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Statutory Research

Catalytic Materials and Processes for Sustainable Development

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

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

Aim of research. The research carried out for the systems $Pd/W_xMo_yO_3$ (Pd = 0.5-4 wt%) aimed to examine the activity and stability of the systems under exothermic cycles of reduction and reoxidations in view of their use as an energy source.

Synthesis and characterization of samples. Apart from the Pd/W_xMo_yO₃ composite with Pd loading (0.5, 1 i 4 wt %) also the Pd/MoO₃ and Pd/WO₃ were studied. The W_xMo_yO₃ was synthesized with hydrothermal method (150°C, 2 h) using Na₂WO₄ x 2 H₂O, (NH₄)₆Mo₇O₂₄ 4 H₂O, 30% H₂O₂, HCl followed by calcination at 600°C, 2 h. The obtained material was crystalline (XRD) with morphology (SEM) similar to that of WO₃ oxide (spherical microcrystallities) but quite different from a plate-like MoO₃ morphology. The EDS analysis showed homogeneous distribution of W and Mo elements through the W_xMo_yO₃ resulting in the atomic ration W/Mo = 1.5 (W_{0.6}Mo_{0.4}O₃) determined also by XPS method.

Incorporation of Pd particles (0.5, 1 and 4 wt%) was obtained by impregnation method using acetone solution of Pd(Ac)₂ followed by the reduction with H₂ (250°C, 2 h). This method was also applied for the preparation of Pd/WO₃ samples (0.5 and 1 wt% Pd). The TPR-H₂ measurements for the impregnated samples showed similar reduction profiles for the 1%Pd/W_{0.6}Mo_{0.4}O₃ and 1%Pd/WO₃ quite different form the reduction profile of 1%Pd/MoO₃. The TPR data as well as XPS analysis demonstrated the complete reduction of Pd²⁺ ions in the reduced samples. All the methods, XRD, SEM and EDS confirmed that the morphology, composition (W/Mo=3) and W, Mo distribution was preserved after palladium incorporation.



Fig. 1 SEM micrographs of studied materials

Thermal effects. The tests with gas flow-through microcalorimeter showed that reduction of catalysts produced hydrogen bronzes $H_{1.9}MoO3$ (Q ~100 kJ/mol H_2), $H_{0.30}WO_3$ (Q ~50 kJ/mol H_2) and $H_{0.32}W_{0.6}Mo_{0.4}O_3$ (Q ~80 kJ/mol H_2). These studies included also the cyclic reduction (H_2 5%/N₂ temp. range 25-105°C) and reoxidation (synthetic air, temp. 25°C) processes. In the reduction stage the hydrogen bronzes were formed with evolution of heat. In reoxidation stage, exothermic reoxidation of bronzes proceeded producing water with regeneration of initial oxide. All the prepared Pd/W_{0.6}Mo_{0.4}O₃ catalysts were effective and displayed stable activity. Irrespective of the Pd loading, the average value of H/(W + Mo) in the range 0.31-0.4 was obtained with the heat of hydrogen bronzes formation 80-87 kJ/mol H₂. The hydrogen reduction stage performed at higher temperature (55, 105°C) produced higher values of H/W + Mo (ca. 0.55) Pd/W_{0.6}Mo_{0.4}O₃. This effect was not observed for the WO₃ and MoO₃ based systems.

Summary. The synthesized microcrystalline composite materials $Pd/W_{0.6}Mo_{0.4}O_3$ displayed ability to the hydrogen bronzes formation of stoichiometry similar to that of WO₃ but higher amount of evolved heat. These materials displayed stable activity in series of cyclic reduction-reoxidation processes, observed in 30 cycles for the 1%Pd/W_{0.6}Mo_{0.4}O₃ sample.

Studies on the properties and application of enzymes with application potential

(Professor Tomasz Borowski, Maciej Guzik PhD, Sangita Kachhap PhD, Anna Miłaczewska PhD, Mateusz Tataruch PhD Eng., Professor Maciej Szaleniec, Agnieszka Wojtkiewicz PhD, Justyna Andrys MSc, Anna Kluza MSc, Justyna Prajsnar MSc, Zuzanna Wojdyła MSc)

a) In studies on new 3-ketosteroid dehydrogenases (KstD) from *Mycobacterium bovis*, the KstD enzymes were isolated from *M. bovis* BCG (vaccine strain) and *M. bovis* DNA isolated from a patient. In both cases the enzymes turned out to be the same variant of the known KstD characteristic of *M. tuberculosis*. Protein products turned out to be insoluble and showed no enzymatic activity. New approaches to developing an effective overexpression system are planned.

