Prajsnar MSc)

a) The aim of the research was to determine the substrate spectrum of (R)-1-(4-hydroxyphenyl)-ethanol dehydrogenase (R-HPED). 11 compounds were tested, i.e. acetophenone and its 9 derivatives (4'-Br, 4'-Cl, 4'-F, 4'-Et, 4'-NO₂, 4'-OCH₃, 4'-OH, 4 and 3'-NH₂,) and 1-indanone. Catalytic tests were performed in a batch mode, at 5 ml scale at pH 5.5 at 30°C using the homogeneous R-HPED catalyst with a specific activity of 31.6 U/mg and 5% isopropanol as the NADH regenerating substrate. The concentration of converted substrates was 2 mM and the reaction time was 24 h. On the basis of the obtained results, it was shown that the conversion was almost complete (> 95%) for compounds with electron-acceptor groups, such as 4'-NO₂, 4'-Br, 4'-Cl, 4'-F, 4'-H and not coupled resonantly with an acetyl substituent (3'-NH₂). On the other hand, for the electron-donor substituents (4'-OCH₃, 4'-OH, 4'-NH₂) reduced conversions were observed, they were in the range from 87 to 49%. Only 9% of 1-indanone was converted, most likely due to its steric mismatch with the R-HPED active site. Chiral chromatographic analyzes confirmed high enantioselectivity of the enzyme (ee% > 95%) and its preference for R isomers. Only for 1-(4'-hydroxyphenyl) ethanol around 10% of the S isomer was observed.

b) Cocrystallisation of FtmF enzyme with its substrate - fumitremorgin B was carried out using initial crystallisation condition for FtmF enzyme (24% PEG 4000, 0.3M MgCl₂, 100mM Tris pH=9, 5% ethanol). The optimisation of condition was performed with changing concentration of: PEG, Tris, MgCl₂, ethanol and pH of crystallisation buffer as well as testing detergents as additional and various crystallisation temperature (4 i 20°C). Different methods were tested for application of slightly soluble substrate: incubation of enzyme with excess of substrate added directly to enzyme solution and centrifuged before setting crystallisation or initial ligand dissolving in DMSO, 40% cyclodextrin solution, 6% SDS solution or 18mM n-decylo-β-D-maltoside and then mixing it with crystallisation buffer or incubation with enzyme in various ratio. Tests were performed for enzyme inhibited by substitution of metal ion (instead of native iron ion) in two variants: 1) nickel ion with the addition of N-oxalylglycine, 2) vanadyl with the addition of succinate. Unfortunately, hitherto all tested crystals of FtmF enzyme did not contained bound substrate (observed lack of electron density in active center derived from substrate)

c) The aim of the computational study was to determine the parameters of the amber force field for the iron cofactor of ectoine synthase (EctC). Three different parameterization methods were used: the method developed by Seminario, the methods implemented in the ParmHess program developed by R. Wang et al. and the method available in the ParamFit program developed by Betz and Walker. These methods were applied to two EctC active site models differing in the Tyr-84 ionization status. The obtained parameter sets were assessed on the basis of geometric criteria (comparison to a reference structure obtained from quantum-mechanical calculations) and the correlation of the energy calculated for a given parameter set with the energy determined by the DFT method.

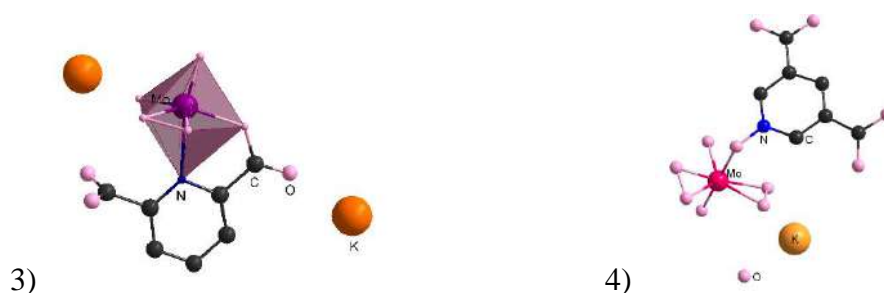
New peroxo and polyoxo compounds of Mo(VI), W(VI) and V(V). Synthesis, structural studies and applications in oxidation processes.

(Professor Wiesław Lasocha, Łukasz Kuterasiński PhD, Adrianna Sławińska MSc)

The conducted investigations concerned the synthesis and structural research of new organic-inorganic peroxomolybdates and polyoxomolybdates. The most important studies can be described as:

- 1) Several syntheses of polyoxomolybdates were carried out with the use of cyclohexanamines. Syntheses under reflux and autoclaves were performed. Tests were carried out for solutions acidified with hydrochloric or acetic acid. The obtained solid deposits were investigated using the methods of powder diffraction and elemental analysis.
- 2) The possibilities of syntheses with 30% H₂O₂, Mo(VI) compounds and dicarboxypyridinic acids were investigated. A number of peroxo compounds with potassium, sodium and ammonium cations were obtained.
- 3) Structural investigations of 1,3-dimethylaminocyclohexane octamolybdate (**1**) and 1,4-diaminocyclohexane trimolybdate (**2**) were performed.
- 4) The solution and refinement of the crystal structures of potassium salts of 2,6-dicarboxypyridine oxodiperoxomolybdate (**3**) and 3,5-dicarboxypyridine oxodiperoxomolybdate (**4**) were performed. The crystallochemical data and structure drawings are presented below.
- 5) For selected compounds from the group of polyoxo and peroxomolybdates, tests of catalytic oxidation of cyclic hydrocarbons and oxidation of cyclohexanone in the Baeyer-Villiger (**BV**) reaction were carried out. In the **BV** reaction, a very high selectivity of some carboxypyridine per compounds towards ϵ -caprolactone (> 90%) was observed.
- 6) Selected peroxo compounds were tested at the *Collegium Medicum* (Jagiellonian University) as part of pharmacological investigations on tumor cell lines. The best compounds show activity comparable to that of cis-platinum used in practical therapies.

The figure below shows the asymmetric units for the compounds (**3,4**). Magenta, black, blue and pink spheres represent Mo, C, N and O, yellow large spheres indicate K atoms.



Crystallochemical data:

(**1**) Mo₈O₂₆ (C₈H₁₈N₂)₂, SG P2₁/m, a, b, c, β ; 13.539617 10.748388 13.508859 90.00000 99.86536, V = 1922.09 Å³, Z=2

(**2**) Mo₃O₁₀ (C₆H₁₆N₂)(H₂O), SG P-1, a, b, c, $\alpha\beta\gamma$; 8.961(1), 11.492(3), 7.625(2), 105.43(2), , 92.51(2) 90.91(2), V=755.9, Å³, Z=2

(**3**) K₃MoO(O₂)₂(C₈H₄NO₄), SG P-1, a, b, c, $\alpha\beta\gamma$; 7.1961(2), 8.0150(1), 10.8977(2), 101.153(1), 91.972(2), 115.502(2), V=551.7, Å³, Z=2

(**4**) K₂MoO(O₂)₂(C₈H₄NO₄) (H₂O), SG P-1. a, b, c, $\alpha\beta\gamma$; 11.757, 7.965, 7.337, 113.94, 94.79, 77.70, V=613.5, Z=2.

Studies of structural effects and influence of support on the catalytic activity of copper-based systems

(Associate Professor Dorota Rutkowska-Żbik, Professor Małgorzata Witko, Professor Mirosław Derewiński, Associate Professor Renata Tokarz-Sobieraj, Anna Micek-Ilnicka DSc, Michał Śliwa PhD, Katarzyna Samson PhD Eng., Małgorzata Ruggiero-Mikolajczyk PhD, Łukasz Kuterasiński PhD, Mariusz Gackowski PhD, Urszula Filek PhD Eng., Małgorzata Zimowska PhD, Wojciech Rojek MSc, Jerzy Podobiński MSc, Natalia Ogrodowicz MSc, Joanna Kaim MSc, Małgorzata Smoliło MSc Eng.)

Within the research task we continued studies aimed to define how the structure of copper-based systems modulates their catalytic activity in the gas-phase conversion of alcohols (e.g. methanol, ethanol, furfural) and processes related to valorisation of furfural.

In order to check if the localisation of copper ions introduced into zeolitic matrices influences its electronic state and properties X-ray absorption spectroscopy (XAS) technique was employed for samples consisting of BEA and FAU zeolites with Cu ions introduced (copper content was 1, 2, and 5 wt%) in a way copper phase was localised on the surface and in the bulk. The experiments were done in the Solaris National Synchrotron Radiation Centre using PEEM/XAS end-line with total electron yield (TEY) (surface sensitive) and partial fluorescence yield (PFY) (bulk sensitive) detection. The samples with copper were subjected to charging during the measurements and as a result, the collected TEY spectra were not of the good quality. The difference between the surface and bulk Cu oxidation state was observed only in case of FAU with 5% Cu; it seems that the higher concentration of Cu(I) is found on the surface of the zeolite than inside the bulk. These results were correlated with the results of the catalytic tests (ethanol oxidation studied *in situ*, with the reaction progress monitored under IR). Ethanol reduces Cu(II) prior to reducing Cu(I). It was found that Cu(I) present in the oxide phase (and thus should be preferentially located at the surface of the sample) is more easily reduced than Cu(I) located in the ion-exchange positions of the zeolite (in the bulk). The experimental results were further interpreted in the light of theoretical studies employing QMPot (one of QM/MM schemes: Polarizable Ions Interatomic Potential/DFT) with the focus on faujasite (FAU) type zeolite, known to exhibit several interesting catalytic and adsorption properties. The *in silico* studies allowed for clarifying the nature of different adsorption adducts observed spectroscopically in Cu(I)-FAU.

Additionally, a series of catalysts in which active phase consisted of H₃PW₁₂O₄₀ heteropolyacid and copper phase was synthesised. As the support, two types of TiO₂ were used: P25 (hydrophilic) and T805 (hydrophobic). The catalysts were characterised by a set of physico-chemical methods: structure was examined with XRD, porosity and surface area were measured by BET, and stability by derivatograph method (TG/DTA). The catalytic and photocatalytic activity of the samples was tested in dehydration of n-butanol in the gas phase at 120-220 °C. It was found that the supported catalysts exhibit higher catalytic activity than pure HPA. The best activity was measured for HPW/P25 and HPW/T805. Light had no effect on the activity.

New catalytic materials for „green chemistry” processes

(Professor Ewa Serwicka-Bahranowska, Roman Dula PhD Eng., Dorota Duraczyńska PhD, Robert Karcz PhD Eng., Joanna Kryściak-Czerwenka PhD, Alicja Michalik PhD Eng., Bogna D. Napruszewska PhD Eng., Katarzyna Pamin DSc, Anna Walczyk MSc)

Two types of new catalytic materials were investigated: a) alkali-activated natural layered mineral sepiolite, b) organocatalysts based on fluorinated N-hydroksyfthalimide (NHPI).

Demand for effective biomass valorization and CO₂ entrapment contributed to the rapidly growing interest in development of new solid base catalysts and adsorbents. Sepiolite, a natural Mg-containing layered silicate mineral with basic properties was chosen as a basis for materials design. Research focused on determining the influence of grinding of sepiolite on the efficiency of alkali activation. Prepared catalysts were characterized with XRD, SEM/TEM, N₂ adsorption/desorption at -196°C, XRF, AAS, XPS, FTIR (MIR, NIR), and ²⁹Si MAS NMR. Surface basicity was determined by titration with benzoic acid. It has been found that grinding influences evolution of phase composition of the alkali activated solid. Unground sepiolite transformed into its Na-form (loughlinite), while ground material underwent transformation to microporous phase of magnesium silicate hydrate (MSH). Prepared materials were tested as catalysts in base-catalyzed reactions, i.e. aldol self condensation of acetone and cyclohexanone oxidation to ε-caprolactone, and as CO₂ sorbents. The observed activity trends depended not only on the materials basicity, but also on their texture and phase composition. Microporous magnesium silicate hydrate formed after alkali activation of ground sepiolite proved to be an exceptionally efficient CO₂ sorbent.

In search for more efficient and environmentally friendly catalytic system for Baeyer-Villiger oxidation of cyclohexanone to ε-caprolactone with molecular oxygen a series of organocatalysts were prepared based on N-hydroxyphthalimide (NHPI) fluorinated in different positions of aromatic ring. It has been reported earlier that NHPI acts as an effective intermediate in the liquid phase aerobic oxidation of hydrocarbons under mild conditions. Synthesized NHPI-type compounds were characterized using XRD and TG/DSC methods. The oxidation of cyclohexanone in the presence of NHPI-type catalysts was performed in a thermostated glass reactor at 40°C for 5 h at atmospheric pressure. The study demonstrated that in the presence of NHPI-type organocatalysts cyclohexanone is effectively converted to ε-caprolactone in the presence of NHPI-type organocatalysts.

Physics and Chemistry of Surfaces and Nanostructures

Mechanisms and kinetics of protein molecule immobilization at solid/electrolyte interfaces and determination of their interactions with macromolecule ligands.

(Professor Zbigniew Adamczyk, Piotr Batys PhD, Aneta Michna DSc, Maria Morga PhD, Małgorzata Nattich-Rak DSc, Agata Pomorska PhD, Marta Sadowska PhD, Lilianna Szyk PhD, Paulina Żeliszewska PhD)

All atom molecular dynamic modeling was applied in order to determine water molecule and electrolyte ion concentration profiles around and inside the myoglobin molecule at various pHs. Significant penetration of counter ions into the molecule was confirmed. The electric potential distribution within and outside the molecule was quantitatively described using the non-linear Poisson-Boltzmann (PB) approach. Using this model, calculations were performed, yielding the surface and zeta potential under various pHs, the electric permittivity, the ion penetration depth and the protein volume fraction (crowding effect). The theoretical results were used for the interpretation of the experimental data acquired under different ionic strengths and temperatures by the DLS, electrophoretic mobility (LDV) and AFM measurements. It is confirmed that the experimental data are adequately reflected for acidic pHs by the non-linear PB model developed in this work. In this way, it is both experimentally and theoretically confirmed that the effective charge of the myoglobin molecule in electrolyte solutions is considerably smaller than the nominal, structure-based, predicted charge. As a result, at physiological conditions prevailing, e.g., in skeletal muscles, the myoglobin molecule should be practically neutral. One can expect that the general approach developed in this work can be applied for predicting charging mechanisms of other protein molecule characterized by an analogous charge vs. pH characteristic, e.g., the SARS-CoV-2 virus spike proteins, and for soft particles with pH responsive characteristics.

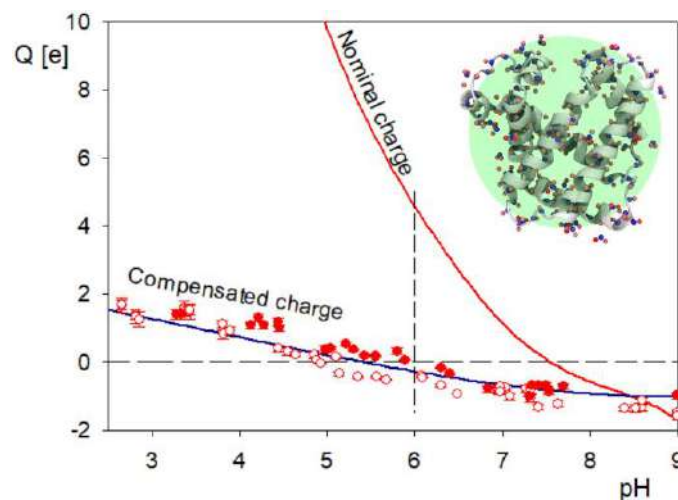


Fig. 1. The dependence of the effective charge of the myoglobin molecule on pH; the hollow and full points denote the experimental data derived from the electrophoretic mobility (LDV) measurements for ionic strength of 0.15 M and the temperature of 298 and 310 K, respectively. The solid (red) line number 1 denotes the nominal charge calculated from the primary molecule structure and the solid (blue) line number 3 shows the theoretical results calculated in this work considering two electric double-layers.

Monolayers of plasmonic nanoparticles of controlled structure and tunable electrokinetic properties

(Professor Zbigniew Adamczyk, Magdalena Oćwieja DSc, Julia Maciejewska-Prończuk PhD, Dawid Lupa MSc Eng., Maria Morga PhD, Monika Wasilewska PhD, Małgorzata Nattich-Rak DSc, Marta Sadowska PhD, Paulina Żeliszewska PhD, Katarzyna Kusak Eng.)

The main aim of undertaken studies was a development of efficient methods of preparation of mixed layers of silver and gold nanoparticles characterized by controlled structure, composition and electrokinetic properties. Silver and gold nanoparticles used in the studies was obtained in a chemical reduction method using silver nitrate and chloroauric acid as precursors and trisodium citrate as a reducing agent. Physicochemical characteristics revealed that the nanoparticles were characterized by spherical shape and narrow size distribution. The average size of silver nanoparticles (AgNPs) was equal to 50 ± 4 nm whereas the average diameter of gold nanoparticles (AuNPs) attained value of 14 ± 2 nm. The nanoparticles exhibited negative zeta potential in a broad range of pH and ionic strength. It was determined that the nanoparticles were stable at $\text{pH} > 3.1$ and ionic strength lower than 3×10^{-2} M.

The processes of sequential deposition of nanoparticles on solid surfaces (mica, silicon) modified by cationic polyelectrolyte – poly(allylamine hydrochloride) (PAH) – were carried out under controlled conditions of temperature, pH and ionic strength. The kinetics of nanoparticle deposition under convection conditions were determined using quartz crystal microbalance (QCM). The electrokinetic properties of formed layers were studied applying streaming potential measurements whereas the structure was determined based on the images and micrographs obtained from atomic force microscopy (AFM) and scanning electron microscopy (SEM).

Conducted research showed that the coverage, composition and structure of mixed layers of plasmonic nanoparticles can be controlled by such parameters as: deposition time of nanoparticles, pH and ionic strength. It was proved that for selected conditions, the order of deposition of nanoparticles of different sizes influences significantly on the structure of formed layers. It was proved that the mixed layers of coverage higher than 10% were characterized by negative zeta potential. Moreover, the high stability of formed mixed layers was demonstrated for a broad range of ionic strength (10^{-4} – 3×10^{-2} M) at pH 5.8.

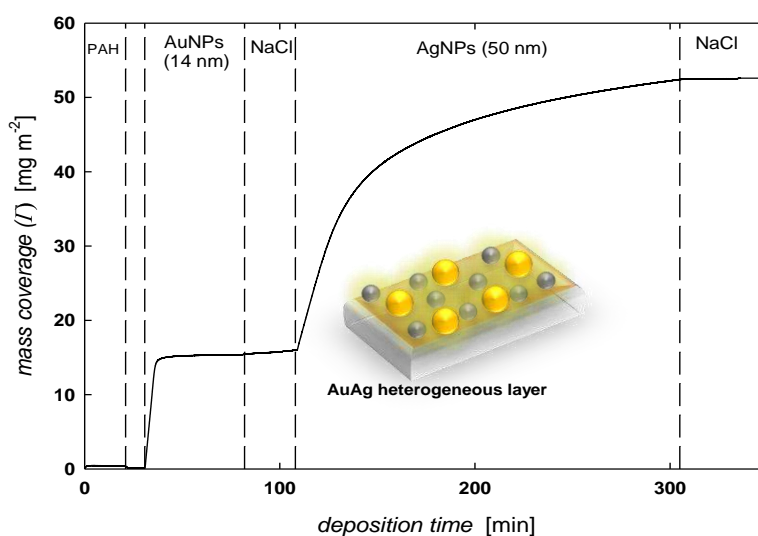


Fig. 1. Deposition kinetics of citrate-stabilized AuNPs (14 nm) and citrate-stabilized AgNPs (50 nm) on PAH-modified sensor. The measurements conditions: $T=298$ K, flow rate $1.33 \cdot 10^{-3} \text{ cm}^3 \text{ s}^{-1}$, bulk suspension concentration 50 mg L^{-1} , pH 5.8, ionic strength: 10^{-4} M for AuNPs and 10^{-2} M for AgNPs.

Modeling of the mechanical properties of biological systems in the micrometer scale.

(Jakub Barbasz DSc Eng., Leszek Krzemień PhD, Agnieszka Kurek MSc)

In statutory research in year 2020 we were working on a model of atomic force microscope indentation measurements using the finite element method.

Our focus was set on a thorough representation of the complex structure of an animal cell. Its crucial constituent was the cell cortex - a stiff layer of cytoplasmic proteins present on the inner side of the cell membrane.

Cortex plays a vital role in the mechanical interactions between cells and external environment. In our model, the cell cortex was modelled by a three-dimensional solid characterized primarily by its bending stiffness. This approach allowed us to interpret the measurements of the mechanical properties of the cells, done by atomic force microscopy, such as elasticity. During the simulations, we probed a broad range of parameters defining cell properties and experimental conditions. Finally, we derived a simple and closed-form formula that approximates the simulated results with satisfactory accuracy.

Our formula was as easy to use as Hertz's function in order to extract cell properties from the measurement, with additional consideration of the cell inner structure.

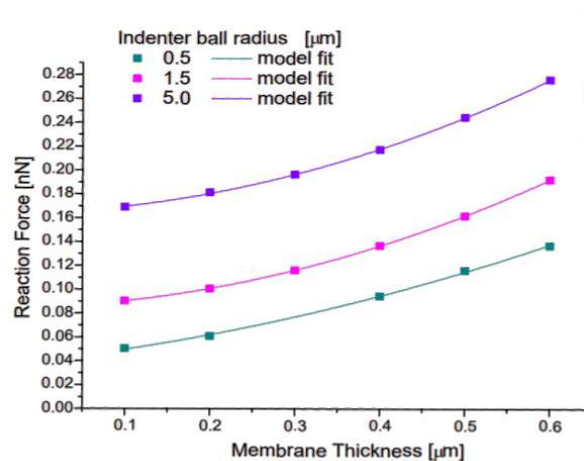


Fig. 1 Dependence of reaction force on membrane thickness for different indenter diameters.