b) In research focused on the optimization of protein production and purification conditions (Rhlb, two homologues of DODA, EctC, DIOX4, DIOX5, DIOX6), finally in order to search for the conditions of their crystallization, it was possible to develop protocols for the production of *P. somniferum* DIOX, *E. coli* DODA and *B. vulgaris* DODA, wherein the DIOX and *B. vulgaris* DODA were produced as MBP fusion proteins. In all cases, a sufficient amount of pure protein sample was obtained to allow for the attempt to crystallize the proteins. All attempts to obtain the recombinant Rhlb protein in *E. coli* were unsuccessful - despite the successful overexpression in bacteria, it was not possible to obtain the Rhlb protein at the purification stage in any of the variants used (use of chaperone proteins, in combination with MBP protein increasing solubility, use of different strains of *E. coli*).

c) Crystallization tests of the studied proteins were successful for the following proteins: *E. coli* DODA, *B. vulgaris* DODA and *P. somniferum* CODM. For some of the crystals obtained, diffraction data sets have already been collected at the BESY II and PETRA III synchrotron beam lines, and for the remaining crystals the data will be collected at the end of March this year. Diffraction data allowed for the solution of crystal structures by the molecular replacement method, and the obtained models are now being refined. In the case of the DODA proteins from *E. coli* and *B. vulgaris*, further work is underway to co-crystallize the proteins in a complex with their ligands.

d) The aim of the computational research was to determine the structure of enzyme-substrate complexes and mechanisms of cyclization reactions catalyzed by EctC and CAS enzymes. The molecular dynamics simulations for enzyme-substrate complexes provided insight into possible low-energy conformations of the substrate and protein residues interacting with it. In the case of EctC, two models are investigated, differing in the geometry of the active site and the way iron interacts with ligands: in the first model, based on the available literature, iron is 4-coordinated, has a tetrahedral geometry; in the second model, iron is 6-coordinate and has octahedral geometry. The calculations so far suggest that model 1 should be rejected due to the high energy barrier accompanying the substrate cyclization. Research on the second model is ongoing. Two possible positions of the substrate (proclavamate) relative to the active site have been identified for CAS. In the first, the atoms between which the new bond is formed are presented to the active site, according to the typical predicted ODD-catalyzed cyclization mechanism. The second, on the other hand, requires the reorientation of the substrate molecule. The two complexes are the starting point for further modeling by QM/MM methods to determine if one of the positions is more favorable to the reaction and to describe the role of substrate reorientation in the selectivity of the reaction.

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

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

The work carried out concerned the synthesis, structural and physicochemical studies of new organic-inorganic peroxomolybdates and polyoxomolybdates. The most important research directions and the obtained results are briefly summarized below.

- 1) Several syntheses were carried out with the use of several isomers of cyclohexanamine. Syntheses under reflux and autoclaves were used. Tests were carried out for solutions acidified with hydrochloric or acetic acid. The obtained solid phases were examined 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 oxodiperoxo compounds with sodium cations were obtained. Compounds with potassium and ammonium cations were synthesized for the purposes of physicochemical, mainly catalytic and pharmacological, research.
- 3) The crystal structures of the 2,6-dicarboxypyridine oxodiperoxomolybdate (1) and 3,5-dicarboxypyridine oxodiperoxomolybdate (2) were solved and refined. The crystallochemical data and drawings of the asymmetric units are presented below.
- 4) For selected compounds from the polyoxo groups and peroxomolybateates, tests of catalytic oxidation of cyclic hydrocarbons and cyclohexanone in the Baeyer-Villiger (BV) reaction were carried out. In the BV reaction, a very high selectivity of some carboxypyridine peroxo compounds to ε-caprolactone was observed (> 90%).
- 5) Selected oxodiperoxo- compounds were tested at the *Collegium Medicum* (Jagiellonian University) as part of pharmacological tests on tumor cell lines. The best compounds show activity comparable to the activity of cis-platinum used in practical therapies in medicine.

The figures below shows the asymmetric units for compounds (1) and (2), respectively. Magenta, black, blue and pink spheres denote Mo, C, N and O, large yellow spheres denote Na atoms.



Crystallochemical data:

(1) $Na_2[MoO(O_2)_2C_5H_3NO(COO)(COOH)]_2.2H_2O$,

SG P-1, a,b,c, $\alpha\beta\gamma$; 12.2307(7), 12.2653(7), 8.9485(6), 97.167(4), 101.840(3) , 87.893(5), V = 1303.48(14)Å^3, Z=4.

(2) Na[MoO(O₂)₂C₅H₄NO(COO)].2H₂O, SG P 2(1)/c, a,b,c, $\alpha\beta\gamma$; 11.6753(2), 13.4514(3), 7.2919(2), 90.0, 93.602(2), 90.0, V = 1142.92(4)Å³, Z=4.

Studies of structural effects and influence of suport 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-Mikołajczyk 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.)

The studies were aimed at finding a correlation between the structure of catalysts containing copper as the active phase and their reactivity in alcohol conversion processes. In 2021 the focus was put on two types of supported oxides: 1) the one in which Cu phase was deposited on zeolite-based supports and 2) the second in which copper phase was deposited on TiO_2 and accompanied with $H_3PW_{12}O_{40}$ heteropolyacid (HPA).