Structural, electronic and dynamics properties of surface and nanostructures studied with microscopic and spectroscopic techniques under ultra-high vacuum conditions.

(Professor Nika Spiridis, Professor Józef Korecki, Jacek Gurgul DSc, Kinga Freindl PhD Eng., Ewa Madej PhD Eng., Ewa Młyńczak PhD, Piotr Mazalski PhD, Robert Socha PhD, Dorota Wilgocka-Ślęzak PhD Eng., Joanna Wojas MSc, Natalia Kwiatek MSc)

Research carried out in the framework of the statutory activity by the "Surface Nanostructures" group concerned metallic and oxide nanostructures, in particular grown by molecular beam epitaxy, with potential spintronic and catalytic applications.

Research in the field of model catalysis was continued; the adsorption of CO on Au nanoparticles on the magnetite Fe_3O_4 (111) surface with different, precisely controlled termination and on the rutile TiO_2 (110) surface modified with Fe was investigated under ultra-high vacuum (UHV) conditions, using a comprehensive methodology involving, among others, scanning tunneling microscopy and temperature-programmed desorption .

We have continued studies of oxygen superstructures formed at high temperatures (500-1200°C) on the tungsten W(110) surface. A new explanation of the observed superstructures has been proposed as the moiré effect resulting from the mismatch between the adsorbed oxygen monolayer and the tungsten (110) surface lattice.

The study of the FeRh alloy, in which the antiferromagnetic (AFM) / ferromagnetic (FM) phase transition occurs near room temperature (RT), was continued. For the FeRh islands formed on W(110), depending on the islands height two types of the magnetic domain structure at RT was observed, which was related to the different relaxation of stress generated at the interface due to the lattice mismatch of the alloy and the substrate.

The oxidation of the two-component NiFe alloy system, in which there is a large variety of crystal phases, with magnetic properties depending on the stoichiometry, was analyzed. The research was carried with the goal to optimize the composition for metal-oxide heterostructures with spontaneous reorientation of magnetization. An alloy layer with nominal stoichiometry of $\text{Ni}_{0.7}\text{Fe}_{0.3}$ and a thickness of 15 monolayers was prepared by co-deposition of Ni and Fe and subjected to UHV annealing, which led to the formation of regions with different crystal structures: fcc (111) and bcc (110). The fcc regions were enriched in Ni and the bcc in Fe. Oxidation at a temperature from the range of 250-300° C, with an O_2 partial pressure of 1×10^{-6} mbar, led to surface segregation and preferential oxidation of Fe for both alloy phases. Using Mössbauer spectroscopy, it was found that in the initial stage an FeO (111) layer was formed, which transformed into Fe_3O_4 (111) during prolonged oxidation, and that a small amount of $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ spinel was formed between the metallic alloy and the surface FeO_x layer.

The second group of tasks, related to materials prepared *ex situ*, concerned the analysis of the elemental surface composition and electronic states of in various types of catalytic, photovoltaic, and electrochemical systems.

A significant amount of group efforts was devoted to measurements, calibration and operation of the PEEM/ XAS beam line at the National Synchrotron Radiation Center "Solaris", and above all to making the end-stations available to external users, both as a result of the open calls for the beamtime as well as in the framework of the CERIC/ERIC consortium and internal ICSC experiments.

Molecules with biological importance in reference to their interaction with a surface and refining their theoretical description

(Professor Tomasz Pańczyk, Associate Professor Wojciech Płaziński, Agnieszka Brzyska PhD)

The conducted research and their results concerned three research problems concerning (i) the application of external forces in quantum-chemical studies of conformational transitions within various molecules, (ii) the analysis of the influence of the external magnetic field on the dynamic trajectories of molecules with partial charges, and (iii) the use of molecular modeling methods for predicting conformational equilibrium of molecules.

Conformational changes in molecules, i.e. transitions between their different structural states, can be caused by various environmental factors (pH changes, temperature, effectors, radiation, etc.). External mechanical forces can also induce permanent conformational changes in molecules. Quantum-chemical methods (EGO, SEGO, CGO) were used to describe enforced structural changes in various molecular systems. The mechanism of the intramolecular proton transfer reaction in the 2-methylfuran molecule, leading to the formation of a series of compounds with a bivalent carbon atom in the system (carbenes), was proposed. SEGO methods allowed to automatically locate all relevant transition states. The EGO and SEGO studies on mechanophores were also carried out. For spiropyran molecule covalently anchored between two polymer chains, a theoretical description of the conformational transition: spiropyran-> merocyanine induced by external forces was proposed.

Literature quite often includes works based on the use of classical molecular dynamics and the Monte Carlo method to describe the dynamics and thermodynamic equilibrium of molecular systems under the influence of an external, static magnetic field. Since these works are often cited in order to support the experimentally observed effects related to e.g. water magnetization, a rigorous theoretical analysis of the possible physical foundations of such phenomena was carried out. Based on the Bohr-van Leeuwen theorem, it can be proved that on the basis of classical statistical physics for systems in statistical equilibrium it is impossible to justify the existence of the phenomenon of magnetism. Thus, the observations of the influence of a static magnetic field on the state of systems modeled using classical molecular dynamics must be erroneous. As part of the research, the impact of algorithm for integrating equations of motion as a source of artifacts generating effects similar to the Lorentz force has been analyzed. However, the main factor responsible for the observation of the significant influence of the magnetic field on the trajectories of classical molecular dynamics is the intentional interpretation of statistical fluctuations.

Chirality plays an essential role in numerous processes of either chemical or biochemical nature. At the molecular level, the effects associated with this phenomenon can be studied by using the molecular dynamics simulations techniques. Several alternative approaches suited for the molecular dynamics-based free energy calculations in chiral systems were proposed: (i) biased sampling in the two-dimensional space, along the coordinates defined by the values of the selected torsional angles; (ii) biased sampling along the path-based coordinate(s); (iii) rational alteration of the system's Hamiltonian in order to enable the interconversion between stereoisomers; (iv) using the free energy landscape generated within approaches (i) or (ii) as time-independent bias in order to further improve sampling efficiency and simultaneously account for multiple chiral centers. All approaches have been tested on a set of model compounds which lead to demonstrating their good performance but also some differences in the range of their applicabilities.

Determination of mechanisms of synthesis, structure, and transport parameters of supported colloidal particle multilayers

(Associate Professor Paweł Weroński, Karolina Pałka MSc)

The radial distribution function, also called the pair-correlation function, is one of the most important statistical functions of many physicochemical systems, including layers of colloidal particles. Its knowledge allows the determination of important parameters of these systems, both on the microscopic and macroscopic scale. The correlation function determines, e.g., roughness of the surface covered with a monolayer of nanoparticles, which is described by another statistical function, the so-called power spectral density. Traditionally, the radial distribution function of a monolayer is calculated by analyzing its image and determining the geometric centers of all adsorbed particles. This allows us to determine the probability of occurring a pair of particles at a certain distance. However, this method is computationally expensive and burdened with a relatively high measurement uncertainty, especially in the range of high surface coverage. As the results of analytical considerations show, the pair-correlation function can also be determined by another method of image analysis, in which there is no need to identify individual particles or their geometric centers. This alternative method is based on measuring the monolayer height function and calculating its power spectral density, and then calculating the Hankel transform of the algebraic expression linking the obtained numerical results.

The aim of our research was to verify the correctness, accuracy and usefulness of the new method of calculating the radial distribution function. For this task, we have developed numerical algorithms and computer programs to determine the necessary discrete, ensemble averaged statistical functions of spherical particle monolayers. We have also developed an algorithm and a computer program for calculating the discrete Hankel transform. We generated statistical ensembles of monolayers with several values of coverage and different surface areas, adsorbed according to the classical RSA model. Then, using the developed tools, we determined the average functions of the power spectral density of the monolayer, single particle and disk slice for all the investigated ensembles. After determining these statistical functions, we computed the inverse Hankel transform of the algebraic expression, which gave numerical values of the radial distribution function as a result of this transformation.

Our results suggest that to obtain a good-quality correlation function, a high-density sampling of the investigated area is necessary. The minimum measurement resolution depends on the nature of correlation function of the monolayer and on the surface coverage. In the case of RSA systems with coverage 0.5, in which the correlation function changes rapidly at the distance of two particle radii, very dense surface sampling on the order of 100 measurements per particle radius is necessary to obtain a good quality distribution function. In practice, this means limiting the size of the analyzed area to a circle with a radius equal to ten particle radii, because such a system already requires the use of very high image resolution of 2048 x 2048. Statistical analysis of an image with such a small surface area and the number of adsorbed particles requires averaging over a very large ensemble to reduce noise. Increasing the radius of the analyzed area to one hundred particle radii allows to obtain a good-quality correlation function from a much smaller number of systems, but requires the use of approximately 10 times higher image resolution, which seems unattainable with the current level of measurement technology. However, further intensive development of digital technology may make this method an optimal tool for determining the radial distribution function in the future.

„Functional multilayer polyelectrolyte films”

(Professor Piotr Warszyński, Marta Kolasinska-Sojka DSc)

During this year's research, we have continued the studies and description of structural changes as a function of incubation time for selected phospholipid bilayers (SLB), modified with model quantum dots (QD) of various size, deposited on polyelectrolyte films.

Quantum dots incorporated inside the lipid bilayers increase their bioanalytical potential, enabling, for example, the tracking of vesicle fusion on the cell membrane surfaces by registering QD fluorescence in the bilayers. Taking into account the benefits of using such hybrids, there is a need for better understanding of the role of quantum dots (or other inorganic nanoparticles) in lipid reorganization and the morphology of nanoparticles/lipid bilayer membranes. Currently, little is known about how the presence of nanoparticles changes the structure and physicochemical properties of SLB also during deposition of supported lipid bilayers on selected surfaces.

The main goal of the presented research was to describe the structure changes as a function of incubation time for the POPC/POPE phospholipid bilayer - palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine/1-palmitoyl-2-oleoyl-sn-glycero-3-phospho-ethanolamine) containing hydrophobic cadmium sulphide quantum dots of various sizes deposited on a positively charged polyethyleneimine film adsorbed on a silicon substrate.

Structural changes over time for the POPC/POPE bilayer with quantum dots (CdS QD) were monitored using the X-ray reflectometry (XRR), while their morphology was characterized using atomic force microscopy (AFM).

We proved the dependence of the structure of lipid bilayers deposited on a polyelectrolyte film on the incubation time for bilayers containing selected quantum dots. The thickness increased with increasing incubation time with simultaneous increase of the density for the studied systems. In addition, we observed the exclusion of quantum dots from the inside of the bilayer to its outer part, which leads to the more orderly packing of lipid molecules inside the bilayer, while the outer part, which is in constant contact with water, is more flexible, leading to easier adaptation to the presence of nanoparticles.

Our results as the first detailed description of the structural evolution of the lipid bilayer containing hydrophobic nanoparticles, adsorbed on a polyelectrolyte film, will be used for further research leading to the use of SLB-QD systems as biosensors.

Nanoparticles as neuroprotective substance carriers

(Associate Professor Krzysztof Szczepanowicz, Marta Szczęch MSc, Professor Piotr Warszyński, Anna Pajor-Świerzy PhD)

Despite many chemicals show a protective effect on neuronal cells, they are less effective in clinical trials, which may be related to their poor absorption and distribution as well as adverse reactions of the immune system after systemic applications. Nanotechnology creates new perspectives because formulations in nano-form can possess unique pharmacokinetic and pharmacodynamic properties, that can contribute to their high effectiveness in therapeutic action while minimizing undesirable side effects. The scientific aim of this task is to develop a methodology of the synthesis of biodegradable and biocompatible nanocarriers for neuroprotective substances. Final results will broaden knowledge in the field of neuropharmacology, particularly concerning the design and synthesis of novel, nano-scale drug delivery systems for neuroprotective agents.

In 2020, we were focused on the optimization of the encapsulation of a selected neuroprotective drug (Edaravone) into multilayered polymeric nanocarriers with controllable physicochemical properties and proper functionality. The method of the encapsulation of Edaravone into biocompatible and biodegradable polycaprolactone (PCL) nanoparticles was optimized. Furthermore, drug-loaded PCL nanoparticles were functionalized by the formation of a multilayered shell. The polyelectrolyte multilayer shell was constructed by sequential adsorption of polyelectrolytes (layer-by-layer) method. Polyelectrolyte multilayer shells were constructed with biocompatible and biodegradable polyelectrolytes: poly-L-lysine (PLL) as polycation and poly-L-glutamic acid (PGA) as polyanion. The average size of drug-loaded multilayered nanocarriers was 90 nm (Fig. 1). Synthesized multilayered nanocarriers were tested for their cytotoxicity and activity of the encapsulated drug.

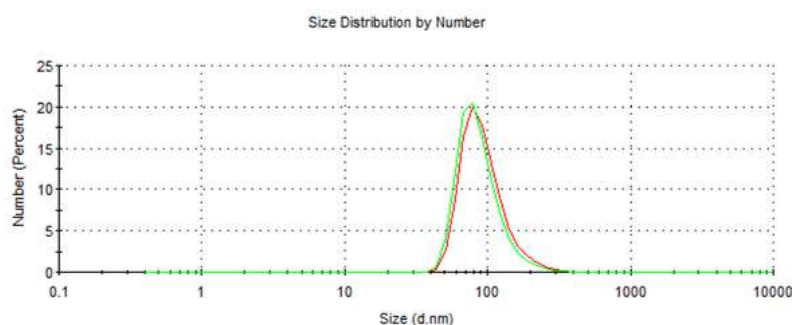


Figure 1. The size distribution of PCL nanocarriers containing Edaravone.

Influence of initial adsorption coverage at liquid/gas interface on stability of foam and wetting films under dynamic conditions

(Associate Professor Jan Zawala, Agata Wiertel-Pochopień MSc Eng., Dorota Gawel MSc Eng., Mariusz Borkowski MSc, Georgi Gochev PhD)

The aim of this research task was to investigate the stability of single foam films formed at the solution/air interface under dynamic conditions, i.e. during single bubble collision with the free solution surface. In the reporting period the influence of solution concentration of n-octanol and n-hexadecyl-trimethyl-ammonium bromide (C₁₆TAB) on the foam films stability was determined. The experiments were planned in a way allowing correlation of the initial adsorption coverages at the detaching bubble surface with the architecture of the dynamic adsorption layer, and investigate the influence of both parameters on the kinetics of drainage of the foam films.

During experiments, the initial adsorption coverage at the detaching bubble surface (liquid/gas interface) was controlled using the “bubble trap” elaborated in our laboratory, allowing immobilization of the bubble in solution of surface-active substance (SAS) for desired time, associated with the SAS adsorption kinetics. This time was called adsorption time (t_{ads}). The initial adsorption coverages of the bubble were calculated. Their influence on the stability of single foam films was determined in the experimental set-up allowing automatic determination of a single bubble lifetime at the solution/air interface. The lifetimes were directly correlated with the times of drainage of foam films. The lifetime values obtained experimentally were used in theoretical calculations of final thickness of the foam films (so-called critical thickness of rupture), using Radoev, Dimitrov and Ivanov (RDI) model. This model allowing to consider the influence of state of dynamic adsorption layer at the rising bubble surface on the foam film drainage kinetics (modifications of the hydrodynamic boundary conditions). It was found that, when the foam film was formed by the bubble release far away from the solution/air interface (distance 150 mm) and was rising with terminal velocity, the film stability was depending on the solution concentration, only. For constant concentration, the increasing initial adsorption coverage had no influence on the single bubble lifetime. It was rather surprising result, indicating that despite the fact of initial adsorption coverage increase, the rate of drainage of formed foam films and their critical rupture thicknesses were practically identical (70-80 nm – see Fig. 1). It was a proof that the interfaces creating the liquid (foam) film have similar surface mobility, which can be associated with similar structure of the adsorption layer induced at the rising bubble surface.

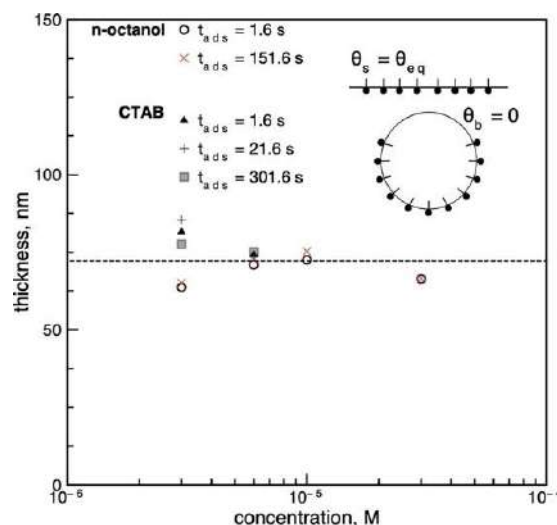


Fig. 1. Thicknesses of the foam films at the moment of their rupture, calculated using experimentally determined bubble lifetimes, according to the RDI drainage model

New cathode materials for high-temperature fuel cells with a reduced working temperature – continuation.

(Michał Mosiałek DSc, Dmitry S. Kharitonov PhD, Małgorzata Zimowska PhD, Robert P. Socha PhD, Grzegorz Mordarski PhD)

YBaCuCoO_{5+δ} (YBCC), YBaFeCoO_{5+δ} (YBFC), YBaCuFe_{0.2}Co_{0.8}O_{5+δ} (YBFCC1), YBaCuFe_{0.6}Co_{0.4}O_{5+δ} (YBFCC2), and SrTi_{0.2}Fe_{0.8}O_{5-δ} (STF) mixed oxides revealing perovskite structure were investigated. Materials were milled, then its microstructure was investigated by scanning electron microscopy (SEM). X-ray photoelectron spectroscopy was used for the surface analysis of the layered perovskites. Electronic states of included elements were described. Oxides in the form of powders were mixed with ink vehicle (Nexceris) forming pastes. Working and reference electrodes were fabricated applying investigated pastes on the surface of the Ce_{0.8}Sm_{0.2}O_{1.9} (SDC) disk using a mask, whereas the whole opposite surface was covered with a thin film of La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-δ} cathode ink (Nexceris) forming a counter electrode. Cells were sintered at 900–1100 °C. Electrochemical measurements were conducted in the single chamber, three-electrode setup in oxygen and mixtures of oxygen and argon using the chronoamperometry, the cyclic voltammetry, and the electrochemical impedance spectroscopy (EIS).

Thermal expansion coefficient values of YBCC, YBFCC1, YBFCC2, and YBFC within the temperature interval 20–780 °C, are equal to $14.3 \times 10^{-6} \text{ K}^{-1}$, $14.9 \times 10^{-6} \text{ K}^{-1}$, $13.9 \times 10^{-6} \text{ K}^{-1}$, and $16.0 \times 10^{-6} \text{ K}^{-1}$, respectively. Values of its high electric conductivities are between 6 and 10 S cm⁻¹ in the range 600–800 °C. Obtained cells examined by SEM reveals enough large porosity, desired grain sizes, and were well sintered to the electrolyte surface without delamination. On the base of EIS measurements, it was shown that the lowest polarization resistance (R_p) revealed YBCC and STF (Fig. 1). For example, at 800 °C and $P(\text{O}_2) P^{-1} = 0.2$ for YBCC and STF it was 0.24 and 0.47 Ω cm², respectively. The oxygen reduction reaction (ORR) mechanism was determined by examining the dependence of the reaction resistance on the oxygen partial pressure, which is expressed by the formula: $\log(R_p) = a - m \log(P(\text{O}_2))$, where a and m are coefficients. Coefficients m at 800 °C are equal to: for YBCC and STF 0.45 in the range of $P(\text{O}_2) P^{-1}$ 0.001–1; for BFCC1 0.37 and 0.16 in the ranges of $P(\text{O}_2) P^{-1}$ 0.1–1, and 0.001–0.05, respectively; for YBFCC1 and YBFC 0.32 and 0.30 respectively, in the range $P(\text{O}_2) P^{-1}$ 0.001–0.5. The dependence of R_p on the oxygen partial pressure indicates a different mechanism of the ORR on the YBCC and STF cathodes compared to the others. Here, the limiting step of RRT is an elementary reaction whose rate is proportional to $(P(\text{O}_2) P^{-1})^{0.5}$ with the participation of oxygen in the molecular form, such a reaction is the adsorption of the O₂ molecule with simultaneous dissociation on the cathode surface. For other materials with the higher polarization resistance, the charge transfer process significantly delays RRT. The activation energy for the reciprocal polarization resistance was determined. For YBCC, STF, YBFCC1, YBFCC2, and YBFC in the range 600–800 °C E_A is equal to 1.28, 1.32, 1.58, 1.49, and 1.14 eV, respectively.

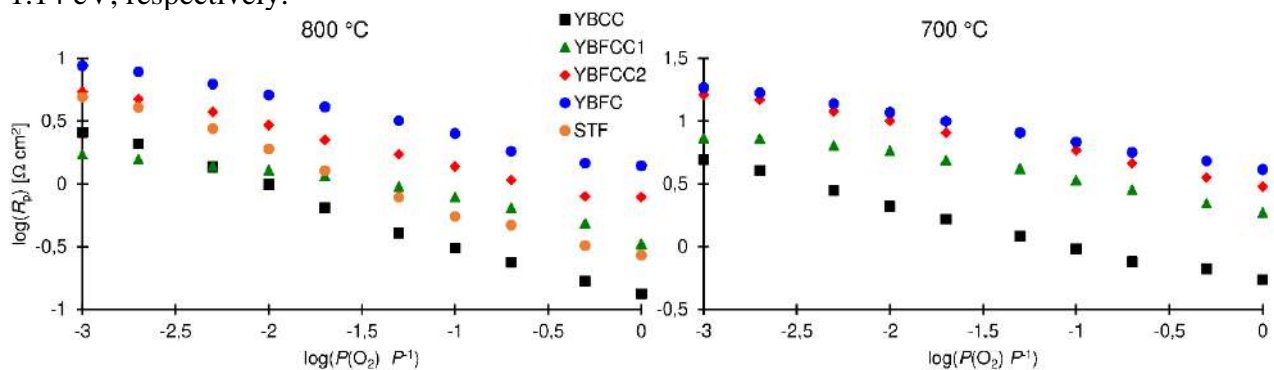


Fig. 1. The dependence of the polarization resistance on the oxygen partial pressure for the tested cathodes.