Ad 1) The Y zeolite (Si/Al = 2.5) was selected as support for the copper phase which was introduced via ion exchange and wet impregnation methods. The redox properties of the samples were studied by H_2 TPR and TPO techniques, while Cu speciation was probed with FT-IR spectroscopy with CO and NO as probe molecules. It was found that copper deposited on Y zeolite is present as Cu(I) in S_{II}, S_{II*} sites, and as Cu(II) in S_{II}, S_{II*}, and S_{III} sites. The H₂ TPR and TPO studies showed that the reducibility of copper depends on its effective charge, resulting from the interaction with the support (oxygen atoms from zeolite and/or oxygen atoms from the Cu_xO oxide phase). The more positive copper cations are, their reduction is easier, the lower their charge is, the more electrodonor they are in the oxidation process.

Ad 2) As the support, two types of TiO₂ were used: P25 (hydrophilic) and T805 (hydrophobic). The copper phase was introduced via wet impregnation and capillary impregnation methods and the samples were heated at 150 °C (Cu@TiO₂(150)) and at 400 °C (Cu@TiO₂(400)). As the next step, the H₃PW₁₂O₄₀ heteropolyacid was introduced via wet impregnation. The Cu@TiO₂@HPW catalysts were characterised by a set of physico-chemical methods: XRD, SEM, EDS, XRF, FTIR, porosity and surface area by BET, as acidity by TPD NH₃. The XRD analysis indicated the presence of copper salts in Cu@TiO₂(150)@HPW, and the crystalline CuO phase in samples Cu@TiO₂(400)@HPW. In order to determine copper oxidation state, x-ray absorption spectroscopy (XAS) method was used. The experiments were done in the Solaris National Synchrotron Radiation Centre using PEEM/XAS end-line. The partial fluorescence yield (PFY) detection was employed providing signal from the bukl of the samples. The studies showed that the surfaces of the samples with 5% of Cu contains both Cu(II0 and Cu(I). The catalytic activity of the samples was tested in dehydration of n-butanol in the gas phase at 120-220 °C. As compared to the reference systems (HPW@P25 and HPW@T805) the introduction of copper results in the increase of reaction selectivity towards butanal formation and increase of selectivity to trans-2-butene at a cost of cis-2-butene. The application of hydrophobic form of TiO₂ as well as the presence of copper as CuO (in the Cu@TiO₂(400)@HPW sample calcined at 400 °C) enabled for the synthesis of materials of high catalytic activity. The results of the TPD NH₃ measurements correlated with the catalytic test data showed that the medium acid centers are decisive for the catalytic activity. In summary, high catalytic of copper-based systems on TiO₂ is due to the presence of copper in the form of CuO, high concentration of sites of medium acidity, and a facile accessibility of the active centers at the surface.

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)

Solids with basic properties gain rapidly on importance, due their potential for catalytic valorization of biomass or as alkaline adsorbents favoring capture of acidic CO₂ molecules. Talc, 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 talc on the efficiency of alkali activation with 2M NaOH. Prepared catalysts were characterized with XRD, SEM/EDX, N₂ adsorption/desorption at -196°C, AAS, FTIR, and ²⁹Si MAS NMR. Surface basicity was determined by titration with benzoic acid. Catalytic activity was tested in the aldol self-condensation of acetone.

The obtained results showed that grinding combined with alkali activation were efficient tools in shaping the surface basicity of talc derived catalysts and, in consequence their performance in basecatalyzed reaction. Grinding caused destruction of talc lattice manifested by depolymerization of tetrahedral silica sheet and formation of kerolite–like structure (highly disordered variety of talc). Alkali activation affected primarily the Si-O sub-lattice. Its impact was enhanced by previous grinding, as depolymerized species were particularly prone to alkali attack. Alkali activation of ground samples was associated with increase of Mg/Si ratio, formation of Mg(OH)₂ and layered magnesium silicate hydrates (MSH) of mixed T-O and T-O-T character. MSH contributed to increase of the specific surface area and reconstruction of platy morphology. Catalytic activity of talc-derived materials depended strongly on the manner of modification. On the optimized catalyst (ground for 30 min. and treated with NaOH for 20 h at 90°C) the yield of the aldol condensation was more than 50x higher than on the untreated talc. **Physics and Chemistry of Surfaces and Nanostructures**

Determination of the mechanism of protein corona formation on the surface of nanoparticles for the myoglobin/latex system

(Małgorzata Nattich-Rak DSc, Marta Sadowska PhD, Monika Wasilewska PhD, Paulina Żeliszewska PhD, Professor Zbigniew Adamczyk, Magdalena Oćwieja DSc)