Physicochemical properties of functional nanocarriers based on dendrimers and proteins

(Professor Barbara Jachimska)

Purpose of the task

The task was to optimize the PAMAM dendrimer system as carriers for cancer drugs. Two generations of positively charged poly (amidoamine) dendrimers (PAMAMs) were selected for research as potential carriers of 5-fluorouracil (5FU). 5FU is most commonly used to treat gastrointestinal and breast cancer.

Scientific and practical effects:

Analytical techniques such as UV-Vis and NMR spectroscopy have shown that the most crucial factor determining the formation of the PAMAM-5FU complex is the initial degree of protonation of the dendrimer molecule and the form in which the drug molecule occurs. Changes in the system's protonation degree were monitored depending on the pH and ionic strength. The observed shifts in the ¹H NMR spectrum confirm the presence of drug molecules both inside the dendrimers' structure and on the surface of the molecule. The functional properties of the obtained PAMAM-5FU complexes were tested by cytotoxicity tests (MTT and MTS). The results show no effect of dendrimers against fibroblast cells (L929) and regular activity of the PAMAM-5FU complex against five human cell lines: malignant melanoma (A375), ovarian cancer (MDAH), glioma (SNB-19), prostate cancer (Du-145) and colon adenocarcinoma (HT-29). The action of the drug in the obtained complexes is correct despite its immobilization in the carrier structure.

Physics and Chemistry in Cultural Heritage Protection

Quantitative assessment of risk to heritage objects due to microclimatic conditions in the environment

(Associate Professor Łukasz Bratasz, Magdalena Soboń MSc Eng., Leszek Krzemień, PhD)

As part of the research task, work was carried out on the further development of software for the quantitative assessment of risk of physical damage of cultural objects due to climate variations - HERIE. As a result of the continuous improvement of the concept of risk assessment based on the response of a historic object to microclimate changes, and due to the new data being published, it was necessary to update the database of dimensional responses of panel paintings and restrained wooden elements on which HERIE was based. Taking into account new material data and better computer models will allow for a more reliable and less uncertain risk assessment for users, conservators, curators and property owners - who do not have the appropriate knowledge and skills to make such assessments themselves.

In the first step, the finite element models used to simulate the behavior of real objects were modified. One of the changes was to standardize the calculation procedure between different types of wood. For this purpose, functions describing the mechanical properties of wood were adjusted to one scheme and the moisture diffusion coefficient in the wood was expressed using the equation given in the literature, independent of the type of wood. Moreover, the main parameter characterizing the risk was modified from total strain to elastic strain. This allowed to take into account the correction coming from a small but not zero response of the paint layer to fluctuations in relative humidity. In the case of a restrained wood, which is a model of furniture or elements of wooden structures, the method of imposing boundary conditions has also been optimized so that it better reflects the structure of historic objects.

In the next step, wooden object response matrices, constituting the database for HERIE, were adapted to the introduced changes. For this purpose, a number of computer simulations were carried out for artificially generated sinusoidal climates with strictly defined parameters, ensuring coverage of all climatic scenarios that can occur in museum and historic interiors. As a result, functions of elastic strain of a wooden object depending on time were obtained. They were used to determine new parameters of the so-called "elementary strain cosines", the superposition of which allows for the reconstruction of the response of a real historic object under the influence of climatic data entered by the HERIE user.

The changes introduced to the models also influenced the length of the time windows in which the Fourier transformation is performed on climate data. This transformation allows for the decomposition of the periodic function into a series of periodic functions, and the resulting transform shows how the individual frequencies make up the original function. This is the foundation of HERIE. The time windows have been re-selected in such a way as to make the transformation over a period long enough to allow the panel painting or restrained wood to respond to a given fluctuation in relative humidity.

In the next step, a comparative analysis of the results obtained in the finite element model and using HERIE - based on the new database - was carried out. Both the artificially generated sinusoidal climates and the real climates recorded in museums and historic interiors showed a very good compatibility between the simulations and the developed tool.

Development grant

Application of nanomaterials for the fabrication of conductive layers on power contacts.

Development grant I KiFP PAN
(dr Anna Pajor-Świerzy PhD)

In recent years, a significant increase in electricity consumption has been observed, especially in areas with a high population density. It is associated with the risk of overloading the power network, which forces increasing the efficiency of working of high-voltage lines. Therefore, their elements such as the contacts, involved in the energy transmission and distribution process, have to operate under more critical conditions (higher temperature, loads, etc.).

In particular, their resistance affects the smooth operation of the contacts. If it is too high and unstable over time, it can lead to overheating of the contact and its shortened life. One of the ways to prevent the increase in contact resistance is to protect their surfaces against the formation of the passivation oxide layer and mechanical damage. Therefore, **the main objective of the research implemented in the project was to obtain a new product in the form of inks or pastes based on metallic nanoparticles (e.g. "core-shell"), which will be used to produce conductive coatings that protect power contacts.**

In order to obtain a uniform, high-conductive coatings on metallic substrates (aluminum), the properties of the inks based on nickel-silver "core-shell" nanoparticles were optimized by selecting the type and concentration of the wetting agent and/or polymer, which enabled their effective deposition by using two different methods: bar and spray coating. Metallic films with optimal wetting properties for the bar coating method were obtained for the ink modified with Surfynol PSA 336 (0.015%) and PVP MW 360,000 (1%). In the case of the spray coating method, the ink containing the PVP at a concentration of 0.5% were deposited on aluminum substrates with the fabrication of uniform coatings.

In the next stage of the research, the metallic coatings, (with optimal properties) deposited by a bar and the spray coating methods, were sintered by annealing process, which allows to transform the non-conductive coating to a layer with a low resistance value.

During the sintering of the deposited coatings, the stabilizer, covering the surface of the nanoparticles, is desorbed, which allows NPs to coalesce and combine into compact, conductive structures. The conditions of sintering process were optimized according to the temperature in order to obtain films with high conductivity. Therefore, the sintering process was carried out in the temperature range of 250-370°C for 30 minutes. The lowest resistance values (Fig. 1) were obtained after the sintering process at a temperature of 300°C of coatings obtained by using the spray coating method, and 350°C for coatings deposited by a bar coating method.

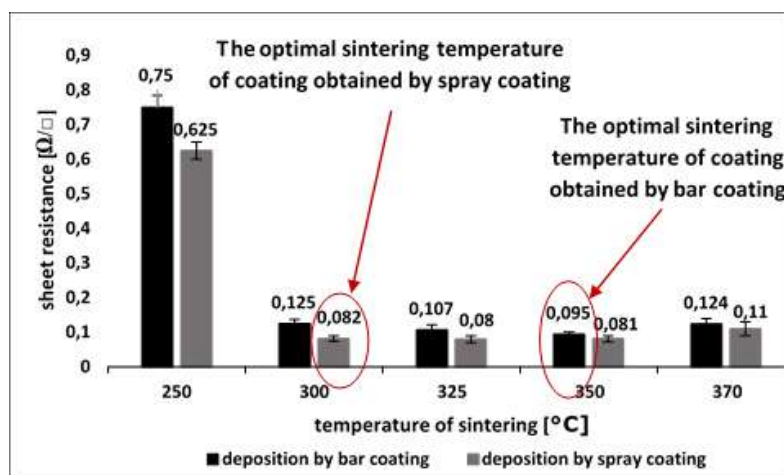


Fig. 1. The effect of sintering temperature of coatings based on Ni-Ag NPs deposited by spray and bar coating methods.

**"Sonata Bis" Research Projects
of the National Science Centre**

2-Oxoglutarate dependent oxygenases in the biosynthesis of pharmacologically active alkaloids - structure, catalytic mechanisms and rational redesign.

"Sonata Bis" research project NCN 2014/14/E/NZ1/00053 [2015-2021]

(*project leader: Professor Tomasz Borowski*)

Within this project we pursue a tightly integrated structural, biochemical and computational studies on two groups of 2-oxoglutarate dependent dioxygenases (ODD) involved in biosynthesis of alkaloids. Structures of these proteins are not known, as are the detailed mechanisms of their catalytic reactions.

For one of the proteins, an attempt was made to change the regioselectivity of the catalyzed reaction. To this end, with the help of Rosetta enzyme design, protein variants (2300 variants, 167 new sequences) were generated capable of stabilizing a substrate position that promotes new regioselectivity. The variants were then verified on the basis of short MD simulations (5 independent 100 ps simulations) and the most promising were selected for experimental testing. The proposed mutant variants were produced in *Escherichia coli* bacteria in order to experimentally validate their activity against the substrate. After cost and time calculation, sequences of the two base mutants were ordered. The obtained genes were cloned by ligation-independent cloning into the pMCSG19 plasmid allowing the expression of the mutants as an MBP fusion protein. Previous studies confirmed that the expression of this native enzyme as an MBP fusion protein is efficient and allows for an active version of the protein to be obtained after proteolytic cleavage of MBP with TEV protease. Another eight mutant sequences were obtained based on the cloned genes and the QuikChange mutation introduction protocol. All mutants were produced in *E. coli* BL21 (DE3) bacteria and confirmed to be in the soluble protein fraction. In further studies mutants will be purified by affinity chromatography and subjected to activity tests against the substrate.

On the basis of the obtained protein structures with the second substrate, computational studies (QM / MM) on the catalysed reaction mechanism were performed, the role of iron ion coordination in the selectivity of the reaction was determined.

At the same time, kinetic tests for the enzyme and its truncated version were started and the pH optimum was determined. Kinetic tests were also started on a different enzyme, as in the previous case, to further analyze the activity of the mutants generated in the earlier studies.

Attempts to crystallize a truncated version of the second protein with substrates were continued. The protocol for the crystallization of the enzyme with the NOG co-substrate analogue was optimized, however, no data indicating the presence of bound alkaloids have been obtained so far. However, high-resolution data were obtained for the enzyme-NOG complex.

As part of the computational studies, QM/MM investigations were also carried out to identify the mechanisms used by ODD to control the selectivity of reactions, in order to potentially be able to use this knowledge in the future to modify the activity of selected enzymes. Calculations were performed for the CAS enzyme, the way the enzyme controls the selectivity of the two reactions was identified and a publication was prepared based on the results obtained.

Conformational properties of model monosaccharides and interaction of selected saccharides with proteins

"Sonata Bis" research project NCN 2015/18/E/ST4/00234: Molecular mechanics force field for structure, dynamics and conformation of carbohydrates involving furanoses [2016-2020]
(*Project leader: Associate Professor Wojciech Plaziński*)

In previous tasks related to this project, a series of simulations was planned and initiated, aimed to investigate various aspects of carbohydrate-protein interactions investigated within different molecular models. The research covered a number of different molecular mechanics force fields describing this type of systems (namely: GROMOS, CHARMM and GLYCAM/AMBER). The free energies of carbohydrate-protein binding, supplemented with basic structural and dynamic parameters of the relevant complex were the main subject of our studies. The comparison revealed a number of qualitative and quantitative discrepancies between the predictions of the tested force fields. These discrepancies include types of carbohydrate-protein contacts, differences in intermolecular hydrogen bonds as well as the RMSD and RMSF parameter values for carbohydrate bound to protein. All tested force fields properly reproduce the key CH \cdots O-type interactions, but the magnitude of the predicted total free energies of carbohydrate-protein binding differs depending on the set of applied parameters.

The second aspect of the research was an attempt to implement the machine-learning potentials in order to study the conformation of monosaccharides of furanosidic molecular topology. While this method appears to be useful for systems containing only the given monosaccharide, the implementation of the explicit solvent effect results in a drastic reduction in efficiency and limits the applicability of this type of approach.

The third raised problem was the systematic study of ring conformational properties for a complete set of heterocyclic compounds with saturated, unsubstituted, heterocyclic five-membered rings. Investigation relied on energy scans carried out at the MP2 theory level. The obtained results allow to conclude that the tested compounds exhibit high conformational heterogeneity, while the calculated energies corresponding to individual ring conformers indicate numerous populations of structures with different ring shapes. Although it is not possible to deduce the preferred type of ring shape from the known molecular topology, the magnitude of the pseudorotation amplitude is similar for most compounds.

**"Sonata" Research Projects
of the National Science Centre**

Lipase-mediated biosynthesis of novel lactose esters. Physicochemical and anticancer studies.

"Sonata" research project NCN 2015/17/D/ST4/00514 [2016-2020]
(*project leader: Maciej Guzik PhD*)

The project was completed and a final report for the NCN was prepared. Based on the results, an application for an application grant was prepared and submitted to the National Centre for Research and Development and the NCN - Tango Path A, for which Sonata is the basic project. The results of in vitro tests on cancer cells, obtained in 2020, also allowed to prepare the patent application.

Stage 3: Characterization of physicochemical properties of sugar esters.

In order to determine the critical micellisation concentration (CMC) values, measurements were taken of the change in surface tension depending on the surfactant concentration in water. Due to the mixture solubility limit, it was not possible to determine exact CMC values for mPHN-lactose and mPHN-glucose esters. Only in the case of mPHN-glucose esters was it possible to determine the CMC value of the mixture surface tension. Higher surface activity may be determined by a higher content of sugar diesters with shorter seven-carbon hydrophobic chains as those whose solubility will be higher than the theoretically more active C9 esters. The pH values of mPHN-galactose and mPHN-lactose solutions were in the range 6.5 to 5.5, which confirms the absence or negligible presence of unreacted mPHN acid substrates in the product fraction. A decrease in pH to 4.5 for mPHN-glucose indicates the presence of traces of organic acids in this mixture. The conductivity values of all ECTs did not exceed $140 \mu\text{s cm}^{-1}$ which, however, confirms the non-ionic nature of the compounds. To sum up, the tested ECGT mixtures are not able to form an emulsion on their own without adding even a small amount of another cosurfactant.

Stage 4: Determination of antiproliferative properties of sugar esters

Microscopic analyses of cancer and healthy cells were carried out for the influence of compounds on morphology. On this basis, the range of concentrations in which ECCs influence their normal morphology was determined. Based on these analyses, further standard microplatelet MTT survival tests were performed to determine cytotoxicity and minimum inhibitory IC₅₀ concentrations. Cells were incubated with compounds for 24h, 72h and 120h at concentrations of 0.5, 0.25, 0.125, 0.0625mg ml⁻¹. The experiments were conducted on the cells: DU145 (prostate cancer), HTB140 (melanoma) and used as controls: PNT2 (prostate epithelium), HSF, HaCAT (human skin fibroblasts). IC₅₀ values obtained in the experiment indicate the antiproliferative properties of lactose-based esters and nonanoic acid, unmodified and fluorinated mPHN monomers against cancer cells. These properties were also demonstrated by glucose and galactose esters based on fluorinated mPHN. It was observed that modification of PHN monomers resulted in increased cytotoxicity to compounds based on nonanoic acid and unmodified mPHN. The control compounds were adequately (glucose, galactose, lactose, nonanoic acid, unmodified mPHN, fluorinated mPHN). They were characterized by many times lower cytotoxicity compared to the tested esters. The inhibitory concentration of IC₅₀ for control line (healthy) cells was 2-4x higher than for neoplastic cells.

Influence of ZrO₂ crystallographic structure on activity of Cu/ZrO₂ and Cu/ZrO₂-ZnO catalysts doped with Ga, Mn, Ni in low temperature steam reforming of bio-ethanol.

"Sonata" research project NCN 2016/23/D/ST4/02492 [2017-2021]
(project leader: *Michał Śliwa PhD*)

The CuZr and CuZrZn catalysts modified with Ni, Ga and Mn were synthesized by co-precipitation method using Na₂CO₃ and NaOH, by complexation method with citric acid and by wet impregnation of ZrO₂ support. The physicochemical properties of catalysts were studied by means of XRD, BET, H₂-TPR, N₂O chemisorption. Additionally, the ratio of tetragonal ZrO₂ phase (t-ZrO₂) to monoclinic ZrO₂ phase (m-ZrO₂) was determined by Raman spectroscopy for two synthesised ZrO₂ supports. The XRD measurements revealed that CuO is the major crystalline phase in the catalysts. The addition of promoters increases the copper dispersion, BET surface area and leads to decrease of CuO crystallites. The H₂-TPR experiments showed that catalysts are reduced in lower temperature in comparison with standard CuO.

The catalytic steam reforming of ethanol (SRE) was performed at 350 °C. The ethanol to water ratio was 1 to 10. The reaction was carried out in the fixed-bed flow reactor connected online to GC equipped with TCD and FID detectors. All catalysts exhibit high conversion of ethanol, ranging from 85 to 100%. Since all catalysts possess basic surface sites, which was confirmed in CO₂-TPD experiments, the main carbon containing products are acetaldehyde and acetone. The formation of these products was also observed in temperature-programmed desorption of ethanol, using mass spectrometer (QMS) as detector. Moreover, spent CuZr catalyst synthesized by co-precipitation with Na₂CO₃, were tested in TPO experiments in order to evaluate the amount of coke. Based on recorded TPO profiles and the peak positions (< 450 °C), the presence of amorphous carbon on the surface of spent catalysts was stated. The positive effect of promoters on amount of carbon deposit was observed. The addition of modifiers limits the formation rate of carbon deposit.

From a single molecule to smart material - understanding the polypeptide complexes formation and properties

"Sonata" research project NCN 2018/31/D/ST5/01866 [2019-2022]

(project leader: Piotr Batys PhD Eng.)

The interactions between polypeptides in solutions have a key impact on the properties of the resulting polypeptide complexes. There are no studies in the literature describing the polypeptide complexation processes at the molecular level, which makes it difficult to understand this process and limits the possibilities of its control.

As part of this project, preliminary theoretical calculations of the complexation of poly-L-lysine (PLL) and polyglutamic acid (PGA) were performed using the classical molecular dynamics method (MD) and the method with replica exchange, Hamiltonian Replica Exchange Molecular Dynamics (HREMD). The HREMD method turned out to be much more efficient in modeling strongly interacting polypeptides, allowing for more efficient sampling of the conformational space, Fig. 1.

In the experimental part of the project, research was carried out on the use of an analytical ultracentrifuge to determine the interaction between peptides. The developed methodology allows, to determine the dissociation constant and the molecule' shape.

In addition, on model systems of polyelectrolyte complexes, experiments were carried out using the attenuated total reflection infrared spectroscopy (ATR-FTIR) method, allowing to determine the properties of water molecules in polyelectrolyte complexes.

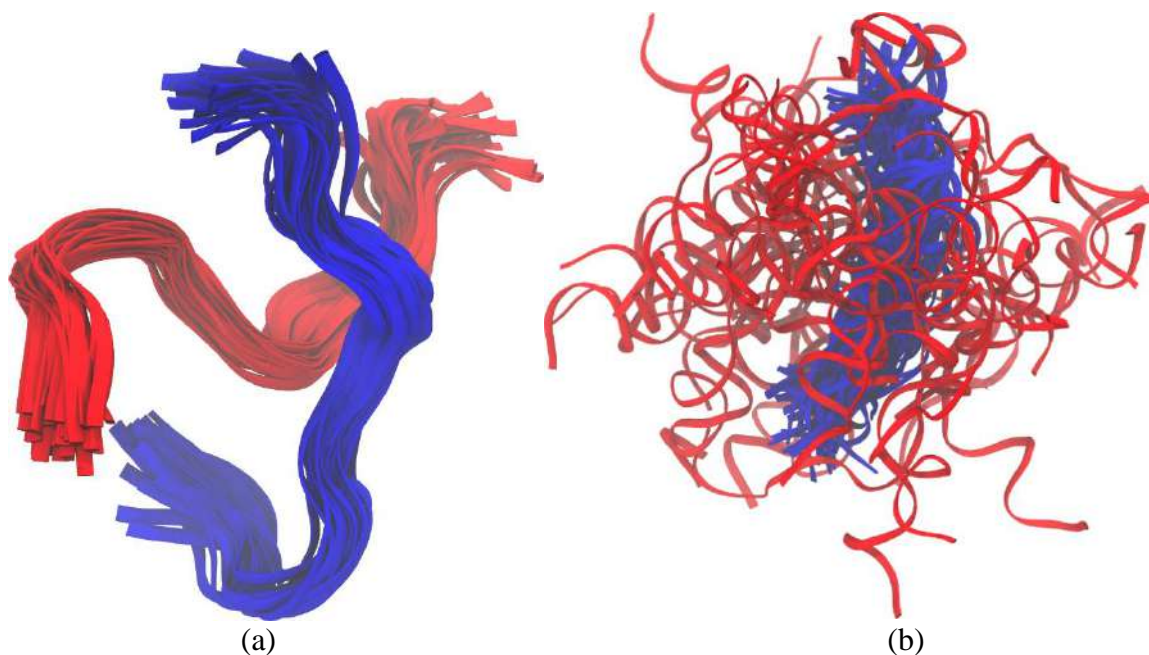


Fig. 1. PLL (blue ribbon) and PGA (red ribbon) complex conformations obtained using the (a) MD and (b) HREMD methods. The ribbons represent the positions of the polypeptides at 1 ns interval.