Despite the significant importance for stabilization of coronavirus particles, mechanisms of protein corona formation are not sufficiently understood. Therefore, the main objective of this study was to quantitatively describe the adsorption of myoglobin at polymer carrier particles, which leads to corona formation using in situ experimental methods and efficient theoretical modeling. Myoglobin, an essential globular protein responsible for oxygen storage and its transport to muscles. It also serves as an efficient biomarker of acute myocardial infections, cardiac injury and renal failure. Adsorption mechanism of myoglobin molecules at negatively charged polystyrene microparticles was studied using the dynamic light scattering (DLS), the electrophoresis (LDV) and the solution depletion method involving the atomic force microscopy (AFM). The measurements were carried out at pH 3.5 and NaCl concentration of 10⁻² M and 0.15 M. Initially, the stability of myoglobin solutions and the particle suspensions as a function of pH were determined. Afterward, the formation of myoglobin molecule corona was investigated via the direct electrophoretic mobility measurements, which were converted to the zeta potential. The experimental results were quantitatively interpreted in terms of the general electrokinetic model. This approach yielded the myoglobin corona coverage under in situ conditions. It was equal to 0.9 mg m⁻² for the NaCl concentration in the range 0.01 M to 0.15 M and pH 3.5. Subsequently, the electrokinetic properties of the corona were investigated using the electrophoretic mobility measurements for a broad pH range (see Fig. 1). The obtained results confirmed that thorough physicochemical characteristics of myoglobin molecules can be acquired using nM amounts of the protein. It was also argued that this method can be used for performing electrokinetic characteristics of other proteins such as the SARS-Cov-2 spike protein exhibiting, analogously to myoglobin, a positive charge at acidic pHs.



Fig. 1. Dependence of the zeta potential of on pH derived from the LDV measurements for 0.01 M, NaCl: \blacksquare , myoglobin molecules in the bulk, \bullet , the myoglobin/particle corona (the coverage of 0.85 mg m⁻²) \blacktriangle , bare polystyrene particles in the bulk. The lines are fits of experimental data.

Monolayers of plasmonic nanoparticles of controlled structure and tunable electrokinetic properties

(Magdalena Oćwieja DSc, Małgorzata Nattich-Rak DSc, Julia Maciejewska-Prończuk PhD, Marta Sadowska PhD, Lilianna Szyk-Warszyńska PhD, Monika Wasilewska PhD, Paulina Żeliszewska PhD, Katarzyna Kusak Eng. Professor Zbigniew Adamczyk)

The main aim of this study was to develop efficient method for the preparation of mixed layers of gold and platinum nanoparticles with controlled structure, composition and electrokinetic properties. The preparation was optimized based on the processes of sequential deposition of the nanoparticles using their suspensions of fixed ionic strength and pH. The plasmonic nanoparticles were obtained with the use of seed-growth method applying trisodium citrate as a shape-directing and stabilizing agent. It was found that the control of: a) weigh ratio of nucleating seed to the metal precursor, b) concentration of trisodium citrate, c) the number of cycles of the reduction process one can obtain stable gold and platinum nanoparticles of an average size ranging from 3 to 150 nm. Based on micrographs recorded with the use of transmission electron microscopy (TEM) it was determined that the nanoparticles were characterized by quasi-spherical shape and narrow size distribution (PdI< 0.25). The dynamic light scattering (DLS) measurements showed that the nanoparticles dispersed in aqueous solutions were highly stable for pH > 3.5 and ionic strength < 0.03 M. It was also established that the nanoparticles exhibited negative zeta potential which grew with an increase of ionic strength and pH.

The electrostatically-driven deposition of plasmonic nanoparticles at the surfaces of mica and silica modified by poly(allylamine hydrochloride) (PAH) was carried out under diffusion and convection transport conditions. The kinetics of nanoparticle deposition and the processes of monoand bimetallic layer formation were determined with the use of gravimetric measurements conducted using quartz crystal microbalance (QCM). Moreover, the layers were investigated using atomic force microscopy (AFM) and scanning electron microscopy (SEM). It was found that the maximum coverage of monometallic nanoparticle monolayers increases with an increase of ionic strength at pH range 5.5 < pH < 6.2 for each type of plasmonic nanoparticles. The maximum coverage of monometallic monolayers equal to 30% was obtained at ionic strength of 10-2 M.

It was shown that by applying the sequential deposition of plasmonic nanoparticles from the suspensions of increasing ionic strength one can prepare stable bimetallic nanoparticle monolayers of controlled composition, morphology and coverage. The results indicate also that the sequential deposition of plasmonic nanoparticles of diverse sizes conducted under controlled ionic strength enables to prepare bimetallic monolayers of maximum coverage higher than the coverage of monometallic monolayers formed under the same conditions of ionic strength and pH.

The plasmonic nanoparticles dispersed in water suspensions and deposited in the form of monolayers were applied for the detection of erlotynib which belongs to the selective EGFR kinase inhibitors used for the treatment of lung and pancreatic cancer. The measurements were conducted by surface enhanced Raman spectroscopy (SERS) and resonant surface-enhanced infrared spectroscopy (SEIRA). Based on recorded SERS spectra it was found that the aromatic phenylacetylene ring of erlotynib is vertically oriented in respect to the surface of the gold nanoparticles. This functional group binds most strongly to the substrate via C=C bonding. It was also found that the phenylacetylene moiety is not involved in the interaction of the drug with the surface of platinum nanoparticles. The visible enhancements of the bands derived from the aromatic ring in the SEIRA spectra and the increase in their intensity indicated the close position and perpendicular orientation of the ring in relation to the surface of the platinum nanoparticles. Thereby, it was proved that bimetallic monolayers composed from two types of plasmonic nanoparticles show promising application potential as modern substrates for spectroscopic studies.

Physicochemical and mechanical properties of "bio" systems Physicochemical and mechanical properties of biosystems

(Aneta Michna Dsc, Maria Morga PhD, Agata Pomorska PhD, Agnieszka Kurek MSc, Jakub Barbasz DSc Eng., Piotr Batys DSc, Leszek Krzemień PhD, Dawid Lupa PhD)

The aim of the task was to study bio-systems in terms of their physicochemical (such as charge, shape and size distribution of molecules and particles as a function of environmental parameters) and mechanical (such as Young's modulus, structure of spatial packing) properties.

This task was an extension of the 2020 statutory task with the participation of members of the newly formed group "nano- and microscale systems".

Continuing our 2020 statutory research, we expanded a finite element model of indentation measurements using atomic force microscopy. In this regard, we developed a new model based on the filling of the cell interior by a viscoelastic fluid, which provides a better approximation than commonly used models that do not take into account energy dispersion because of the frictional forces. As in the previous year, the model took into account the complex structure of the animal cell, but also allowed us to simulate more complex plant cells - this was developed in 2021. The major advantage of the proposed model is its simplicity. It is easy to use, comparable to the Hertz model, to extract cell properties from the indentation measurements, with the additional consideration of the internal structure of the cell.

We prepared two publications on this topic during 2021, one is currently under consideration and the second one is being prepared for submission.

We also worked on the behaviour of macro ions depending on the parameters of the environment.

We have also performed studies on the structure of substrates for the deposition of proteins and polyelectrolytes (including DNA) taking into account simulation parameters representing real experimental systems rather than stoichiometric values derived from approximations that do not take into account the small volume of the simulation box. The results of simulations were confirmed experimentally and an article summarizing the obtained results is currently under preparation.

In 2021 we also studied the applicability of diffusion models used conventionally to describe biological systems to model macroscopic phenomena. In the field of this sub-activity, we published a paper "Physics of free climbing" in the well-established journal Phys Rev E (140 Ministerial points).

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., Bohdana Blyzniuk MSc, Natalia Kwiatek MSc)

Statutory activity by the "Surface Nanostructures" group concerned metallic and oxide nanostructures, in particular grown by molecular beam epitaxy, and their chemical, structural, electronic, magnetic and functional properties.

Fe(001) epitaxial films are used in our group as a model ferromagnetic system in which quantum well states formed by d electrons in are responsible for many fundamental phenomena that oscillate with layer thickness, such as magnetic anisotropy or magnetoresistance. Using momentum microscopy and angle-resolved photoemission, we mapped in unprecedented detail the quantized electronic states of Fe(001) in a broad photon energy range starting from soft x-ray (160 eV) down to vacuum ultraviolet (8.4 eV). We demonstrated electronic states that can be responsible for the oscillations of the magnetic anisotropy in Fe(001) thin films with periods of about 5 and 9 monolayers. We also observed magnetization-dependent spin-orbit gaps with the symmetry lower than the bulk symmetry.

We also studied in-plane current induced magnetization switching in model epitaxial Au(001)/Fe(001) bilayers grown on MgO(001) using the planar Hall effect combined with magnetooptical Kerr effect (MOKE) microscopy. We showed reproducible electrical switching of the magnetization between multiple stable states that correspond to different arrangements of magnetic domains with magnetization direction along one of the in-plane easy magnetization axes of the Fe(001) film. We found that the physical mechanism of the current-induced magnetization switching of the Au/Fe/MgO(001) system at room temperature can be fully explained by the Oersted field, which is generated by the charge current flowing mostly through the Au layer.

Using low energy electron microscopy (LEEM) we monitored in real time and at the micrometer scale oxidation of iron on Pt(111). We studied the role an epitaxial of graphene layer in blocking iron segregation and iron oxides formation under oxidative conditions.

Another type of carbon-based nanostructures were multiwall carbon nanotubes (MWCNTs) including iron nanoparticles. We studied the effects of combined chemical and mechanical (grinding) functionalization on the magnetic properties. Grinding revealed a unique impact of -COOH groups (compared to -COONH4 groups) on the magnetism of functionalized MWCNTs and strong dependence of the mill type used (steel or agate).

We continued studies of the influence of ion irradiation on the magnetic properties of epitaxial cobalt films sandwiched between heavy metals, Au and Pt. Polar magnetooptical Kerr effect magnetometry and Brillouin light scattering spectrometry were used to measure the magnetic anisotropy and the strength of Dzyaloshinskii-Moriya interaction (DMI). Our results, showing relations between the ion fluence and magnetic properties can be used for the adjustment of DMI interaction in the manufacturing of magnonic nano-devices.