**"Opus" Research Projects
of the National Science Centre**

Magnetic nanoparticles on periodic iron oxide templates: control of magnetism using particle - substrate interaction and external electric field

"Opus" research project NCN 2016/21/B/ST3/00861 [2017-2021]

(project leader: Professor Nika Spiridis)

Hematite, $\alpha\text{-Fe}_2\text{O}_3$, is a prototypical insulating antiferromagnet that can be applicable in emerging spintronics based on antiferromagnetic (AFM) materials with no net magnetic moment, which makes them stable and resistant to external fields. The hematite crystals undergo a magnetic spin-flop transition at the Morin transition (Morin temperature $T_M=263$ K), from a canted easy-plane phase to a purely (or better “almost purely” according to more recent studies) AFM phase with spins along the c -axis. However, in (0001)-oriented hematite epitaxial films, T_M could be much lower or even not exist, depending on the film/substrate lattice mismatch or doping. Using our experience in growing hematite films on Pt(111) by oxidation of magnetite films, we have developed preparation technology of $\alpha\text{-Fe}_2\text{O}_3(0001)$ films on MgO(111) with a Pt buffer- or cap-layer. *In situ* conversion electron Mössbauer spectroscopy (CEMS) measurements proved perfect stoichiometry of the hematite films with a typical thickness of 10 nm (Fig.1a). The hematite films in the studied thickness range, from 5 to 15 nm, did not exhibit Morin transition down to the lowest achievable measurement temperature (100 K) of our UHV CEMS spectrometer. This means that in our antiferromagnetic insulator the Fe^{3+} magnetic moments stay in the (0001) plane, with a weak ferromagnetic component along three equivalent in-plane directions. For such films we were able to reproduce the recently demonstrated electrical switching of the tri-state AFM order by spin-orbit torque [Cheng et al., Phys. Rev. Lett. 2020, 124, 27202]. We patterned our sample into 8-leg Hall crosses (Fig. 1b), where the width of the two voltage terminals is 5 μm and the other six legs (60° apart) are 10 μm wide. Figure 1c shows a reversible control of the tristate Hall resistance switching after a sequence of ten current pulses (50 mA, 1 ms). More interestingly, for the sample with the buffer Pt layer, the switching is stable with no detectable decay with increasing number of the switching events.

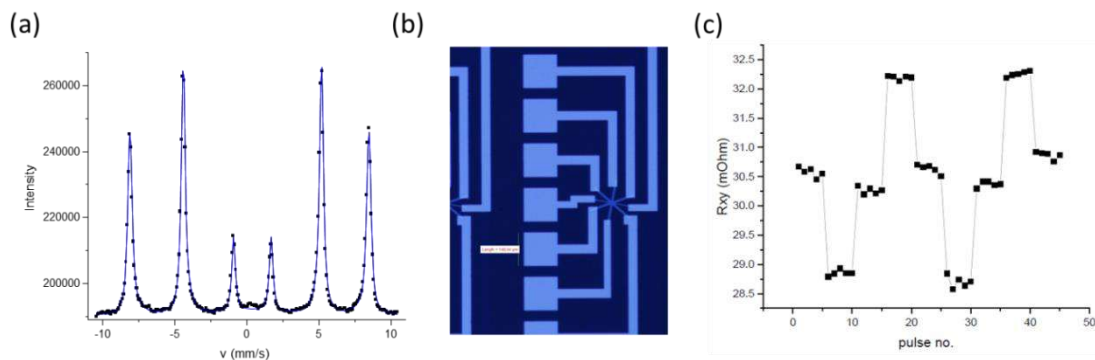


Fig.1. (a) CEMS spectrum of a 10 nm $\alpha\text{-Fe}_2\text{O}_3(0001)$ epitaxial film on a Pt-buffered MgO(111) substrate. (b) Optical microscopy image of contacts and eight-leg Hall-cross lithographically patterned in the $\alpha\text{-Fe}_2\text{O}_3(10\text{ nm})/\text{Pt}(7\text{ nm})$ bilayer. Leg width is 10 μm . (c) A plot of Hall resistance (R_{xy}) measurements after current pulses applied along legs (L_i) in the sequence: $L_1, L_2, L_1, L_3, L_1, L_2, \dots$

Development of modern generation technology of stable biological surface film for various bio-medical applications (antibacterial or regeneration properties)

"Opus" research project NCN 2016/21/B/ST8/02107 [2017-2022]
(*project leader: Marcel Krzan PhD*)

During the project, we want to develop technology for generation and application of stable thin films of surface formulated from mixtures of hypoallergenic, non-toxic biological polymers, mainly biosurfactants (proteins, polysaccharides, glycolipids and phospholipids). The scientific goal of the project is to investigate the competitive adsorption processes occurring in multi-component solutions, where the main substrates are various surface-active bio-polymers. During the project, we want to investigate which of the available biopolymer formulations have sufficient surface activity to be used in cosmetic products. We want to determine the minimum described above necessary to carry out wetting or to create the surface effect of surfactant concentrations. To achieve this effect, we plan detailed research on the tested solutions of biopolymers. We want to set the above-described minimum concentrations necessary to carry out wetting or to create a surface surfactant concentration effect. In order to achieve this goal, the project conducted research activities related to two thematic areas of the project during 2020:

- The systems of solid surface films made of solutions and suspensions based on alginate compounds, chitosan and hylauronic acid, which were additionally refined with silver nanoparticles, were investigated. In the foreseeable future, these systems (films) could be used as natural and ecological coating substances, inhibiting the growth of pathogenic bacteria and fungi. A rheometer system was used in the research to test the viscous-elastic properties of solutions and suspensions. The particle sizes of alginate, chitosan and hylauronic acid in suspensions (DLS) were also tested. The solidified films were examined by means of contact angle measurements (for polar and non-polar liquids) to determine their hydrophobicity and free surface energy.

- Research was carried out describing foams produced in solutions of the biodegradable surfactant lauryol ethyl arginate LAE, in which additional stabilization of the foam system was introduced by means of added nanocellulose particles with different functional groups (carboxyl, sulfone). The aim of the work is to describe the effect of particles on the activity and surface elasticity of solutions and to study the stability of foam systems produced in the double syringe system.

In addition, in 2020, two conference presentations (Eufoam / Scotland / online) were presented based on the research carried out in the project and 3 publications were published in ISI / JCR journals.

Due to limitations related to the COVID-19 pandemic, the project was extended until 2022.

The mechanism of regioselective oxidative dehydrogenation of 3-ketosteroids catalyzed by Δ^1 -cholest-4-en-3-one dehydrogenase from *Sterolibacterium denitrificans*

"Opus" research project NCN 2016/21/B/ST4/03798 [2017-2021]
(project leader: Professor Maciej Szaleniec)

The aim of the project is to evaluate the reaction mechanism of steroids dehydrogenation catalyzed by Δ^1 -cholest-4-en-3-one dehydrogenase (AcmB). The enzyme is produced by the denitrifying bacterium, *Sterolibacterium denitrificans*, and belongs to the FAD-dependent 3-ketosteroid dehydrogenases. It catalyzes the oxidative dehydrogenation of 3-ketosteroids that leads to the formation of a double bond between C1 and C2 atoms of a steroid ring A. The project focuses on the elucidation of the enzyme's structure together with the characterization of its catalytic properties. Furthermore, the theoretical calculations are applied for the study of the reaction mechanism.

The fourth year of the project enabled the refinement of the crystallographic structure of AcmB. Thanks to the now available structure the QM:MM:MD calculations of the reaction mechanism were undertaken which aimed at verification of the mechanistic hypothesis also for AcmB and not only KSTD from *R. erythropolis*. In parallel the much more advanced calculations for KSTD were conducted, that concentrated on modeling kinetic isotope effect and elucidation of the unexpected experimental results (i.e., observed KIE for substitution at C1 and C2 in the range of 1.5-2). Based on the analysis of kinetic parameters from the modeling as well as results obtained for KSTD in '60 we managed to propose an explanation of the observed phenomenon.

The kinetic studies were also continued using both steady-state and pre-steady-state approach, providing information on substrate specificity for both studied enzymes. The analysis also allowed the determination of the kinetic constants collected in the presence of the propylated cyclodextrin. This was possible thanks to the determination of the equilibrium constants for the formation of the steroid-cyclodextrin guest-host complexes. Finally, the ping-pong mechanism was also confirmed for KSTD from *R. erythropolis*.

To further explain the low value of the observed KIE the kinetic solvent viscous effect was studied for KSTD with glycerol acting as a microviscosity agent. Steady-state experiments showed that both formation of the ES, as well as decomposition of the EP complex, can be subjected to diffusion limitation. The pre-steady-state experiments showed that the diffusion limitation influences steps before the reaction (i.e. FAD reduction observed in the experiment). The origin of KSVE may be either in slow diffusion of the substrate to the active site or in a diffusion-limited change of the enzyme conformation during ES complex formation. Regardless of this KSVE may be one of the reasons why the observed KIE is lower than predicted iKIE. (approx. 4).

Finally, a series of applied experiments have been conducted. It was demonstrated that AcmB can be efficiently oxidized by atmospheric O₂. Under aerobic conditions, both O₂ and produced in situ H₂O₂ also oxidized DCPIPH₂. In cooperation with Silesian Technical University AcmB was immobilized on silica support functionalized with APTS. The obtained catalyst exhibited specific activity in the range of homogenous catalyst with significantly improved operational stability enabling reaction for 27 days. Also, different forms of the catalyst (such as whole-cells, crude enzyme extract) were tested and used for the up-scaled synthesis of dehydrogenated steroids. For the first time dehydrogenation of saponin diosgenon to (25R)-spirosta-1,4-dien-3-on was demonstrated and the IP to this inversion was secured with a Polish patent application.

Theoretical and Experimental Studies on the Mechanism of Oxidative Dehydrogenation (ODH) of Light Alkanes over Vanadium-containing Hierarchical Zeolite Materials

"Opus" research project NCN 2016/23/B/ST4/02854 [2017-2021]
(project leader: Associate Professor Dorota Rutkowska-Żbik)

The aim of this joint experimental and theoretical work is to gain understanding in the nature of the V species responsible for their catalytic activity in the oxidative dehydrogenation (ODH) of light alkanes into light alkenes and to determine the mechanism of the ODH process.

Three series of vanadium catalysts which differ by the type of zeolitic support and the amount of vanadium were tested in the ODH of propane: 1) the V_x FAU ($x = 1, 3, 6$) series in which faujasite zeolite was impregnated with 1 – 6 %mas of vanadium; 2) the V_x FAUdes ($x = 1, 3, 6$) series in which desilicited faujasite zeolite was impregnated with 1 – 6 %mas of vanadium; 3) V_x SiBEA ($x = 1, 2, 3, 6, 7$) series in which 1 – 7 %mas of vanadium was introduced into beta zeolite. The catalytic tests were run in a fixed-bed gas flow reactor with a gas chromatograph to detect substrates and reaction products at a temperature range from 400-500 °C, with varying contact times. Out of the tested samples, the V_6 FAUdes appeared the most active.

The analysis of the obtained results for the FAU and FAUdes samples suggested that the activity of the vanadium catalysts should be ascribed to three parameters: vanadium location, porosity of the samples, and their acidity. The higher selectivity of the V_x FAUdes catalysts over V_x FAU is probably due the presence of the dispersed vanadium ions in the tetragonal coordination environment, as seen by the UV-VIS spectra. The conversions of C_3H_8 are higher for the V_x FAU series than for the V_x FAUdes series. The microporosity prevails over the mesoporosity in the V_x FAU systems. The narrow pores hinder the diffusion of reagents inside the zeolite, resulting in the increased probability of the catalytic reaction. On the other hand, the prolonged contact with the active sites may lead to the combustion of propane. This explains the overall higher selectivity to propene found for the V_x FAUdes systems. Low total acidity of the catalysts, as found for $V_{3.0}$ FAU and $V_{6.0}$ FAUdes, favors a high selectivity to C_3H_6 . The presence of weak acid sites promotes hydrocarbon adsorption on the catalysts' surfaces, while the lack of strong acid sites impedes propane cracking. Similar observations were done for the V_x SiBEA series of the catalysts.

The geometries and electronic structures of models of BEA zeolite substituted with vanadium atoms placed in all inequivalent T-sites were compared and analysed based on the DFT(PBE/def2-TZVP) calculations. The results indicate that vanadium could substitute T atoms in all available crystallographic positions in BEA. As the V–OH group, vanadium center is bound preferentially in the T2 position. Vanadium could be present as the V=O moiety in T2 or T3 positions (the distinction between the two sites is disabled due to the too low difference in energies). The introduction of the V=O center generates an additional acidic site in its proximity, which may act as an anchor for reagents. The most energetically favored position for the V(=O)(–OH) group is T3. The analysis of Mulliken charges accumulated on oxo and hydroxyl centers indicates their nucleophilic character. Their dominance in the valence band suggests that all studied oxygen species may play an active role in catalysis, in particular in redox processes. The parameters of the V=O, V–OH, and V(=O)(–OH) groups present in the BEA zeolite were then compared with the characteristics of the same species on the most abundant (010) V_2O_5 surface. The V=O species are more nucleophilic being introduced into the BEA structure than on the (010) V_2O_5 surface. In the former system, they can become the sites actively participating in catalytic events. On contrary, on the unmodified (010) V_2O_5 surface, there exist sites of higher nucleophilicity than V=O—triply and doubly coordinated oxygen atoms—which may be more relevant for catalysis. Similarly, the V(=O)(–OH) group has more nucleophilic character when introduced into BEA and hence would be more relevant for catalysis than a similar group on V_2O_5 .

The influence of counterions on the formation and functionality of polyelectrolyte membranes

"Opus" research project NCN 2016/23/B/ST8/03128 [2017-2021]

(project leader: Marta Kolasińska-Sojka DSc)

The scientific goal of the project is to investigate the dependence of the structure and properties of polyelectrolyte multilayers on selected ions from the Hofmeister series. The impact of the interaction of counter-ions from the liotropic series on the resulting polyelectrolyte films is unknown and thus, understanding the mechanisms responsible for creating such structures may contribute to the design of materials with well-defined parameters, which will improve the properties of selective membranes, biomaterials and nanocontainers in the future.

The ongoing work concerned the comparison of the effect of monovalent anions: CH_3COO^- , Cl^- , Br^- , NO_3^- , ClO_4^- on the formation of PAH/PSS and PDADMAC/PSS multilayer polyelectrolyte films. The quartz crystal microbalance was used to study the kinetics and efficiency of the multilayer deposition process in the presence of selected basic electrolytes: NaCH_3COO , NaCl , NaBr , NaNO_3 , NaClO_4 at ionic strength $I = 0.15$ M. The results of this part of the work are presented in Fig. 1.

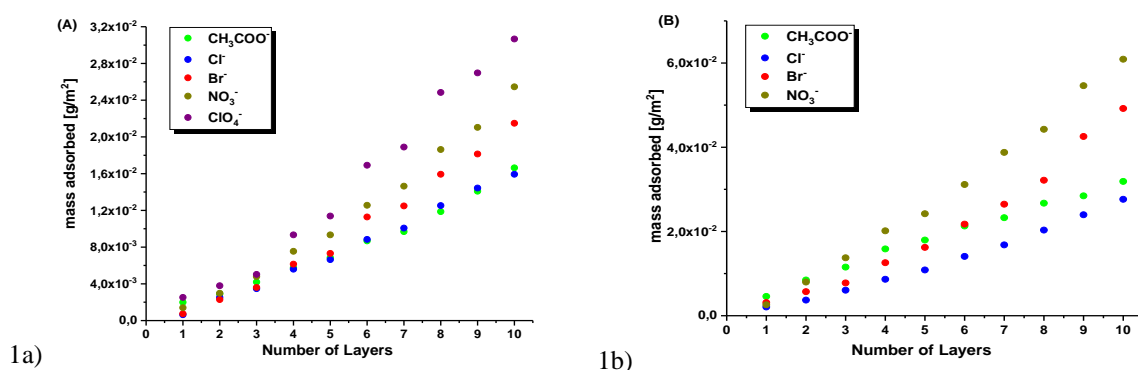


Fig. 1 Mass of deposited polyelectrolyte films as a function of adsorbed layers for the systems studied: a) PAH/PSS and b) PDADMAC/PSS.

The mass adsorbed in the case of the PDADMAC/PSS (1b) system is bigger than for films with an analogous number of layers but made of PAH/PSS polyelectrolytes (1a), which is consistent with our previous research. In the case of the PDADMAC/PSS multilayers, a more indicated effect of the counterion on the adsorbed film is observed. For 10-layer PDADMAC/PSS systems, the lowest mass is for a film with Cl^- counterion while the highest is for films adsorbed in the presence of NO_3^- . PAH/PSS films show analogous dependency on counteranions, except that films with ClO_4^- were additionally studied, which was not possible for PDADMAC due to precipitation in the solution.

Then, permeability to electroactive probes was tested for analogous polyelectrolyte films, built up in the presence of selected monovalent cations on gold disc electrodes. As a redox system an equivalent mixture of $1\text{mM } \text{K}_3\text{Fe}(\text{CN})_6 / \text{K}_4\text{Fe}(\text{CN})_6$ in 0.15 M NaCl was used.

It has been shown that the permeability of multilayers towards the selected electroactive agent is reduced as a result of covering of the gold electrode with a polyelectrolyte film. The degree of permeability also depends on the counterion used. In the case of 10-layer films, the effect of blocking of the electroactive agent by the polyelectrolyte film terminated with negatively charged layer plays an important role and the differences in permeability depending on the counterion used are much more subtle, although still visible.

Dendrimers as a platform for designing biologically active carrier

"Opus" research project NCN 2017/ST5/02788 [2017-2021]

(Project leader: Professor Barbara Jachimska, co-investigator: Magdalena Szota PhD, Wojciech Jasnosz PhD, Kamil Rakowski PhD, Paulina Komorek PhD)

Dendrimers are nanosized, non-immunogenic, hyperbranched polymeric systems. Dendrimer synthesis can be precisely controlled in size, shape, molecular mass, composition, and reactivity. Two generations of positively charged poly (amidoamine) dendrimers (PAMAMs) were selected for the study as potential carriers for 5-fluorouracil, a drug primarily used in treating colorectal cancer. Analytical techniques such as DLS, UV-Vis, LDV have shown that the most critical factor determining the formation of the PAMAM-5FU complex is the starting components' protonation degree. The change in the system's protonation degree was monitored using the zeta potential measurement as a function of the system's pH and ionic strength. As a result of the dendrimer molecule interaction with the drug, a systematic decrease in charge of the complex was observed, indicating the dendrimer molecule's charge compensation. However, these measurements do not provide precise information about the location of 5FU molecules in dendrimers' structure.

Additionally, using the QCM-D method, the adsorption efficiency, and the number of drug molecules immobilized in the dendrimer structure was determined. The tests confirmed the system's ability to attach about 20 5FU molecules per one dendrimer molecule for the fourth generation dendrimer and approximately 25 molecules for the sixth generation dendrimer. Comparing these values with the nominal number of amine groups present in the dendrimer structure, a system yield of 16% for G4PAMAM and 5% for G6PAMAM dendrimers was obtained. These results correlate well with the spectroscopic studies.

In search of effective and environmental friendly frothers and emulsifiers – quantitative description of thin liquid film stability in solutions of “green” surfactants

"Opus" research project NCN 2017/25/B/ST8/01247 [2018-2021]
(Project leader: Associate Professor Jan Zawala)

The presented research project is aimed to investigate potential application of bio-surfactants as new, effective and environmental-friendly stabilizers of foam and emulsion films under dynamic conditions. Scientific tasks of the project are performed according to the new methodology and by use of the new experimental set-up elaborated within the project framework. The experimental set-ups allow description of kinetics of drainage of single symmetrical liquid films (foam and emulsion), formed at the liquid/gas and liquid/liquid interfaces by the colliding bubbles and /or droplets in solutions of biodegradable and environmental-friendly surfactants.

In the reporting period the experimental set-up for determination of time of drainage of single emulsion films under dynamic conditions, i.e. during collision of a single oil droplet with liquid/liquid interface, was developed. The set-up consisted of single droplet generator elaborated and build in our laboratory as well as a system for visual observations of the formed films. Times of drainage of single emulsion films, so-called lifetimes of droplets at the liquid/liquid interface in solution of given concentration, were registered automatically by the CCD camera. The lifetime was determined a time span from the moment of the droplet first collision with the interface to the moment of its rupture (coalescence). Using determined lifetime time values the influence of surface-active substances on stability of emulsion films was assessed.

The experiments were focused on determination of influence of pH of the BSA (bovine serum albumin) solutions on the droplet's lifetimes. The BSA was used as a model globular protein. The single droplet lifetimes (times of the emulsion film drainage) as a function of pH were determined in the BSA solutions of concentration 6×10^{-7} M. Next, the set-up was modified and equipped with the reflectance probe and proper optical system allowing direct determination of the thickness of the emulsion film and its evolution in time (drainage). The longest lifetime was registered for natural pH and pH corresponding to the isoelectric point of the protein molecule (pH_{IEP}). It was found that the emulsion films have relatively high initial thicknesses. However, the drainage of the liquid film was significantly slower for pH_{IEP} comparing to the acidic pH. The obtained results suggest that the observed trends are caused by different rheological properties of the liquid/liquid interfaces, at which the BSA is adsorbed under different pH conditions. Systematic studies of the rheological properties of interfaces are planned at the next project's stages.

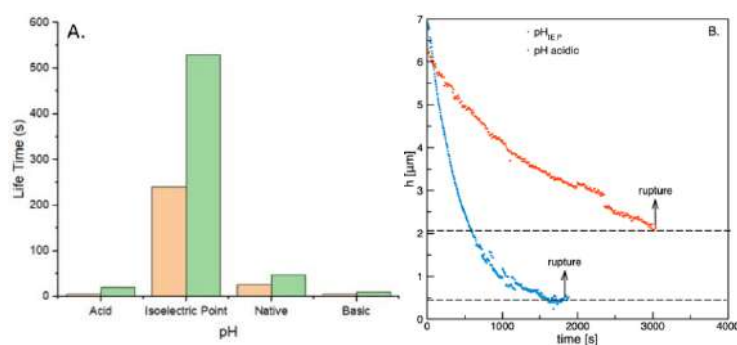


Fig. 1. Lifetimes of single emulsion films formed under dynamic conditions in solution of 6×10^{-7} M BSA of different pHs (A), and kinetics of drainage of single films at acidic and IEP pH values (B)

The pH stimuli responsive surfactants and copolymers for nanovehicles formation

"Opus" research project NCN 2017/25/B/ST4/02450 [2018-2021]

(Project leader: Professor Piotr Warszyński)

The main project objective, realized by the consortium of two research groups from Jerzy Haber Institute of Catalysis and Surface Chemistry of the Polish Academy of Sciences and from Wrocław University of Science and Technology, Faculty of Chemistry, is to develop scientific background of a novel strategy of formation of pH sensitive nanostructures: thin films or nanocapsules. Using newly-synthesized amphoteric surfactants with hydrophobic chains of different lengths, mixed with polyelectrolytes and/or amphiphilic polyelectrolytes with hydrophobic groups grafted on the polyelectrolytes backbone by pH-labile linker, we will construct nanostructures which decomposition can be trigger by change of pH. Application of this type of components will allow to obtain nanostructured thin films with controlled hydrophobicity, or antimicrobial properties sensitive for changes of environment.

We synthesized amphiphilic polyelectrolytes on the basis of poly(4-styrenesulfonic-co-maleic acid) (PSS/MA) with hydrocarbon chains (C12 or C16) linked by pH-sensitive, amide and ester groups. Obtained degree of hydrophobization was 15% or 40%. Using the QCM-D technique, we investigated the adsorption of hydrophobized and unmodified PSS/MA copolymers at the liquid /solid interface. The copolymers were adsorbed on surfaces covered with a multilayer polyelectrolyte film (PSS/PDADMAC). The adsorbed polymer films were then treated with solutions at pH 3 and pH 11. The wettability of the surface of silicon wafers coated with a multilayer film (PSS / PDADMAC) with adsorbed copolymers was also tested. We found that the adsorption of hydrophobized polyelectrolytes leads to an increase in wetting angles on surfaces covered with a multilayer film. After exposure of the films to solutions with pH 3 and pH 11, we observed a decrease and an increase in their mass, respectively, the changes being reversible and related to a changes in film hydration. After the films were coated with hydrophobized polyelectrolytes, the films were more stable than those coated with unmodified PSS/MA. The use of the ATR FTIR technique allowed for the correlation of changes in the differential spectra in the wave number range of 2800 - 3800 cm^{-1} corresponding to stretching vibrations for a water molecule with the degree of hydrophobicity of the film.

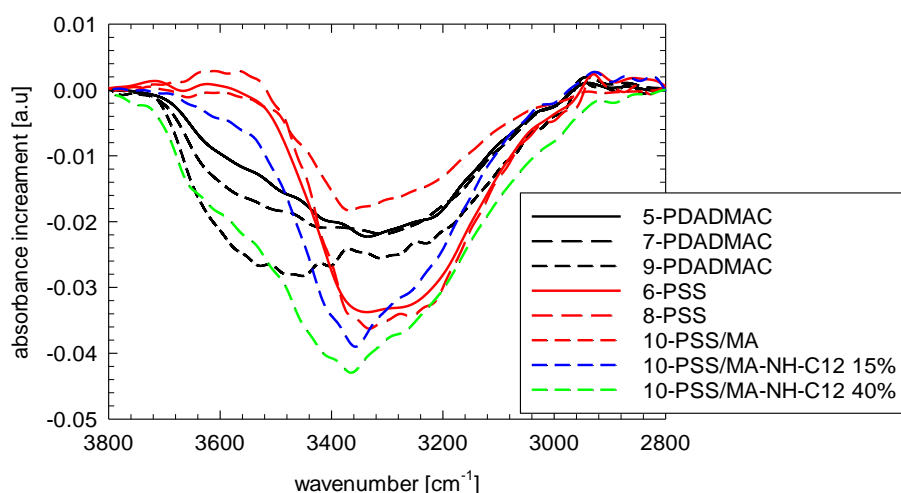


Fig. 1. Differential IR spectra of multilayer polyelectrolyte films in the range 2800 - 3800 cm^{-1} obtained after applying the next layer.

Studies of the interactions of carbon nanotubes with telomeric DNA by means of the molecular dynamics simulations

"Opus" research project NCN 2017/27/B/ST4/00108 [2018-2021]

(Project leader: Professor Tomasz Pańczyk)

Calculations were carried out to model a complex system made of nanotubes with chirality (10,0) and (20,0) and a length of approximately 75 Å, and a telomeric DNA (iG) chain containing a total of 90 residues of nitrogen bases. In the middle of this chain, non-canonical forms were created, i.e. iM and Gq (i-motif and G-quadruplex). The aim of the calculations was to investigate how the interaction of iG with a functionalized carbon nanotube influences the thermodynamic stability of iM and the role of the guanine-containing functional group in the stabilization of the entire system.

As a result, several important conclusions were drawn regarding the complex structure of fCNT + iG. Namely, it has been shown that the presence of a guanine-containing functional group has a major impact on the site of the nanotube attack on DNA. That is, the presence of this group causes the nanotube to attack the place where iM and Gq structures are formed with its forehead, and then a static system is created. The lack of a functional group leads to the situation that the nanotube and iG shift relative to each other and iG interacts with the outer wall of the nanotube. This is an important finding helpful in designing drug carriers based on CNT structure as it allows to predict how CNT functionalization affects the site of CNT attack on DNA.

Calculations were also performed on the interaction of the i-motif, iM sequence with functionalized carbon nanotubes with chirality (10,0) and (20,0). The systems were designed in order to determine whether the structural changes of the iM sequence in the pH function of the environment could be used for the controlled release of doxorubicin. A model was constructed to investigate the intercalation ability of doxorubicin by iM molecules non-covalently attached to the surface of a carbon nanotube (10,0). It turned out that such mixed systems do indeed form stable ternary structures. However, removal of doxorubicin from the system significantly diminished the efficiency of iM binding to CNT. Therefore, the method and efficiency of doxorubicin binding in the three-component system and then in the two-component system were investigated in more detail - which allowed for a deeper study of the mechanism of doxorubicin binding to iM. The determined values of the binding energy, the number of formed clusters and the surface available for the solvent in the three-component systems suggested that DOX binds more strongly at neutral pH than in acidic pH and it will probably detach under conditions when the iM obtains the form typical for acidic pH. The studies in a two-component system confirmed this hypothesis because the determined free energies of detachment DOX from iM turned out to be of the order of 20 kJ/mol at acidic pH, while at neutral pH they were of the order of 160 kJ/mol.

The conducted research leads to the conclusion that DOX can be immobilized in the iM system forming a cluster at neutral pH and released in an acidic environment. It is an additional possible mechanism not described in the literature so far. Previous literature data postulated that DOX must be intercalated within the duplex at neutral pH and released when the duplex breaks at acidic pH and the spatial form of iM is formed. This kind of mechanism thus assumes that the Watson-Crick pairs must break in favor of Hoogsten pair formation - which seems unlikely from a thermodynamic point of view. The mechanism proposed by us does not require such an assumption and leads to the same phenomenon on a macroscopic scale.

Biopolymers as templates for preparation of nanostructured hydrotalcite-like materials and their calcined mixed oxides derivatives for catalytic applications

"Opus" research project NCN 2017/27/B/ST5/01834 [2018-2021]

(Project leader: Professor Ewa Serwicka-Bahranowska)

The project sets the frame for fundamental research into designing nanostructural hydrotalcite-like compounds (Ht) with aid of commonly available, cheap and environmentally friendly natural biopolymers (e.g., starch, gelatin), used in the capacity of soft biotemplates. The approach represents an alternative to the use of the more expensive, more complex and less green procedures based on synthetic templating agents (e.g., surfactants, block copolymers). Research focused on a) determination of catalytic activity of Mg-Al Ht prepared in the presence of potato starch and differing in the nature of compensating anion in the Baeyer-Villiger oxidation of cyclohexanone to ϵ -caprolactone with use of H_2O_2 as an oxidant, and b) determination of main synthesis parameters of Cu-Mn-Al Ht samples prepared in the presence of potato starch, to be used as precursors of mixed oxide catalysts for combustion of toluene.

Catalytic testing of Mg-Al systems showed that the nature of the compensating anion had a significant influence on the course of the catalytic oxidation of cyclohexanone (Fig. 1). Best results were obtained for nitrate-form of Ht.

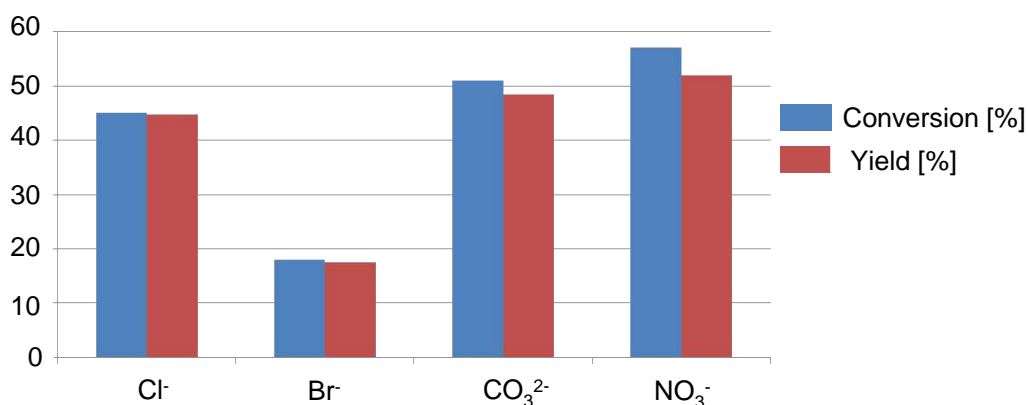


Fig. 1. Conversion of cyclohexanone and yield of ϵ -caprolactone over Ht Mg-Al catalysts prepared in the presence of starch and differing in the nature of compensating anion.

Synthesis of Cu-Mn-Al Ht samples were carried out by co-precipitation at pH=9. The investigated synthesis parameters included the nature of the precipitating agent (NaOH/Na₂CO₃ or TBAOH), synthesis temperature, the manner of precipitate washing, and temperature of calcination. The materials were examined with XRD, SEM/EDS and FTIR. Tests of toluene combustion demonstrated very high activity of prepared materials. In the case of catalysts obtained from unwashed precursors, the samples precipitated with TBAOH were more active than those prepared with NaOH/Na₂CO₃. Poorer performance of the latter was due to the detrimental effect of sodium retained by the catalysts obtained with inorganic precipitant. Catalytic properties of samples synthesized with NaOH/Na₂CO₃ could be significantly improved by careful washing of precursors prior to calcination.

New polysaccharide-based biomaterials as an effective platform for adsorption and release fibroblast growth factors: applications in diagnostics and treatment of diseases of affluence

"Opus" research project NCN 2018/31/B/ST8/03277 [2019-2022]
 (Project leader: Aneta Michna DSc)

The aim of this research project is: to develop a quantitative description of the adsorption of biocompatible macroions forming multilayers on solid surfaces and to explain the mechanisms of binding the fibroblast growth factors (FGF) to the obtained biomaterials and to determine the FGF release rate from these biomaterials.

During the reporting period, a procedure of the packed macrocation (PAMAM dendrimers of generation 8 (PAMAMG8), branched polyethyleneimine (bPEI), polyallyldimethylammonium chloride (PDADMAC), chitosan (CHIT)) layer formation on solid surfaces was developed. The thoroughly physicochemical characteristics of the macroion monolayers and their stability were also evaluated. The obtained monolayers were further applied as anchoring layers enabling the adsorption of lambda-carrageenan (λ -CARR), a negatively charged polysaccharide with proven antiviral and antibacterial activities.

The mono- and bilayers were characterized by electrokinetic (streaming potential measurements), gravimetric (quartz microbalance with energy dissipation), optical (optical waveguide lightmode spectroscopy) methods, and atomic force microscopy. The effects of the transport type (diffusion and convection), adsorption time and the macroion mass concentration in the bulk as well as the ionic strength and pH of the simple electrolyte on the formation and stability of mono- and bilayers were determined. The macroion hydration degree was also evaluated.

It was shown that packed anchor layers are formed when the macroions are adsorbed under convective controlled transport conditions, with a low volumetric flow of the macroion solution of $Q = 0.0025$ - 0.02 ml/s. The mass concentration of the macroions and adsorption time were also low and equal to 5 mg/L and 20 min, respectively. The measurements, carried out in the pH range of 4.0-7.4, showed a slight dependence of the solution pH on the macroion adsorption.

It was confirmed that the hydrodynamically coupled electrolyte amount in dendrimer monolayers is many times larger than the internally coupled electrolyte responsible for swelling.

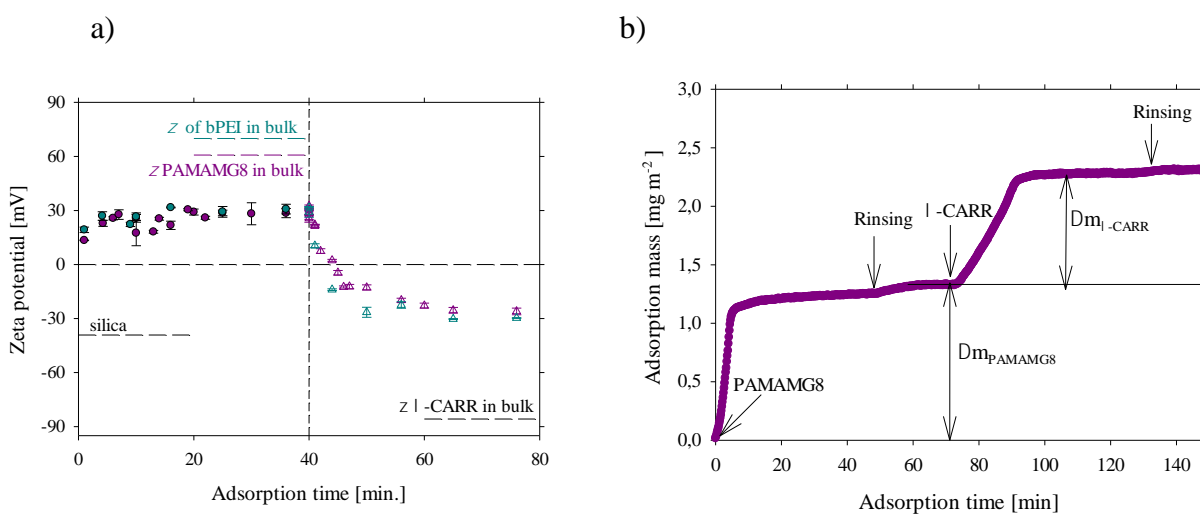


Fig. 1 a) Formation of a complete lambda carrageenan (λ -CARR) (Δ, Δ) layer on an anchoring layer formed by dendrimers (PAMAMG8) (\bullet) and polyethyleneimine (bPEI) (\bullet) under convection controlled transport conditions, $Q=0.02$ ml/s (streaming potential measurements). b) Adsorption kinetics of lambda carrageenan on PAMAMG8 layer under convection controlled transport conditions ($Q=0.0025$ ml/s). The measurements were carried out in simple electrolytes of defined ionic strength of 0.01 M at pH 5.8. Bulk concentrations of the macroions were equal to 5mg/L.

Novel composites of smectite minerals and TiO₂ nanoparticles prepared by inverse microemulsion method for photocatalytic applications

"Opus" research project NCN 2018/31/B/ST5/03292 [2019-2022]

(Project leader: Professor Ewa Serwicka-Bahranowska)

The scientific aims of the project are: a) to obtain TiO₂/clay composites according to a novel design based on the synthetic procedure employing exfoliated organoclays and inverse microemulsion of TiO₂-based nanoparticles, and (b) to test the newly engineered materials as photocatalysts for purification of water from organic pollutants. The proposed novel synthetic procedure offers a number of possibilities for control of composite properties via a) changing the nature of clay, b) changing the organocation, c) modification of oxide nanoparticles size by appropriate choice of the microemulsion synthesis parameters. Moreover, inverse microemulsion method enables synthesis of multicomponent oxides, which opens way for chemical modification of TiO₂ nanoparticles.

Research concentrated on investigation of the effect of various synthesis parameters on structural and textural properties of composites TiO₂/montmorillonite. Among others the role of TiO₂ loading in the composite (Fig. 1) was examined, the use of organic and inorganic form of smectite was compared, and modification of microemulsion synthesis parameters was investigated. The experimental set-up for photocatalytic measurements was assembled and preliminary tests of photocatalytic decomposition of rhodamine B were carried out.

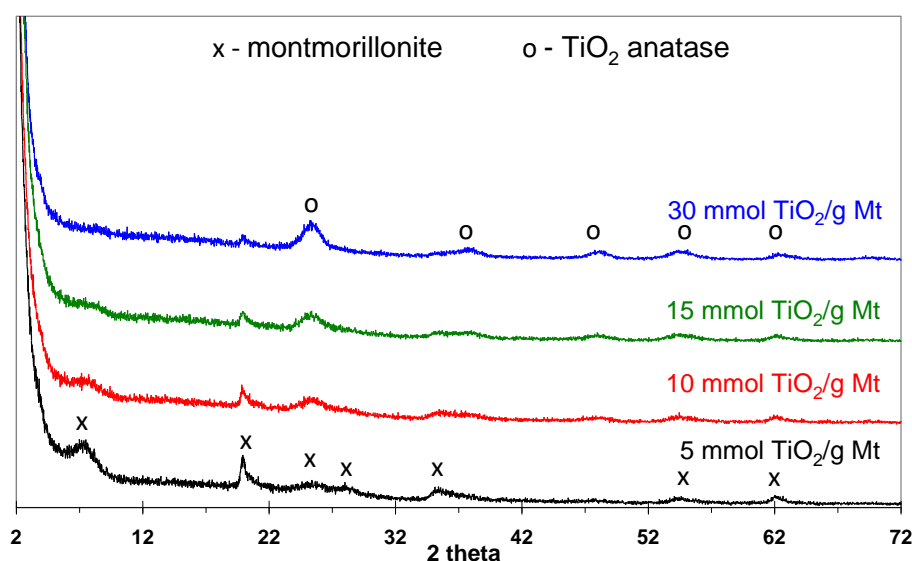


Fig. 1. XRD patterns of calcined composites TiO₂/montmorillonite with different loadings of titania.

Conformational properties of glycosaminoglycan building blocks

Coarse-grained modeling of carbohydrates

"Opus" research project NCN 2019/35/B/ST4/01149 [2020-2024]

(Project leader: Associate Professor Wojciech Plaziński)

In the early stages of the project, the conformation of glycosaminoglycans was considered at the level of the accuracy of the all-atom simulations and in the context of their building units.

The systems containing all possible building blocks (dimers) of glycosaminoglycans, i.e. the most important and diverse group of natural glycans, were built. The systems under investigation include different types of monosaccharides, different sulfation patterns, different anomeries and topologies of glycosidic bonds. Two types of molecular dynamics simulations were performed: (i) standard molecular dynamics simulations aimed at investigating the conformational properties and provide the data for the subsequent coarse-grained parameterization procedures; (ii) the enhanced-sampling simulations to compute the two-dimensional free energy maps related to glycosidic bond orientation.

The second aspect of the research concerned the general design of a computational procedure that would allow to estimate the value of persistent length for a given polysaccharide based on the knowledge about the conformation of glycosidic bonds between the monosaccharides that build it.

**"Preludium" Research Projects
of the National Science Centre**

Effect of controlled adsorption time on kinetics of three-phase contact formation at solid surfaces with different hydrophobicity

“Preludium” research project NCN 2017/27/N/ST4/01187 [2018-2020]

(PhD student: Agata Wiertel-Pochopień MSc; supervisor: Associate Professor Jan Zawala)

The goal of this project is to determine the effect of controlled time available for adsorption of surface-active substances (SAS) at an air bubble (gas/liquid) interface on kinetics of its attachment and three-phase contact (TPC – gas/liquid/solid) formation at a solid surface of different hydrophobicity.

Experiments on kinetics of three-phase contact (TPC) formation by colliding bubble with quartz surface in solution of surface-active substances with identical hydrophilic group – alkyltrimethylammonium bromides C_nTAB (octyltrimethylammonium bromide - C8TAB, dodecyltrimethylammonium bromide - C12TAB, hexadecyltrimethylammonium bromide - C16TAB, octadecyltrimethylammonium bromide - C18TAB) were performed.

During the experiments the quartz sample was located at two different distance from capillary orifice (L=3 and 150 mm) to determine the influence of dynamic adsorption layer (DAL) on time of three-phase contact formation (t_{TPC}) (Fig.1). It was shown that initially the t_{TPC} was longer when the DAL was fully formed (L=150 mm). After some threshold concentration the TPC was formed slower when the distance covered by the bubble after detachment from the orifice was too short for the DAL establishment (L=3 mm) and induction of non-uniform adsorption coverage. The opposite situation was observed for C8TAB, what can be caused by very fast adsorption of C8TAB molecules or high contamination with octanol molecules.

It was proved that the dynamic adsorption layer has a big influence on kinetics of three-phase contact formation. The change in the trend of t_{TPC} correlates well with variations of quartz surface hydrophobicity what confirms two different mechanism of rupture of the wetting liquid films.