Several tasks were related to XPS studies aimed at determination of the chemical and oxidation state of catalytic materials., such as cerium and iron doped titania, silica supported molybdenium and tungsten bronzes and others.

Finally, the group is involve in operation of two beamlines at the synchrotron Solaris. In this year the PEEM microscope was transferred to the undulator beamline DEMETER, which will significantly improve the performance of the instrument. Nevertheless, despite intensive experimental works during the commissioning phase, several synchrotron PEEM and XAS experiment were completed, including for example extensive studies of thermoelectric composites (in cooperation of Bulgarian Academy of Science).

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

(Professor Tomasz Pańczyk, Professor Wojciech Płaziński, Agnieszka Brzyska PhD, Paweł Wolski PhD)

The conducted research and their results concerned the three research problems: (i) the interaction of molecules of β -D-glucuronic acid (GlcA), N-acetyl- β -D-glucosamine (GlcNAc), their dimers and hyaluronic acid (HA) with the surface of single-walled carbon nanotubes (CNT); (ii) the analysis of the mechanism of GlcA and GlcNAc interactions with the surface of carbon nanotubes at the quantum-chemical level and (iii) the study of the interactions of a molecule containing daunosamine in its skeleton with the surface of carbon quantum dots, CQD.

Adsorption of hydrophilic molecules on the surface of carbon nanotubes is one of the most widely used methods to improve the hydrophilicity and biodistribution of inherently highly hydrophobic carbon nanomaterials. Studies of the adsorption of GlcA, GlcNAc, their dimers and HA molecules showed that these molecules have the ability to bind to the CNT surface, and they show significant differences in terms of the geometry and energetics of this process. Studies based on simulations by the classical molecular dynamics method with the use of the GLYCAM/AMBER force field have shown that in the group of monosaccharides, the GlcNAc molecule is the most strongly bound to the CNT surface, and regardless of the degree of surface coverage, it always adsorbs with the same side in reference to the CNT surface. It also creates the most uniform adsorption layer in the range of large surface coverages. The GlcA molecule binds to the CNT surface weaker but also shows a preferential orientation to the surface (opposite to the GlcNAc molecule). It was found that the adsorption of the GlcA molecule is additionally stabilized by the presence of an energy (or entropy) barrier towards its desorption. GlcA-GlcNAc and GlcNAc-GlcA dimers showed a greater tendency to stably adsorb on the CNT surface, but at the same time displayed an inclination to group into larger assemblies forming local multilayers. On the other hand, the HA molecule forms a helical structure and only in this case significant deformations of the glycosidic linkages were found. Quantumchemical calculations confirmed the fundamental conclusions concerning the energetics and geometry of GlcA and GlcNAc molecules on the CNT surface obtained with the use of the classical force field. Moreover, a confirmation of the significant role of CH- π interactions in the overall energy balance of binding these monosaccharides to the surface of carbon nanotubes was obtained.

An important molecule containing the daunosamine aminosaccharide in its structure is doxorubicin (DOX) - a well-known anti-cancer drug. The interaction of DOX with the surface of carbon quantum dots is important for the use of CQD as drug carriers. A CQD model was developed containing various groups on the surface that may undergo protonation/deprotonation depending on the pH of the environment. The CQD core was modeled using the manybody potential and the DOX and functional groups using the GAFF force field. The obtained results indicate that electrostatic interactions, together with hydrogen bonding, play a major role in the processes of DOX binding and release. At neutral pH, the CQD-DOX interaction becomes stronger as the number of oxygen-containing groups on the sidewalls of CQD increases, while at acidic pH the trend is reversed. The observed effects were attributed to the more favorable orientation of the DOX molecule on the CQD surface. At neutral pH, as the density of oxygen-containing groups increases, DOX molecules bind mainly on the sidewall of the CQD and more selectively interact with the functional groups of the carrier through their polar functional groups, thus resulting in stronger electrostatic CQD-DOX interactions.

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

(Associate Professor Paweł Weroński, Karolina Pałka MSc)

The power spectral density (PSD) of layer height function of deposited particles is an important statistical function for a quick and precise description of the layer roughness. In the so far PSD research for monolayers of spherical particles, we have limited ourselves to relatively large systems with circular symmetry and radius $R_s >> a$, where *a* is the particle radius. The aim of our recent research was to theoretically determine the quantitative relationship between the radius of analyzed circular area and the error in the PSD calculations of this area, resulting from neglecting the last term in the analytical equation of this function. The research included computer simulations of adsorption of monodisperse spherical particles with different coverage and radius of adsorption area, according to the random sequential adsorption model. We have determined the discrete PSD function for each system. We also numerically calculated the correction represented by the last term of the equation for PSD and the relative error resulting from neglecting this term, as a function of wave number *q*. The results of our calculations for the radius $R_s = 10a$ and $R_s = 400a / 9$ are presented in Fig. 1.