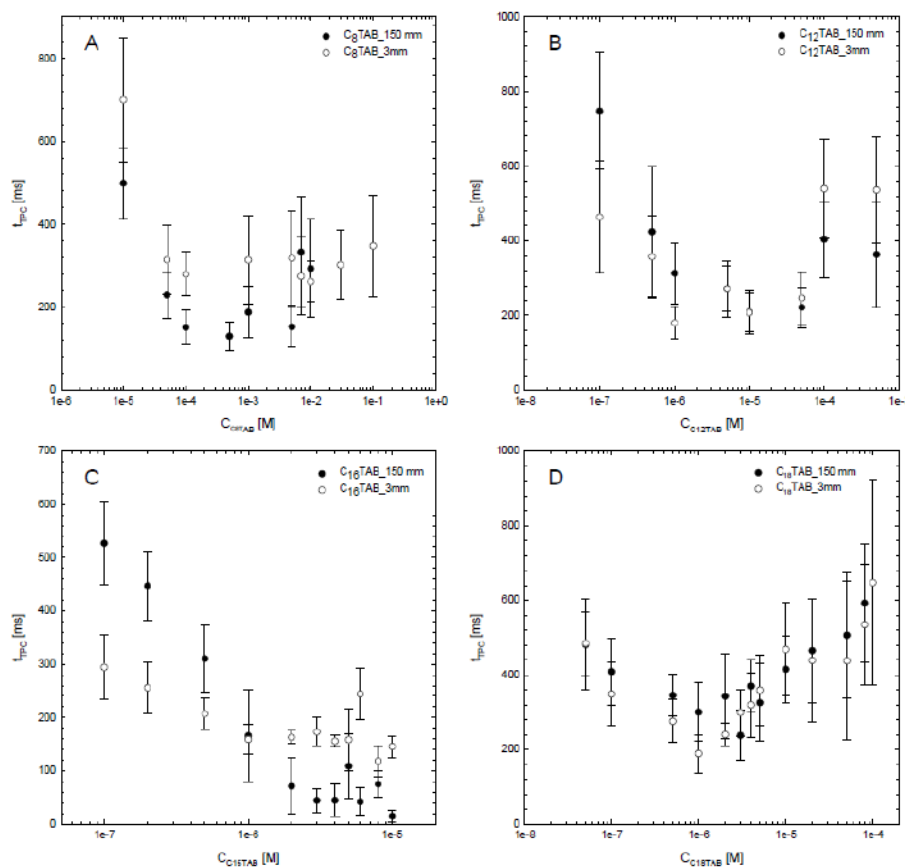


Fig. 1. Time of three-phase contact formation by colliding bubble with quartz surface in solutions of (A) C₈TAB, (B) C₁₂TAB, (C) C₁₆TAB and (D) C₁₈TAB.

Tungsten-containing aldehyde oxidoreductase from *Aromatoleum aromaticum* - study of catalytic reaction mechanism

“Preludium” research project NCN 2017/27/N/ST4/02676 [2018-2021]

(PhD student: Agnieszka Winiarska MSc; supervisor: Professor Maciej Szaleniec)

Tungsten aldehyde oxidoreductase (AOR) enzymes catalyze a reversible oxidation reaction of aldehydes to the corresponding carboxylic acids in the presence of ferredoxin, and because of their broad substrate spectrum, they are assigned a role in detoxifying harmful aldehyde metabolites in the fermentative degradation of amino acids. The AORs known so far are derived from anaerobic bacteria and archaea, and among them the tungsten aldehyde oxidoreductase is characterized by the lowest sensitivity to oxygen from *Aromatoleum aromaticum* (AOR_{Aa}). This enzyme is characterized by more complex structure (($\alpha\gamma\beta$)₂) than other known AORs (of structure α_2).

The research planned in the project is aimed to provide knowledge about the structure of the active enzyme centre and its reactivity, which will enable determination of the AOR_{Aa} reaction mechanism.

To obtain protein for testing, bacterial cultures in fermenters were grown. The bacteria *Aromatoleum evansii* was cultured, that contains a new AOR_{Aa} expression system, with a tag enabling protein purification by affinity chromatography, which enables to prepare the enzyme for research in a much simpler way.

In the AOR_{Aa} active center, the main catalytic function is assigned to the tungsten cofactor. The exact coordination of tungsten is difficult to determine by both crystallographic and spectroscopic methods, and knowledge of it is necessary to propose the catalyzed reaction mechanism. Thanks to the X-ray absorption study for the tungsten atom, it will be possible to determine the ligand system in the metal cofactor located in the active center of the enzyme. AOR samples were prepared and shipped to University of Saskatchewan (Canada), to study the protein tungsten-containing cofactor by EXAFS spectroscopy.

In continuation of the modelling of various possible versions of the tungsten cofactor using DFT and molecular dynamics methods, an attempt was made to improve the geometry of the tungsten cofactor in the known structure of the aldehyde oxidoreductase from *Pyrococcus furiosus*, in which it was not possible to unambiguously resolve the ligand position. Thanks to the use of QM: MM modelling, it was possible to determine the most probable structure and its geometry matching the electron density from the crystal structure: with tungsten in the VI oxidation stage and two oxo ligands.

As part of the biochemical characterization of the enzyme, activity tests with various aldehydes and carboxylic acids were continued, broadening the AOR_{Aa} substrate spectrum by i.a. heterocyclic aldehydes.

**"Beethoven" Research Projects
of the National Science Centre**

Domain wall dynamics and magnetic texture behavior in magnetic films with Dzyaloshinskii-Moriya interaction

"Beethoven" research project NCN 2016/23/G/ST3/04196 [2018-2022]

(Project leader: Piotr Mazalski PhD)

In the frame of project ultrathin magnetic layers, in which the Dzyaloshinskii-Moriya interaction (DMI) is expected – layers grown using sputtering techniques and molecular beam epitaxy. One of the interesting studied layers with unsymmetrical type of interfaces was trilayers NiO/Co/Pt where ferromagnetic layers is in contact with nonmagnetic layer (Au) and antiferromagnetic layer (NiO). NiO and Pt layers in contact with Co layer were expected to give big value of DMI. Magneto-optical and Brillouin Light Scattering spectroscopy studies confirm existence of DMI – what was interesting obtained value was one of the biggest in relation to other trilayers with different type of asymmetrical interfaces. Additionally, using magneto-optical microscopy it was possible to visualize magnetic domain structure where presence of DMI was observed by asymmetrical magnetic domain wall movement.

It was also studied multilayered sample like Ir/Co/Pt. In such kind of samples it was observed strong dependence of DMI depending on number of layers repetitions. Interestingly, it was discovered additional ferromagnetic resonance peaks probably coming from magnetic domain walls – resonances was dependent on number of layers repetitions and strength of DMI. There are planned additional experiments related with this phenomenon.

In addition, sample like Pt/Co/Au deposited by molecular beam epitaxy techniques was studied. In the next step sample was modified using irradiation by Ga^+ ions. Performed BLS studies and data analysis show existence of DMI at nonirradiated part of the sample – earlier DMI was observed only in similar composition sample deposited by sputtering. By ion irradiation it is possible to strongly modify magnetic properties of the samples and also DMI – up to zero after irradiation with selected ions fluence.

Additionally micromagnetic simulations of magnetization distribution were performed taking into account variation of magnetic anisotropy and DMI coefficient in the simulated layers.

Part of the results were presented at international conference (as “oral” presentation) and used for accepted publication.

**"Beethoven Life" Research Projects
of the National Science Centre**

Structure and function of fumarate-adding glycyl radical enzymes: biochemistry, modeling and application

"Beethoven Life" research project NCN 2018/31/F/NZ1/01856 [2020-2023]

(Polish leader: prof. dr hab. Maciej Szaleniec, German leader: prof. dr. Johann Heider)

The project aim is the investigation of the biochemistry and reaction mechanisms of glycyl radical enzymes which catalyze the addition of fumarate (fumarate-adding enzymes, FAE). The prototype representative enzyme of the FAE class is benzylsuccinate synthase (BSS) from *Thaurea aromatica*, which catalyses radical addition of toluene to fumarate yielding (*R*)-benzylsuccinate. The planned research utilizes a combination of theoretical and experimental techniques for elucidation of the reaction mechanism of the FAE class as well as the development of the microbiological expression platform for other FAE enzymes. These recombinant microorganisms will be tested for potential use in the production of optically pure succinate derivatives. The project is conducted in the Polish-German joint research team.

During the first year of the project, we focused on the modeling of BSS, aiming to explain experimental results from Prof. Heider's team. In particular, the observed changes in catalytic activity and substrate specificity of mutated variants of BSS were explained with MD simulations. The results from MD simulation predicted expansion of the BSS substrate specificity in an I617V mutant, resulting in the ability of the mutated enzyme to add fumarate to *m*-xylene (Fig. 1). In an R508K mutant, which adds 3-acetyl acrylate instead of fumarate to toluene, the simulation explained this newly gained activity. The crucial role of Arg508 for activity was also confirmed in the binding analysis of the fumarate in the active site. The statistical analysis of the distances between the catalytic cysteine residue of BSS and the methyl group(s) of the substrate(s) provided an additional explanation of the changes in activities. With help of the MM/PBSA method, it was also possible to study the influence of fumarate protonation on the catalytic process.

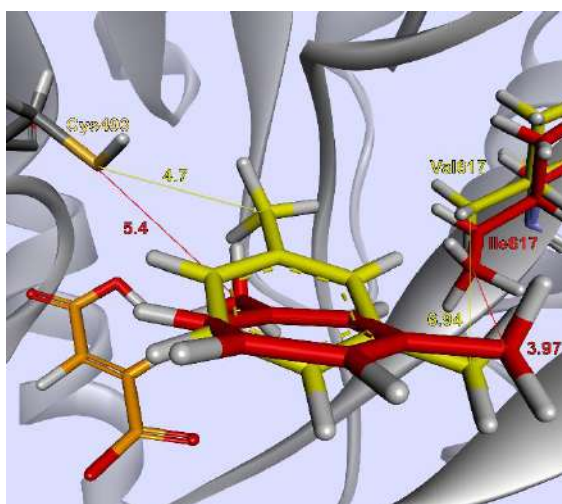


Fig. 1. BSS:*m*-xylene complex for the wild type (red) and I617V mutant. The numbers provide the most frequent distances between the substrate CH₃ substituents and Cys493 or Ile/Val617 residues.

The reaction mechanism was studied with the cluster-model and QMMM approach. The already studied pathway for monoprotonated fumarate was accompanied by calculations conducted for a completely deprotonated substrate.

Finally, experimental studies on BSS were also initiated in the Polish laboratory. These encompassed the cultivation of *Aromatoleum evansii* containing plasmid encoding BSS genes as well as the development of the analytical method for determination of enantiomeric excess of benzylsuccinate and dimethyl 2-benzylsuccinate esters.

**"Solar-Driven Chemistry" Research Projects
of the National Science Centre**

SolarMethaChem: Solar light-driven photochemical processes for methane chemical conversion to valuable product

„Solar-Driven Chemistry” research project NCN nr 2019/01/Y/ST4/00024 [2020-2023]
(Project leader: Associate Professor Dorota Rutkowska-Żbik)

Direct conversion of methane into fuels and platform molecules has been for a long time a “holy grail” in chemistry. The high C-H bond energy (434 kJ mol^{-1}), absence of functional groups and of the polarity result in a very low methane chemical reactivity. High temperatures and high pressures are generally required to accelerate methane chemical transformations and operation at practical rates. These harsh conditions, however, lead to huge energy consumption, often important emission of CO_2 , parasitic formation of by-products and fast catalyst deactivation. Solar light is an ideal alternative energy source and is largely used in combination with semiconductors to drive chemical reactions. The major goals of this project are *i*) the nanoengineering of new efficient materials for efficient oxidative coupling of methane under light, *ii*) identification of the reaction mechanisms of methane coupling and *iii*) optimization of the photochemical reactor and operating conditions.

In order to examine the electronic properties of the Ag/HPA/ TiO_2 catalyst, which catalyses methane coupling to ethane with yields up to 10%, the electronic structure of the following nanocrystals of TiO_2 was elucidated: $(\text{TiO}_2)_{84}$ of the bipyramid shape, $(\text{TiO}_2)_{78}$ of the cut bipyramid shape, and spherical $(\text{TiO}_2)_{78}$ nanoparticle. In the next step the theoretical models of the catalyst fragments were (HPA/ TiO_2 , Cu/ TiO_2) based on the results obtained for the support.

**"GRIEG" Research Projects
of the National Science Centre**

GRIEG Craquelure – Model of paintings with craquelure patterns for evidence-based environmental control in museums

"GRIEG" research project NCN 2019/34/H/HS2/00581 [2020-2022]

(Project leader: Associate Professor Łukasz Bratasz;

co-investigator: Mohammad Yaghoub Abdollahzadeh Jamalabadi PhD, Lindsay Oakley PhD,

Noemi Zabari PhD, Katarzyna Poznańska MSc Eng.)

In the framework of GRIEG Craquelure project, the research team prepared the scope of work and performed the measurements for experimental part of the project specified in subtask 1.1 - Development of a comprehensive database of material properties and structural features of the pictorial layers. Material selected to be included in the database and laboratory tests were selected based on technical research and available literature from historical sources. Together with Dr. Aleksandra Hola, the conservator of painting at the Academy of Fine Arts in Krakow, we have prepared a procedure for tempera paints with egg yolk as a binder for pigments like lead white, yellow ochre and azurite, while distemper paint with animal glue as a binder used only azurite. Appropriate proportions were defined for each pigment based on mechanical criteria and qualitative assessment by qualified conservator. As part of the project, samples of rabbit glue were prepared.

The laboratory tests have been performed to select and optimize methodology for samples testing in universal testing machine placed in climatic chambers for determining mechanical parameters and in a dynamic mechanical analyzer (DMA), as well as on a microbalance for determination of water vapor adsorption isotherms and measuring moisture-related swelling.

Simultaneously, a three-dimensional model of a panel painting was created with developed crack network to simulate development of new cracks under hygric loads. Two typical load modes were adopted in the model. One, uniaxial, generated by the moisture response of the wooden support, second isotropic, related to drying shrinkage frequently called annealing shrinkage. A mixed mode in which both modes are present were also considered. For verification of the results, stresses in the ground surface were compared in 3D and 2D models. The verified 3D model was used to determine the critical distances between the cracks along and across the wood grain below, which new cracks will not form. The model explained the cracks parallel to the wood grain and the square-shaped cracks observed in real paintings as well as their superposition. The model did not explain the cracks perpendicular to the wood grain. The model is currently under further development and optimization.

In the framework of the project, the image processing algorithms to isolate cracks from selected image fragments are developed. Among other, binarization, thinning methods and filtering algorithms were used to search for sets of neighboring pixels, for which the intensity takes local extremes in the direction of the main curvature, allowing for the separation of the crack lines on a single background. Currently, the algorithms are tested on mock ups of panel paintings with a craquelure pattern resulting from the exposure to humidity cycles in a climate chamber. They also allowed for the statistical characteristics of the cracks, i.e. the average length of the cracks, orientation of each crack or the directional average density of cracks. Numerical calculations were also carried out based on selected real works of art with a developed craquelure pattern.

**"Miniatura" Research Projects
of the National Science Centre**

Searching of novel bacterial ketosteroid dehydrogenases for oxidative dehydrogenation of steroids

"Miniatura" Research Projects NCN 2018/02/X/ST4/01963 [2018-2021]
(Project leader: Agnieszka M. Wojtkiewicz PhD)

The aim of the project is the identification of a physiological role for potential FAD-dependent 3-ketosteroid dehydrogenases (KstD) from two strains: *Sterolibacterium denitrificans* Chol-1S (two genes) and *Pseudomonas putida* KT2440 (three genes). In particular the project will help to answer following questions: i) is the expression of mentioned genes leading to catalysts with KstD activity; ii) are active enzymes regioselective in the direction of Δ^1 or Δ^4 products; iii) are substrates of the reaction only non-branched four-ring steroids as androstendione or branched at C17 as cholestenone or 3-ketopetromyzonole or two- or five-ring systems as well; iv) are functional catalysts differ in pH optimum or in the preference of an electron acceptor.

In the first stage of studies the necessary materials for the project were bought: components for genome DNA isolation from bacterial strains and for latter genes visualization. Oligonucleotides used as primes for genes isolation from genomic DNA were designed and ordered (for two sequences from *S. denitrificans* (SMB21450, SMB25049) and three from *P. putida* (Pp_2607, Pp_2600, Pp_2605)). Amplification of mentioned genes was confirmed by horizontal electrophoresis. For each gene a product of 1.7 kbp was obtained. Amplified genes were isolated for further construct preparation and bacteria transformation.

Genes encoding studied enzymes were amplified using molecular biology tools for all five putative enzymes. Three of them, genes from *P. putida*, were introduced to pMCSG7 plasmid, the plasmid that contains ampicillin resistance and histidine tag. Furthermore, plasmids with genes were cloned to *E. coli* XL-Gold and sequenced to confirmed its identity with the template. Next, plasmids with genes were cloned to the production strain: *E. coli* BL21(DE3)/MAGIC. After bacteria cultivation and protein production induction the protein expression was confirmed as well as the enzymatic activity. In the case of genes from *S. denitrificans*, for one of them the plasmid with gene for cloning to *E. coli* BL21(DE3)/MAGIC was prepared, while for the other one studies on preparation of the plasmid with the gene are still ongoing.

Ultrasonic synthesis of faujasite type zeolite as catalysts for the decarbonylation of furfural into furan

"Miniatura" research project NCN 2019/03/X/ST4/00149 [2019-2021]

(Project leader: *Lukasz Kuterasiński PhD*)

Sonochemical synthesis of zeolites seems to be an alternative method in respect to the classical techniques due to the possible reduction of the process time and the easing of temperature and pressure conditions. The application of this method in the long term could lead to a reduction or even elimination of the use of expensive (and often harmful) reagents. That causes a reduction in the costs of zeolite synthesis and is in line with the green chemistry policy.

In the undertaken research, it was performed the attempts to the synthesis of FAU-type zeolites via ultrasonic technique as catalysts for the production of furan from furfural. With reference to a well-known hydrothermal synthesis of zeolites, a special and the innovative aspect is a total replacement of the hydrothermal procedure with ultrasonic irradiation. The choice of faujasite from other zeolite structures (more than 250) implies from a very wide its application in chemical industry. For the obtained systems, the following parameters were determined: the time needed for the crystallization of the zeolite with the FAU-type structure depending on the sonication conditions, crystallinity, structure, morphology and acidity.

Preliminary XRD results indicated that in the case of ultrasonic treatment of the gel for 8 h, the presence of FAU-type zeolite phase was found. Nevertheless, the crystallinity of obtained material was not too high. Nevertheless, these XRD results showed that the synthesis of zeolites via total replacement of hydrothermal conditions with sonochemical technique is feasible, but this procedure requires further improvements and investigations.

Analysis of the porosity of FAU-type zeolites, prepared in the presence of ultrasounds indicated that it is possible to obtain mesoporous zeolites without the application of post-synthesis modification. It was also found that higher duration of ultrasonic irradiation caused gradual decrease of microporosity with simultaneous increase of overall mesoporosity. The application of ultrasonic irradiation allows to obtain active and selective mesoporous catalysts for the production of furan from furfural.

The acidity studies (NH₃-IR and CO-IR) showed that the application of ultrasound in the synthesis and modification of FAU-type zeolites led to the reduction of both Brønsted and Lewis acid sites. Analysis of the IR spectra of samples directly after activation at 400 °C (prior to the adsorption of probe-molecules) led to the conclusion that protonic acid sites are mainly in the form of bridged hydroxyl groups (hydroxyl nests). These OH groups are characterized by a low acid strength. Hence, CO sorption did not allow to estimate accurate acid strength of this OH groups type. The presence of hydroxyl nests implies from the existence of mesopores in such prepared samples.

In the near future, for the prepared materials, catalytic tests will be carried out in the decarbonylation of furfural into furan. Furthermore, the conducted research will be extended to zeolites with other structures, such as ZSM-5, beta or mordenite.

'Confinement effect' - 5-fluorouracyl in mesopores

"Miniatura" research project NCN 2019/03/X/ST5/01756 [2019-2021]

(Project leader: *Mariusz Gackowski PhD*)

As part of the scientific activity Miniatura 3, a number of works were carried out in 2020. The aim of the scientific activity is to introduce the drug 5-fluorouracil into mesoporous materials. SBA-15 mesoporous silica and mesoporous zeolites were purchased and synthesized. Various solvents were tested for the efficiency of incorporation of 5-fluorouracil into porous materials. Methanol, acetone and water were checked. Organic solvents were characterized by difficulty in evaporation from the carriers and low drug solubility values. Water was the best solvent for introducing the active substance. The process of applying 5-fluorouracil to carriers using water was optimized. The pre- and post-drug materials were characterized by solid state NMR spectroscopy in the ^1H and ^{13}C CP MAS experiments. NMR measurements were also made after dehydration, i.e. after the water had been removed by heating the samples in vacuum at 120°C for 20 hours. For comparison, 5-fluorouracil was also introduced into microporous materials (zeolite ZSM-5). The plans for the next year include completing the physicochemical characteristics of the obtained samples.

Preliminary examination on the impact of rare-earth alloying on corrosion mechanisms of magnesium alloys and its prevention by inorganic inhibitors

"Miniatura" research project NCN 2019/03/X/ST4/00749 [2019-2021]
(Project leader: Dzmitry Kharytonau PhD)

Magnesium alloys are widely used in various areas due to their highest strength-to-weight ratio. However, Mg alloys have low corrosion resistance causing significant exploitation problems. These materials contain many alloying elements forming a heterogeneous structure, usually composed of a large variety of intermetallic phases, which makes them highly susceptible to local types of corrosion.

The aim of the project was to investigate the influence of the microstructure of magnesium alloys alloyed with rare earth metals on their corrosion behavior and to explain the inhibition mechanisms of selected inorganic inhibitors on a macro and micro scale.

In the first stage, the microstructure of magnesium alloys QE22, ZRE1, and WE43 containing various rare earth metals was examined using scanning electron microscopy. The added rare earth elements formed intermetallic particles in the structure of the tested Mg alloys. Scanning Kelvin probe force microscopy was used to assess the local Volt potential differences within the microstructure of Mg alloys.

In the second stage, the influence of intermetallic phases on the local corrosion of Mg alloys doped with rare earth elements was investigated using electrochemical methods. Corrosion tests carried out in 0.05 M aqueous NaCl solutions showed high corrosion rates of all tested alloys. Based on the results of electrochemical impedance spectroscopy and linear voltammetry, the polarization resistances of the tested alloys are arranged as $QE22 < ZRE1 < WE43$.

At the same time, the effectiveness of inorganic anionic corrosion inhibitors was tested on the example of vanadates and molybdates. It has been shown that the selected inhibitors affect the corrosive mechanisms of all tested alloys. The highest corrosion inhibition efficiency was obtained when 100–150 mM sodium molybdate was added to 0.05 M NaCl solution. On the other hand, the highest calculated values of the corrosion inhibition efficiency of ca. 95% were obtained for the WE43 alloy (Figure).

Raman spectroscopy and X-ray photoelectron spectroscopy were used to understand the mechanisms of corrosion inhibition by selected inhibitors. The mechanism of the corrosion inhibition is based on the formation of a surface oxide layer of the inhibitor.

Isothermal titration calorimetry (ITC) in biochemical characterization of α -ketoglutarate dependent enzymes. Internship at McGill University in prof. Mittermaier group.

"Miniatura" research project NCN 2019/03/X/ST4/01639 [2019-2021]
(Project leader: Anna Milaczewska PhD)

From January to March 2020 I have chosen and prepared two α -ketoglutarate dependent enzymes (kanamycin B dioxygenase - KanJ, hyoscyamine 6 β -hydroxylase - H6H) for ITC measurements. For this purpose, I have cultivated transformed E.coli bacteria in LB medium and I have purified recombinant enzymes (using affinity chromatography with Ni-NTA resin and size exclusion chromatography with Superdex-75 column)

I have bought ligands of appropriate purity, which are needed for planned ITC studies: kanamycin B and N-oxalylglycine. The visit was planned for April 2020. According to the plan, the airplane ticket were bought and room in a hotel was booked in Montreal. Additionally, in reported period, I have proceeded with necessary documents required by McGill University, which were e-mailed.

For the period: April - December 2020, the project was suspended due to COVID-19 pandemic and connected to it restriction in travelling and work in Poland and Canada. Currently, we are waiting for finishing of refund from airlines after flights cancelation, while hotel reservation was cancelled free of charge.

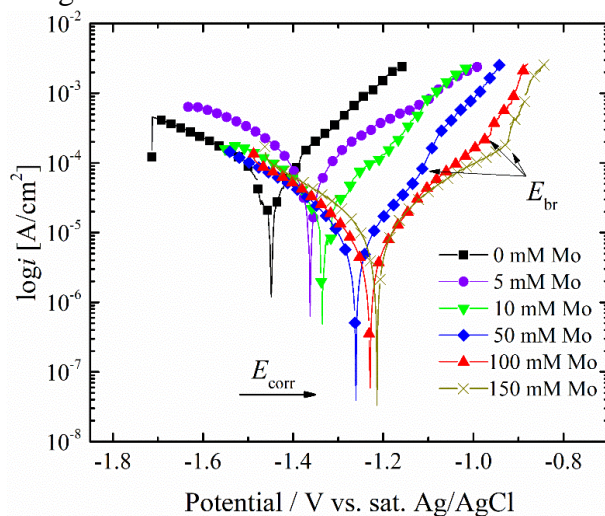


Figure. Potentiodynamic polarization curves of WE43 alloy in 0.05 M NaCl containing varying amounts of Na₂MoO₄ inhibitor.

Effect of doping with transition metals of oxide systems for photocatalytic elimination of volatile organic compounds. Research internship at CSIC - Instituto de Catálisis y Petroleoquímica (ICP) in the group of Prof. M. Fernández-García.

"Miniatura" research project NCN 2019/03/X/ST4/01638 [2019-2021]
(Project leader: Urszula Filek PhD)

The aim of this project is to investigate the photocatalytic and thermo-photocatalytic activity of the titanium oxide - heteropolyacid $H_3PW_{12}O_{40}$ system subsidized with transition metals in the photooxidation reaction of aromatic hydrocarbons with various substituents (toluene, styrene). The reaction will be carried out in a heterogeneous system, i.e. on a solid catalyst in a gas phase flow. Toluene has been chosen as the reference for the photodegradation reaction of organic pollutants present in urban atmospheres, and styrene as an example of photosynthetic reactions to obtain products of high added value of industrial interest.

Samples (catalysts) the Cu-HPW-TiO₂ and Pd-HPW-TiO₂ were synthesized using the traditional impregnation method. Preparations synthesized by the reverse microemulsion method are going to be obtained at the CSIC. Both series of samples are going to be characterized using the equipment available in the receiving team.

Due to the restrictions resulting from the prevailing SARS-CoV-2 pandemic, the project was suspended until the end of April 2021.

**Research Projects
of the National Centre for Research and Development**

Novel functionalised biopolymers for medical applications.

"Leader" programme research project NCBiR 0090/L-7/2015 [2017-2020]
(Project leader: Maciej Guzik PhD)

Stage 4 Biomaterial effectiveness in wound healing on a mouse model - in vivo studies.

The aim of this stage was to evaluate the possibility of using biopolymer dressings to cover wounds in a mouse model.

The studies were conducted on eight-week-old mice males of the C57BL/6 strain. Mice of this strain are a standard animal model, not burdened with metabolic or civilization diseases, without any known skin or allergic problems. The conducted experiments were approved by the 1st Local Ethical Committee for Animal Experiments (Resolution 170/2016 of November 16, 2016).

In the experiment 50 animals were used. Two time variants of the experiment were done, in half of the animals the healing process was observed for 7 days, and in the other half for 14 days. In each of the time variants, the animals were divided into 3 groups (8 animals): 1) control (self-healing wounds), 2) mice with an unmodified biopolymer and 3) mice with a biopolymer modified with an anti-inflammatory compound. Two mice were lost during the surgical procedure due to anesthesia. After the wounds were made and treated, the mice were observed and assessed for 1 and 2 weeks. Animals were euthanized and then tissues were collected for further analysis.

It was observed that in mice in the control group, the wounds contracted more quickly. No inflammation was observed in this group. In both the first and second study groups, it was observed that the applied biomaterial delayed the shrinkage of the wound edges. In both variants, in particular with the 2-week healing process, integration of the material with the animal tissue was observed. The material removed from the wound was clearly thinner than that used when wound was dressed. Moreover the colonization of the biomaterial by animal cells was visible.

In the collected skin fragments the expression of various genes was assessed, including KRT14 – epidermal cells, keratinocytes and progenitor cells for keratinocytes marker; KRT15 – progenitor cells for keratinocytes and skin stem cells marker; TSLP – a cytokine that promotes the maturation of e.g. Langerhans and mieloid cells associated with the skin's immune system; Langerhans cells activation by TSLP induces the synthesis of pro-inflammatory cytokines (e.g. TNFa) and indicates the development of inflammation; IL1A – pro-inflammatory cytokine, produced, inter alia, by macrophages and neutrophils, activates the inflammatory process.

It has been observed that KRT14 expression was lower in the study groups than in the control animals, and the lowest in the group of animals kept for two weeks with a modified dressing. The KRT15 expression was low and comparable in all groups. We also showed low TSLP expression in the tested animals, with no apparent differences between the groups. The IL1A expression was significantly decreased in animals healed for 2 weeks as compared to animals kept for 1 week. In the one-week groups, lower IL1A expression was observed in the study groups compared to the control group, while in the animals that healed for 2 weeks. Similar IL1A expression was demonstrated in the control group and animals treated with modified biomaterial and slightly higher in animals with unmodified dressing.

The conducted studies have not shown a negative effect of the used biomaterials. The reduced expression of IL1A may indicate that biopolymer dressings reduce inflammation process in the healing wound.

Outperforming functionality: composite/mixed matrix porous materials in membrane-based processes

„EIG CONCERT-JAPAN” research project NCBiR EIG CONCERT-JAPAN/1/2019 [2019-2022]
(Principle investigator: Aleksandra Pacula D.Sc. Eng.)

The aim of the research: synthesis and characterization of physicochemical and photocatalytic properties of metal-TiO₂-zeolite composites.

Synthesis: a) preparation of metal nanoparticles (NPs): Ag (diameter ~ 14 nm) or Pd (diameter < 10 nm). Synthesis of metal NPs was performed via chemical reduction (by means of NaBH₄) of silver cations (AgNO₃) or palladium cations (PdCl₂). Ag NPs were stabilized by the addition of organic anions (citrates). Pd NPs were synthesized via reverse microemulsion method “water in oil”. b) deposition of Ag NPs or Pd NPs on TiO₂ and also on physical mixture of TiO₂ and zeolite Y (sodium form of faujasite). The nominal concentration of Ag in the catalysts was 1, 0.5, 0.25, 0.1 and 0.05 wt. %. The catalysts containing unreduced silver cations on TiO₂ were also prepared (nominal loadings: 0.1 and 2 wt. %). The nominal concentration of Pd in the catalysts was 1 wt. %.

Physicochemical properties: specific surface area of TiO₂ and physical mixture of TiO₂ and zeolite Y (95:5) is 60 and 84 m²g⁻¹, respectively. Deposition of Pd NPs (1 wt. %) or Ag NPs (0.05 wt. %) does not affect S_{BET}. Due to low concentration of metal NPs (≤ 1 wt. %) and/or low dimensions of metal crystallites, deposition of metal NPs onto TiO₂ or physical mixture of TiO₂ and zeolite Y does not result in the presence of additional reflections in the XRD patterns besides those characteristic of TiO₂. In the XRD patterns of physical mixtures of TiO₂ with various contributions of zeolites Y (5, 10 and 15 wt. %), besides the reflections characteristic of TiO₂ one additional reflection at 2θ = 6° characteristic of zeolite Y is observed. Its intensity increases with increasing amount of zeolite Y in the physical mixture of TiO₂ and zeolite Y. Spreading of metal NPs (Ag or Pd) on TiO₂ or on physical mixture TiO₂ and zeolite Y does not influence the band gap of semiconductor – TiO₂ (~ 3.2 - 3.3 eV).

Photocatalytic properties: photocatalytic test involved degradation (UV lamp with an emission spectrum between 365 and 367.5 nm was used as an irradiation source) of the dye: methyl orange in the presence of TiO₂ or TiO₂ with deposited Ag or Pd NPs or physical mixtures of TiO₂ with various contributions of zeolite Y (5, 10 and 15 wt. %). Degradation of methyl orange (40, 30 and 29 %) decreases with increasing contribution of zeolite Y in physical mixture of TiO₂ and zeolite Y (5, 10 and 15 wt. %), while for pure TiO₂ it is equal to 83 %. After 1 hr of being irradiated, 26 and 44 % of methyl orange is decomposed in the presence of TiO₂ containing 1 wt. % of Ag NPs or Pd NPs, respectively. It suggests that the surface of TiO₂ particles is more covered by Ag NPs than by Pd NPs. Degradation of methyl orange in the presence of small amounts of Ag on TiO₂ (0.1 and 0.05 wt. %) is comparable with that in the presence of pure TiO₂. After 1 hr of being irradiated, 82 and 85 % of methyl orange is decomposed in the presence of TiO₂ containing 0.1 and 0.05 wt. % of Ag NPs, respectively. It suggests that TiO₂ particles in Ag/TiO₂ (0.1 and 0.05 wt. %) are well exposed to the methyl orange aqueous solution. The degradation of methyl orange in the presence of small amount of Ag NPs deposited on TiO₂ (0.05 wt. %) is comparable to pure TiO₂ after 1 hr (85 vs. 83 %) and 2 hr (91 vs. 94 %).

Summary: the obtained composites have ability for photocatalytic degradation of methyl orange. The addition of zeolite Y and the deposition of metal NPs on TiO₂ reduces the efficiency of photocatalytic degradation of methyl orange in comparison to pure TiO₂ but the negative effect can be minimized by the application of small amounts of Ag NPs on TiO₂ (0.1 and 0.05 wt. %). The prolongation of degradation of methyl orange from 1 hr to 2 hr does not cause drastic improvement.

Technology of biorefining vegetable oils for the production of advanced composite materials

„TechMatStrateg” research project NCBiR TECHMATSTRATEG2/407507/1/NCBR/2019 [2019-2022]
(Project leader: Maciej Guzik PhD)

Task 1

1. Development of fatty acid hydrolysis

Optimization of the hydrolysis process was performed using catalysts other than sulfuric acid. Zeolite catalysts and CalB lipase were tested. Faujasite 31 (98.4% rapeseed oil conversion) turned out to be the best inorganic catalyst. Based on the results from this part of the project, a master's thesis was created.

2. Fermentations leading to aPHA

Several fed batch fermentations were performed in a 5L Sartorius Stedium Biostat® B bioreactor. Free fatty acids from rapeseed oil or oleic acid were used as the substrate. Comparison of samples from both fermentations showed faster biomass growth in case of oleic acid as a substrate. Higher amounts of biomass were observed for fermentations with substrates derived from rapeseed oil. The percentage of polymer was higher for oleic acid. The composition of mclPHA monomers at the end of the fermentation process was comparable for both substrates.

3. Fermentations leading to PHB

Several fermentations were carried out and the obtained results were analyzed. Glycerol as a carbon source is well absorbed by the bacteria *Z. denitrificans* and the use of waste glycerin in the process is possible and gives a chance for waste management after the production of biodiesel.

4. Modeling of fermentation processes

During the analysis of fermentation profiles for PHB, it was noticed that jumps in glycerol concentration above 100 g / l were eliminated, while fluctuations in its concentration did not exceed 60 g / l. The process was scaled up for the final volume of 30l.

5. Management of waste streams

The results of preliminary tests concerning the selection of the type of acids used for hydrolysis were analyzed. Preparations were made for scaling up the process of acid hydrolysis of bacterial biomass

Task 2

Preparatory work has been carried out for the design of the refinery building at the Institute. Planned location of the demonstration line inside the building. Appropriate equipment was purchased to enable its construction in the temporary building

**Exchange of PhD Students
and Academic Staff Programme Projects
of the Polish National Agency for Academic Exchange**

International Scholarship Exchange of PhD Candidates and Academic Staff



Project NAWA PPI/PRO/2018/1/00006/U/001 PROM [2019-2021]

(Project coordinator: Professor Tomasz Borowski)

In accordance with the assumptions of the Project, the following scholarship competitions under the PROM Program were conducted and resolved at the turn of 2019/2020:

1. Competition for scholarships to finance the costs of participation in short forms of education abroad (scientific conference, science school, scientific workshops, scientific courses, scientific training) for doctoral students of ICSC PAS,
2. Competition for scholarships to finance short-term internships in foreign research units for doctoral students of ICSC PAS,
3. Competition for scholarships to finance the costs of short-term internships in foreign research units for representatives of the scientific staff of ICSC PAS,
4. Competition for scholarships to finance short-term internships at ICSC PAS for doctoral students from abroad,
5. Competition for scholarships to finance short-term internships at ICSC PAS for representatives of foreign academic staff.

27 participants were selected for the Project under all of the above competitions. Unfortunately, due to the development of the pandemic, most of the planned trips and arrivals could not be implemented so far, only 2 internships for foreign workers at ICSC PAS were carried out. The contract with NAWA for the implementation of the project was extended by 12 months.

“Polish Returns” Programme - CRAQUELURE



“Polish Returns” Programme NAWA
PPN/PPO/2018/1/00004/U/00001 [2018-2022]

(Project leader: Associate Professor Łukasz Bratasz; co-investigator: Mohammad Yaghoub Abdollahzadeh Jamalabadi PhD, Lindsay Oakley PhD)

The goal of the "Polish Returns" Programme and thus the CRAQUELURE project is to create a project group conducting research on the development of a physical model of paint layers in paintings based on funds obtained from external sources as well as conducting other research in the field of heritage science. Therefore, the second year of project implementation was devoted to submitting applications for research funding and employment of new employees funded from the project the project.

During this period, several applications for external financing were submitted to:

- European Commission, H2020 program, call H2020-MSCA-ITN-2020, application number 956043, for funding research and doctorate - the project has not received funding,
- Ministry of Science and Higher Education, investment grants program, application number 488408 - project under evaluation,
- National Science Center, Preludium program, application number 479395, "Development of rational environmental guidelines for short-term religious, cultural and commercial events in historic buildings", project submitted by Magdalena Soboń, and dr. hab. Łukasz Bratasz acts as a supervisor - the project is under evaluation.
- National Science Center, OPUS-LAP program, application number 2020/39 / I / HS2 / 00911, "Conservation prevention strategies for poly (vinyl chloride) objects", project submitted jointly with the Jagiellonian University and the University of Ljubljana - project in during the evaluation.

At the beginning of 2020, Dr. Mohammad Yaghoub Abdollahzadeh Jamalabadi joined the project group, and developed a three-dimensional physical model of the painting layer of panel painting. Based on the model, calculations were performed to elucidate the effect of cracks parallel and perpendicular to the wood fibers on the process of initiation of new cracks caused by the wood moisture response and ground drying, which is the result of the slow reaching of the thermodynamic equilibrium and deeper packing of the ground structure. The calculations allowed to explain two basic typologies of cracks, i.e. cracks parallel to the fibers and "square" cracks. The model did not explain the cracks perpendicular to the wood grain. Currently, the model is further refined and developed towards the possibility of assessing the development of damage caused by minor defects in the material.

Two competitions were announced for the positions of assistant mechanics and image processing specialists. Parallel to this research, Dr. Lindsay Oakley developed a model of chemical reactions in oil paints with pigments containing metal ions. The developed model allowed to determine the rate of chemical reactions in the initial period of drying of oil paints. In October 2020, Dr. Lindsay Oakley was offered a job as director of the Heritage Science Department of the National Archives and Records Administration in Washington and resigned from the job. Therefore, an additional competition for the position of an assistant was announced, but only one person who did not meet the requirements entered the competition. An additional competition is currently underway, the conclusion of which is planned for January 2021.

Methane selective oxidation to methanol of over metallozeolites catalysts



Research project NAWA no PPN/BIL/2018/1/00069 [2019-2021]

(Project leader: Associate Professor Dorota Rutkowska-Żbik)

The aim of the current bilateral collaboration project between the Jerzy Haber Institute of Catalysis and Surface Chemistry PAS and the J. Heyrovský Institute of Physical Chemistry Czech Academy of Sciences is a targeted preparation of highly structured metal (Fe, Mn) ion/oxo centres stabilized in zeolites of ferrierite (FER) and beta (*BEA) topology, which may serve as active catalysts for CH₄ oxidation to CH₃OH by N₂O.

The Mn-FER samples obtained in last year in which we used FER of various distribution of Al in the zeolite network and in which Mn content was changed in the range of 0-3 wt% were characterized by UV-Vis and FTIR spectroscopy leading to the determination of manganese location in the zeolite framework.

Metal (Fe, Mn) oxidation state introduced into the FER structure was studied by X-ray absorption spectroscopy (XAS) in Solaris National Synchrotron Radiation Centre at the PEEM/XAS end-station. Signals were detected using total electron yield (TEY) (surface sensitive) and partial fluorescence yield (PFY) (bulk sensitive) detection.

The obtained catalysts were tested in the oxidative dehydrogenation of propane in temperature range 100-300 °C.

Switchable surfactants at air-water interface and their role in photo-responsive foam



Project NAWA PPN/BIL/2018/1/00093 [2019-2022]

(Project leader: Marcel Krzan PhD)

In this project we introduce a new class of photo-switchable surfactants and their 2D assemblies at the liquid/gas interface, which make the interface as well as macroscopic foam responsive to light irradiation. This opens exciting new possibilities for foams such as self-healing capabilities or the possibility to adapt foam properties by photo-switching of the surfactants. We have synthesized amphiphilic arylazopyrazole (AAP) derivatives which are superior analogues of azobenzene surfactants due to the less spectral overlap between *trans* and *cis* isomers, a more favorable photo-stationary state (>95 % switching in both directions), and increased thermal stability of the *cis* isomer. Such molecules have anionic or cationic head groups as well as different chain lengths, which allows for tuning lateral interactions and surface rheology as well as structure.

Recently it was demonstrated that novel arylazopyrazole surfactants facilitate superior photo-control of fluid interfaces and colloids. In our research we extended these studies by investigating the effect of added (non-surface active) polyelectrolyte PDADMAC to aqueous solutions of the photo-switchable n-butyl-arylazopyrazole butyl sulfonate (butyl-AAP-C₄S) surfactant. It was found that the polyelectrolyte forms complexes with the surfactant, but what is important, it does not inhibit the surfactant's photo-responsive behaviour at the water/air interface and in foams, i.e. the foams are still responsive to light agitation. On the other hand, the interfacial properties of such complexes are rather different than those of the surfactant alone. We present results obtained by several complementary methods, namely vibrational sum-frequency generation spectroscopy, tensiometry and surface dilational rheometry, and attempt to correlate interfacial to foam stability.

Due to limitations related to the COVID-19 pandemic, the project was extended until end of 2022.

Understanding molecular aspects of the protein misfolding process: in situ spectroscopic and microscopic studies



Project NAWA PPN/BIL/2018/1/00103 [2019-2020]

(Project leader: Professor Barbara Jachimska; co-investigator: Paulina Komorek PhD)

Project research focuses on the characterization of protein layers at the solid/liquid interface. The structural stability and degree of hydration of the layers were monitored using a range of advanced analytical methods such as multi-parameter surface plasmon resonance (MP-SPR), quartz crystal microbalance (QCM-D), and infrared spectroscopy (FTIR). The SPR and QCM-D studies indicate that during the monolayer's filling on the surface, lysozyme molecules' orientation changes from side-on to between/end-on. In the range of high volumetric concentrations, bilayer formation is observed. The degree of hydration of the monolayers and bilayers differ significantly. The hydration degree for the monolayer varies between 35-75%, in the case of the bilayer is higher than 85%. Moreover, correlations between the degree of hydration of the adsorption layer and the layers' viscoelastic properties were observed. In general, an increase in the filling of a layer is characterized by its stiffness. Simultaneously, a higher level of hydration of the system means an increase in the viscoelastic properties.