Fig. 1. Relative error resulting from neglecting the PSD component of the particle monolayer, depending on the size of the analyzed area, as a function of wavenumber q. The left and right graphs show the calculation results for area radius $R_s = 10a$ and $R_s = 400a / 9$, respectively.

Our results indicate that the PSD term dependent on the size of analyzed area has a significant impact on the PSD of particle monolayer. The effect of this term decreases with the increase in the radius of the area. Despite the observed dependence, the influence of area size on the fitting monolayer parameters is negligible even for the area with radius $R_s = 10a$. Our research suggests that particle deformation at the edge of analyzed area is of greater importance.

"Functional multilayer polyelectrolyte films"

(Professor Piotr Warszyński, Marta Kolasińska-Sojka DSc)

The ability to predict and control the formation of lipid bilayers on nanostructured supports represents an important aspect for the investigations of biomembranes and their inherent properties. The formation of complete supported lipid bilayers by vesicle adsorption and rupture was studied in relation to deposition conditions of vesicles and underlying cushion formed from various polyelectrolytes. Lipid vesicles were formed from zwitterionic 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (POPC) and negatively charged 1-palmitoyl-2oleoyl-sn-glycero-3-phosphoethanolamine (POPE) in phosphate buffer of various pH with or without NaCl addition. Polyelectrolyte multilayer films (PEM) were constructed by sequential adsorption of alternately charged polyelectrolytes from their solutions - layer-by-layer deposition (LBL). The mechanism of the formation of supported lipid bilayer on polyelectrolyte films was studied by quartz crystal microbalance with dissipation monitoring (QCM-D) and atomic force microscopy (AFM). OCM-D allowed following the adsorption kinetics while AFM measurements verified the morphology of lipid vesicles and isolated bilayer patches on the PEM cushions providing local topological images in terms of lateral organization. Additionally, polyelectrolyte cushions were characterized with ellipsometry to determine thickness and swelling properties, and their roughness was measured using AFM. It has been demonstrated that the pH value and an addition of NaCl in the buffer solution as well as the type of the polyelectrolyte cushion influenced the kinetics of bilayer formation and the quality of formed bilayer patches.



Fig 1. Frequency shift upon lipid bilayer deposition on PEI film. Dependence on pH value of PBS buffer solution (a) without and (b) addition of 0.15 M NaCl; buffer pH adjusted to three different values: 7.5, 8, and 9.5.

We found that the production of POPC/POPE supported lipid bilayers was affected by the pH value and NaCl addition to PBS buffer solution. The optimal values allowing liposomes' rupture followed by their fusion and formation of lipid bilayer were pH = 9.5 and 0.15 M NaCl in PBS buffer. We found that the type of underlying polyelectrolyte cushion played a crucial role in bilayer formation. The interaction between phospholipid vesicles and polymer support can strongly affect the quality of the final SLB. It had an impact both on the kinetics and the quality of obtained bilayers. Depending on the film underneath, lipid structures on the surface were from homogeneous bilayers for PEI(PGA/PLLpH = 10)₃, bilayers with a fraction of intact liposomes for PEI monolayer as well as patches of lipid bilayers and multilayers for PEI(PSS/PDADMAC)₃ and PEI(PSS/PEI)₃.

Theranostic nanocarriers of anticancer drugs

(Associate Professor Krzysztof Szczepanowicz, Anna Pajor-Świerzy PhD)

Despite very significant progress in cancer research, many people still die due to the lack of effective methods of diagnosing and treating cancer. Late diagnosis and multi-drug resistance of neoplastic cells is a serious clinical problem. The main problem is the low selectivity of chemotherapeutic agents, which mainly results from systemic administration as well as poor solubility of chemotherapeutics in an aqueous medium (there are mainly hydrophobic substances). Therefore, it seems reasonable to use carriers of anti-cancer drugs in order to improve the biodistribution of therapeutic substances in the system, and thus increase their therapeutic index. Nanotechnology creates new perspectives, as it enables the transport of drugs to the target, and moreover, nano-drug preparations may have unique pharmacokinetic but also pharmacodynamic properties.

In 2021, we were focused on the development of novel method of the preparation theranostic nanocarriers for targeted anticancer therapy. A selected anticancer drug (5-Fluorouracil) was encapsulated into mulilayered core@shell nanocarriers formed with poly-L-lysine (PLL), poly-L-glutamic acid (PGA) and pegylated-PGA (PGA-g-PEG). The theranostic nanocarriers were formed by layer-by-layer method and saturation techniques. The size of prepared nanocarriers ranged between 80-200 nm. Biocompatibility of our nanocarriers as well as activity of the encapsulated drug were confirmed by MTT tests. Moreover, the ability to the real-time observation of developed nanocarriers and drug accumulation inside the target was confirmed by fluorine magnetic resonance imaging (¹⁹F-MRI).