Moreover, the protein's interaction with the gold surface has a significant influence on the stability of the native structure of the protein. Based on FTIR spectra analysis, an increase in the content of β -turns and random structures of lysozyme is observed, with a simultaneous decrease in the range of β -sheets. The increase of β -turns in the structure determines the lysozyme stability and prevents system aggregation. The change in the system's ionic strength induces a difference in the water shell structure around the protein molecule. Unbound water dominates at low salt content. The increase in salt concentration is associated with a more significant proportion of bound water, which affects the resulting layers' stiffness and increases the stability of the II structure of the adsorbed protein.

Horizon 2020 Programme

Energy-X: Transformative chemistry for a sustainable energy future



Horizon 2020 Programme no. 820444

(Tasks coordinator: Associate Professor Dorota Rutkowska-Żbik, Professor Małgorzata Witko)

The Energy-X project aims at the formation of an international consortium for Large Scale Initiative whose vision would encompass the sustainable production of synthetic fuels for energy storage and of feedstock for the chemical and materials industry. In the longer-term, the science and technology developed will allow to change the current production system moving to a distributed production.

ICSC PAS is mainly involved in Work Package 6 “Coordination with regional and national funding”) whose aims are to map of European national and regional funding activities and to propose mechanisms and plan for alignment of co-funding. In 2020 within the Work Package 6 the report “Mechanisms and plan for alignment of co-funding” on was prepared (deliverable 6.1) which analyses availability of funding for joint initiatives in energy and transformative chemistry.

The current project resulted in establishing of the SUNERGY consortium, composed of the Energy-X and CSA SUNRISE partners, including ICSC PAS. The aim of the SUNRISE consortium is to lobby for financing of scientific project in the field of new energies and materials.

CollectionCare - Innovative and affordable service for PC monitoring of individual Cultural Artefacts during display, storage, handling and transport

Horizon 2020 Programme no. 814624

(Project leader: Associate Professor Łukasz Bratasz; co-investigator: Arkadiusz Janas MSc, Katarzyna Poznańska MSc Eng.)

The research team carried out a number of tests focusing on changes in the mechanical properties of the canvas, canvas sized with animal glue, animal glue-based ground layer (the gesso), and oil paints as a result of changes in relative humidity. The measurements were made with a universal testing machine and with the use of optical methods.

In this study, each of the parts constituting a painting on canvas was examined, i.e. canvas, canvas sized with animal glue, and animal glue-based ground layer (the gesso) - a stiff material similar in mechanical properties to aged brittle oil paints, having a function of a substitute for the design layer. The results showed that in the tested samples there is a strong anisotropy of mechanical properties depending on the direction on the canvas. The stiffness modulus for the directions corresponding to the "weft" and "warp" directions are an order of magnitude greater (~ 200 MPa) than the diagonal direction on the canvas. By covering the canvas with a layer of animal glue significantly increases the stiffness modulus while maintaining anisotropic mechanical properties is observed. Hence, the canvas-covered with a layer of animal glue is a composite material. The application of an animal glue-based ground layer increases the stiffness modulus by another order of magnitude (~ 2 GPa) and the anisotropic mechanical properties of the material disappear. Cracking of the gesso layer, which is responsible for the formation of cracks in the images, is already observed at deformations of the order of single parts per mille. The measurements were carried out in a wide range of relative humidity, from 30% to 90%. An increase in relative humidity causes a decrease in the material stiffness modulus, while cyclical changes in relative humidity are responsible for the formation of cracks.

Additionally, the mechanical properties of oil paints used in the painting were measured. Of the four 30-year-old samples available, two showed no change in mechanical properties. Measurements of the remaining two samples showed a material shrinkage of about 1%, which is sufficient to generate cracks in the paintings. The samples were subjected to cycles of temperature changes in the range of 20°C - 40°C and changes of relative humidity from 50% to 90%. The results showed no changes in mechanical properties as a result of changes in temperature and relative humidity.

The general conclusion from the work performed so far is that the research described above may help explain the common observation that canvas paintings are often covered with a dense network of cracks. Changes in RH may have fundamental consequences for future conservation recommendations regarding environmental conditions in museums. For further development, further research will be carried out on the influence of environmental conditions on the mechanical properties of samples simulating real paintings.

IPERION HS - Integrating platforms for the European Research Infrastructure on heritage science

Horizon 2020 Programme no. 871034

(Project leader: Associate Professor Łukasz Bratasz, Marcin Strojecki PhD, Magdalena Soboń MSc)

The goal of the IPERION HS project is establishing and operating a distributed pan-European research infrastructure, strengthening key national research facilities of recognised excellence in heritage science. Heritage science is a young and cross-cutting scientific domain embracing a wide range of research disciplines enabling deeper understanding of the past and improved care for the future of heritage. Since 2016, heritage science is included in the European Strategy Forum on Research Infrastructures Roadmap as one of the strategic areas in the domain of Social Sciences and Humanities, where it is represented by the European Research Infrastructure for Heritage Science. IPERION HS will provide to the advanced community of heritage science a further level of pan-European integration, in view of the establishment of European Research Infrastructure for Heritage Science. The project is a further step towards a unified scientific approach to the most advanced European instruments for the analysis, interpretation, preservation, documentation and management of heritage objects in the fields of art history, conservation, archaeology and palaeontology. The IPERION HS project will be offering not only trans-national access to a wide range of high-level scientific instruments and methodologies, but for the first time it will focus on needs of preventive conservation in museums and other memory institutions. One of the key action will be development of the Preventive Conservation Digital Platform (PCDP) enabling users to model and plan future risk scenarios and adjust preventive conservation measures accordingly. The PCDP will be a first step of the heritage science community to actively support the European Open Science Cloud initiative to build a competitive data and knowledge economy in Europe.

In the first year of the project the main components of the PCDP have been defined encompassing databases of relevant data, and decision supporting tools for practitioners, museum professionals and object owners. The institute is responsible for development of a general platform where various tools can be uploaded by project partners as well as for adopting HERIE tool to the PCDP. The research work has been focused so far at development of its structure and requirements.

Analysis of existing data on various degradation mechanisms has shown that frequently it cannot be translated into knowledge enabling to support preventive conservation decision. Another requirement is related to need of significant reduction of complex set of data, dependences and uncertainties into simplified models that can be used by professionals responsible of decisions, which don't necessary have specialised subject knowledge.

The main structure of the model will be based on ten agents of deterioration defined in the manual for the CCI-ICCROM-ICN Risk Management Method as its primary (though not mandatory) framework for organizing risks.

The proposed structure has been preliminarily implemented on www.herie.pl website and is being tested. Additionally, the HERIE tool allowing estimating risk of mechanical damage due to environmental variations, is being adopted to the new decision supporting platform.

EU COST Actions

Computational materials sciences for efficient water splitting with nanocrystals from abundant elements



EU COST Action no 18234 [2019-2020]

(country coordinator: Professor Małgorzata Witko)

This COST Action intends to focus on bridging the knowledge gaps between different theoretical methods (DFT, molecular mechanics and molecular dynamics, Monte-Carlo dynamics, microkinetic modelling) and computer codes in order to facilitate the modelling of all processes which accompany water splitting, in a longer term enabling the discovery of novel electrocatalytic materials.

The project “Extremely small nanocrystals” was initiated. Within the project the researchers involved in the current COST actions constructed models of semi-conducting metal oxide nanocrystals. The group from ICSC PAS proposed two models of V_2O_5 , one of a cube and one of a belt shape, each of 1-2 nm size (see Figure below).

Next step consisted of the elucidation of electronic structure of the proposed structures. Additionally, a nanocrystal of NiOOH was considered. The studies were conducted within Density Functional Theory with PBE functional and def2-SVP basis set. The geometry optimization of all structures were also initiated, but the jobs didn't finish due to the large size of systems under study.

During 2020 four project meetings took place: on 11-13.02. 2020 in Naples, on 7.07.2020 in Haifa (on-line), on 1.12.2020 in Gothenburg (on-line), and on 11.12.2020 in Barcelona (on-line). Seven papers resulted from the action, out of which one was written in ICSC PAS.

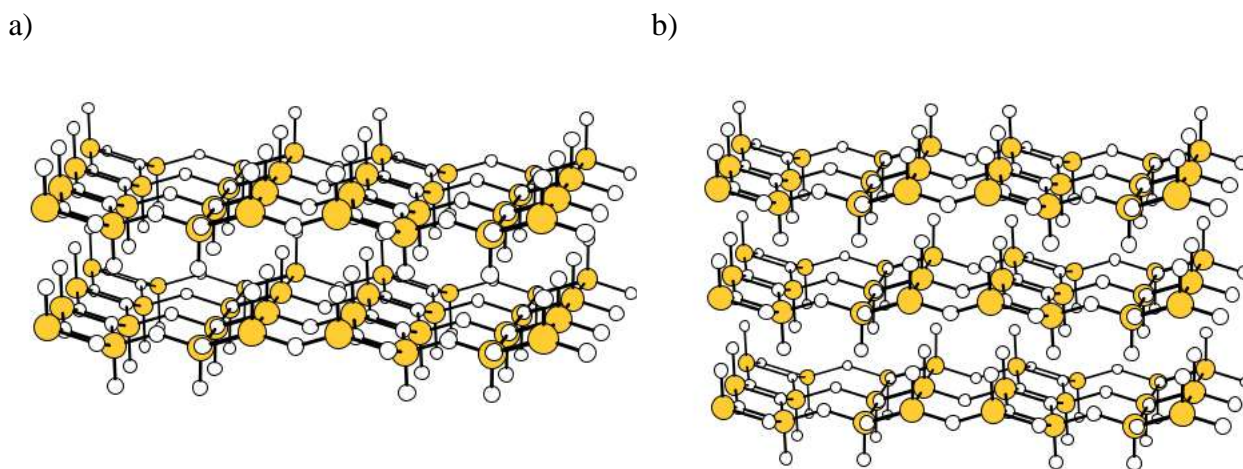


Figure. Structures of V_2O_5 nanocrystals (yellow – vanadium atoms, white – oxygen atoms): a) belt-shape crystal, $(V_2O_5)_{32}$, b) cube-shape crystal, $(V_2O_5)_{36}$.

Projects of the Norwegian Research Council

Sustainable Management of heritage Buildings in a Long-term perspective - SyMBoL



Norwegian Research Council research project 274749 SyMBoL [2018-2021]
(Project leader: Marcin Strojceki PhD)

The research activity conducted within the project was aimed both at experimental and theoretical computer aided modelling. The experimental work covered controlled laboratory tests and long-term monitoring of microclimate impact on two stave churches (Heddal and Ringebu) selected as case studies. In both objects, systems of environmental parameters monitoring (air temperature and relative humidity) and acoustic emission (AE) have been installed. In each church, in cooperation with conservators, two wooden objects were selected as representative architectural and decorative elements, to the surfaces of which the EA probes were attached. The AE signals recorded for all monitored objects come from the stress relaxation in hygroscopic objects induced by changes in relative humidity as a result of climate instability in their surroundings. Additionally, the concentration of particulate matter (PM) suspended in the air is monitored in order to assess the rate of soiling of architectural surfaces and the furnishings.

As part of the theoretical research task, a model of a massive wooden element, a sculpture or a structural element, e.g. a column, was developed, which will become the basis for including this category of objects in the HERIE software. The model is based on the finite element method and was developed in COMSOL Multiphysics. It is used to evaluate the energy release rate in a wooden object due to fluctuations in relative humidity. Exceeding the critical value, which is a characteristic for each material, determines the moment of crack propagation, chosen as a risk indicator. It is a significant modification in comparison to the previous approach known from classical mechanics, in which the risk indicator was the stress level in the material related to critical value of the stress, above which crack grows. Applying fracture mechanics to assess the risk of material damage is more adequate, as it provides information not only about the failure, but also about the size of developed crack and risk to already existing defects in wood.

It was assumed that the cylindrical symmetry is an appropriate approximation for wooden sculptures. The model was optimized in terms of mesh element size and time step size so that the relative humidity change between the borders of each element did not exceed 1% at any point in the simulation. This allowed to ensure a satisfactory accuracy of the model. The energy release rate was calculated on the basis of the J integral equation, widely used in fracture mechanics, adapted to an orthotropic material with properties dependent on relative humidity. The research was carried out for the maximum amplitude of changes in relative humidity from the average level, observed in historic interiors as a result of short-term heating - from 50% to 20%. Using the literature value of the critical energy release rate, the maximum duration of a heating episode safe for massive wooden objects was determined, amounting to 48 hours. Additionally it was shown that drops in relative humidity smaller than 20% are safe for objects independently on duration of heating episode. This information is relevant for conservation recommendations regarding the environmental conditions inside historic churches and other buildings, heated only during religious ceremonies or cultural events.

Projects of EU Structural Funds Programmes

Cross-institutional PhD Studies „Interdisciplinarity for Innovative Medicine” InterDokMed

EU Structural Funds project NCBR POWR.03.02.00-00.I013/16 [2017-2022]
(project leader: Associate Professor Renata Tokarz-Sobieraj)



The Interdisciplinary PhD Project is implemented as part of the Operational Program Knowledge, Education and Development for 2014-2020, action 3.2 **InterDokMed** Doctoral studies, Axis III Higher education for the economy and development. The aim of the project is to increase the quality and effectiveness of education at doctoral studies, through the development of an extended program, its implementation and implementation, as part of InterDokMed's Interdisciplinary for Innovative Medicine.

The project is implemented by a consortium of five scientific units with at least A category and KNOW status. The project coordinator is the Jerzy Haber Institute of Catalysis and Surface Chemistry PAS (ICSC PAS) and partners: Maj Institute of Pharmacology PAS (IP PAS), The Henryk Niewodniczański Institute of Nuclear Physics PAS (INP PAS), Faculty of Chemistry, Jagiellonian University and Faculty of Medicine, Jagiellonian University (JU). The choice of implementing units guarantees the implementation of interdisciplinarity through the implementation of scientific research covering more than one area of knowledge (exact sciences / medical sciences), more than one field (chemical / physical / medical sciences) and several scientific disciplines (physics, chemistry, pharmacology, medicine).

In 2020, 46 doctoral students (out of 50 accepted in two recruitments) continued their education. The study program in 2020 included lectures on "Ethics", "Philosophy of Nature" and "Doctoral Seminar". Due to the epidemic situation, the classes were carried out in a hybrid system: part in stationary mode, part on-line. In 2020, as part of the actions planned in the project, two types of elective classes were organized, thematically addressed to PhD students of interdisciplinary studies. These were: at IKiFP PAN "Workshops on the preparation of interdisciplinary publications and presentations" and WCh UJ lecture "Nanoparticles and reactive oxygen species in medicine - application and detection". PhD students also delivered elective lectures not included in the InterDokMed offer. All PhD students obtained the 3rd year credit.

Doctoral students carry out their research on an ongoing basis, under the supervision of two tutors from two different partner units representing various scientific disciplines. In 2020, doctoral students completed 8 internships abroad, participated in 2 schools / workshops, thematically related to their work. They co-authored 58 publications from the JCR list, 3 book chapters, 10 articles in post-conference materials and 2 popular science articles. They co-authored 34 oral presentations and 31 posters at national and international conferences. 7 PhD students obtained their own research funding projects in external institutions such as the National Science Center (4) and in their own units (3).

InterDokMed PhD students have won many awards, incl. for the best publication, conference speech, they obtained funding for foreign internships at external institutions, conference scholarships and finally scholarships for the best doctoral students in their home units.

In 2020, 8 doctoral students opened the procedure for awarding a doctoral degree, previously 18 people opened a doctoral dissertation.



Unia Europejska
Europejski Fundusz Społeczny



Interdisciplinary Environmental Doctoral Studies "Physical, Chemical and Biophysical Foundations of Modern Technologies and Materials Engineering" (FCB)

Project of Operational Program Knowledge Education Development (POWER) for interdisciplinary doctoral study programs POWR.03.02.00-00-I004/16 [2017-2022]

(*deputy project manager: Anna Micek-Ilnicka DSc. Eng.*)

The project is financed by the Foundation for the Development of the Education System and is a result of a competition announced by The National Centre for Research and Development (NCBiR) in 2017 for interdisciplinary doctoral studies programs. This project is coordinated by the Faculty of Physics and Applied Computer Science (WFiIS) at the AGH University of Science and Technology (AGH) with the participation of the Faculty of Materials Science and Ceramics (WIMiC) at the AGH, the Faculty of Chemistry at Jagiellonian University (WCh UJ), The Henryk Niewodniczański Institute of Nuclear Physics of the Polish Academy of Sciences (IFJ PAN) and Jerzy Haber Institute of Catalysis and Surface Chemistry of the Polish Academy of Sciences (IKiFP PAN).

FCB doctoral studies are interdisciplinary. PhD students are doing research in the field of natural sciences in the discipline of the chemical and physical sciences and in the field of engineering and technical sciences in the discipline of materials science and chemical engineering. Assumptions of this project provided for studying of 75 PhD students. Currently, we educate 74 doctoral students at FCB, including 4 students at the IKiFP PAN.

The FCB study schedule, carried out in the 2019/2020 academic year, included 15 hours of doctoral seminar conducted in the summer semester, from 27/03/2020 groups were conducted via the Skype application. Doctoral students listened to a lecture "Self-organized colloidal systems and Their application in photovoltaics, medical diagnostics, and phototherapy" led by Professor dr hab. Kvetoslava Burda (WFIS AGH). It was completed with an exam.

PhD students soft skills were developed by the participation in on-line course on the Zoom platform, on September 25-27, 2020, titled "Commercialization of scientific research results and developing forms of individual entrepreneurship" conducted by dr. Seweryn Rudnicki (WH, AGH) and in workshop on "Acquiring funding for research projects" carried out by dr. hab. Andrzej Młyniec (WIMiR AGH). In addition, doctoral students within the 30 didactic hours made the instructional movies for WIMiC AGH students in the field of qualitative and quantitative analysis.

PhD students from IKiFP PAN (4 people) published in the academic year 2019/2020 three publications and delivered two lectures. They realized two Opus grants as performers and also one Preludium grant.



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Other International Research Projects

Biocompatible foams and emulsions stabilized by natural surfactants and particles for bio-medical application

Joint research project of the Polish Academy of Sciences and CNR National Research Council of Italy [2020-2022]

(project leaders: Marcel Krzan PhD)

During the project, we wanted to develop technology for generation and application of stable foam and emulsions formulated from mixtures of hypoallergenic, non-toxic biological polymers, mainly “green surfactants”. Such surface thin film could in the close future become the basis of the cosmetic and dermatological composition for the multiple use products. The application of other biologically active particles, like i.e. chitosan, silk fibroin or liposomes will also be carefully studied. Similar multicomponent film layer (created after foam or emulsion injection on the human body) would be the first line of the skin body defence against various pathogens. Thanks for them the skin will be simultaneously protected, lubricated and regenerated. Similar thin surface film (created from our foams or emulsions) could also be used as a pathogen barrier in the food industry as natural preservatives. The same technology may be utilized in the agricultural production in natural green pesticides. The similar application of the technology let us in close future reduce the number of synthetic surfactants incorporated into the natural environment.

During the first year of project emulsification tests were carried out in a system based on saponin as an emulsifier and Migoil MCT oil. The aim was to develop stable emulsion systems for natural triglyceride oil and natural surfactant. The emulsion was produced using the double syringe method, using syringes with a capacity of 5 ml and sets of syringe pumps purchased last year for the project. The stability and other properties of the obtained emulsion systems were studied by rheological and microscopic measurements, including confocal microscopy. In order to better visualize the obtained systems, various fluorescent dyes (rhodamine, coumarin, etc.) were introduced into them, allowing to accurately characterize the morphology of the phases and their changes. In addition, but for the system components, i.e. for saponin aqueous solutions, detailed studies were carried out on changes in surface tension with the concentration of the solution and with time. The surface elasticity of the above-mentioned solutions was also tested.

The obtained results were published in one paper in Coatings journal (IF 2.33). Due to limitations related to the COVID-19 pandemic, the originally 2-years project was extended until end of 2022.

Biocompatible particle-stabilized foams and emulsions for biomedical applications

Joint research project of the Polish Academy of Sciences and the Bulgarian Academy of Sciences cooperation [2018-2021]
(*project leader: Marcel Krzan PhD*)

During the project, we want to develop technology for generation and application of stable foam and emulsions formulated from mixtures of hypoallergenic, non-toxic biological polymers, mainly biosurfactants. The medical impact of the biological foams and emulsions, which could be used as the thin cover film, will be further strengthened by the addition of silver nanoparticles. The application of other biologically active particles, like i.e. chitosan, silk fibroin, liposomes or dendrimers will also be carefully studied. Similar multicomponent film layer (created after foam or emulsion injection on the human body) would be the first line of the skin body defence against various pathogens.

During the third year of the project, measurements of foam formation and foam stability were carried out in a glass column for mixtures of the tested biopolymers with various selected solid particles. Changes in the height of the foam and liquid columns over time were examined automatically in the column, directly from the moment of air dispersion in the solution until the foam phase disappeared. It is assumed that the initial height of the foam fraction characterizes the foaming capacity of the tested solution, i.e. the ability of the tested system to generate foam. In contrast, foam stability is described by the rate at which the foam decays. It has been found that the presence of particles influences the stability of n-dodecyl ethyl arginate foams much more than the foams generated from BSA or methylcellulose. The particles with a diameter below 10 nm significantly increased the durability and height of the LAE foam. Moreover, the obtained results describing the initial heights of the foams were in good agreement with the data obtained on the basis of measurements of changes in dynamic surface tension.

Due to limitations related to the COVID-19 pandemic, the originally 2-years project was extended until end of June 2021.