Figure 1. The size distribution of 5-Fluorouracil nanocarriers.

Elaboration of experimental set-up for examination of interfacial phenomena at fluid interfaces under static conditions

(Georgi Gochev PhD, Professor Piotr Warszyński, Dominik Kosior PhD, Associate Professor Jan Zawała)

The aim of the statutory task was to elaborate and build an experimental set-up for examination of thin liquid layers (films) in Scheludko-Exerowa cell, in order to determine the interfacial phenomena at liquid film interfaces under static conditions. Elaboration of a new methodology will allow for determination of properties of liquid films formed between liquid/gas interfaces in solutions of typical surfactants, polymers/biopolymers, proteins and nanoparticles, in relation to stability of real dispersed systems. Visual observations of the liquid film and interferometric measurements will allow for determination of disjoining pressure, which is a measure of specific intermolecular interactions within the thin liquid layers. In addition such important parameters as kinetics of drainage of liquid films and their stability can be also determined.

In the reporting period the microscope, being already available at Jerzy Haber Institute of Catalysis and Surface Chemistry PAS, was upgraded by additional equipment, namely: environmental chamber, digital camera and thermostat. The environmental (thermostatic) chamber was designed and elaborated in cooperation with professional external company. To test the elaborating methodology, precisely designed Scheludko-Exerowa glass cells were used. By applying the control pressure to the cell it was possible to create the liquid (foam) film of specific radius, which was formed between two liquid/gas interfaces. Preliminary observations of thin liquid films were performed in n-octanol and n-dodecyltrimethyl ammonium bromide solutions of different concentration and their 1:1 mixtures, in order to determine the kinetics of drainage of films to socalled critical thickness of rupture (i.e. liquid films lifetimes). Systematic studies allow determining the synergistic effect, previously observed in our laboratory and described in recent papers for experiments under dynamic conditions in two-phase and three-phase systems. It was found that the minimum (threshold) concentration, ensuring the longer liquid film lifetime (ca. 180 s) in onecomponent solutions was significantly higher (by order of magnitude) comparing to the mixed n-octanol/C12TAB solutions (see Fig. 1). Moreover, qualitative analysis of liquid films photos, taken during the experiments by the digital camera revealed that critical thickness of rupture of the films are different, depending on the solution composition, what indicates different liquid films drainage kinetics.

In the next step, the elaborated set-up will be modified and adjusted for direct determination of thicknesses of the liquid films by means of interferometry.



Fig. 1. Scheme of the thermostatic chamber for measurements of kinetics of drainage of liquid film under static conditions (left) and results of measurements of liquid films lifetime in solutions of n-octanol, C12TAB, as well as their mixtures.

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

(Michał Mosiałek DSc, Dmitry S. Kharitonov PhD, Grzegorz Mordarski PhD Eng., Małgorzata Zimowska PhD)

Mixed oxides NdBaCoCuO_{5+ δ} (NBCC1), NdBaCuFe_{0.5}Co_{0.5}O_{5+ δ} (NBFCC), NdBaCo_{1.5}Cu_{0.5}O_{5+ δ} (NBCC2), and NdBaFeCoO_{5+ δ} (NBFC) were synthetized by the solid-state reactions and examined as potential cathode materials for solid oxide fuel cells (SOFCs). Dense gastight sinters of Ce_{0.8}Sm_{0.2}O_{1.9} (SDC) in the shape of a cylinder with a diameter of 20 mm and a height of 1 mm cut in half were used as the electrolytes.

The powders were grated with an organic carrier in an agate mortar to obtain pastes, which were screen-printed onto the SDC surface and then sintered to obtain electrodes.

After sintering, the morphology of cathodes surface and their cross-sections were investigated using the JEOL JSM-7500F Field Emission Scanning Electron Microscope. The electrochemical tests were carried out using a Gamry 300 series potentiostat/galvanostat/ZRA in mixtures of oxygen and argon at successively changing partial pressure of oxygen, applied potentials, and temperatures. The electrochemical impedance spectroscopy (EIS) spectra were fitted with the software MINUIT using a complex nonlinear regression procedure.

Obtained materials crystallized within the P4/mmm symmetry. The results demonstrate that all prepared materials are chemically and thermally compatible with SDC electrolyte. The lowest values of thermal expansion coefficient (17.4 and $17.7 \times 10^{-6} \text{ K}^{-1}$) were observed for NBFCC and NBCC2 materials, respectively. These materials also possessed the highest electrical conductivity.

The prepared electrodes exhibited porous microstructure with different surface morphologies (Fig. 1). The grain size decreased with decreasing iron content in the examined cathode material. EIS measurements in a gas mixture containing 20 vol.% of oxygen at successively changing temperatures from 800 to 500 °C with a measurement step of 25°C allowed the calculation of the activation energy of the reciprocal of the polarization resistance for NBCC1, NBFCC, NBCC2, and NBFC electrodes are 1.26, 1.76, 1.41, and 1.31 eV, respectively.

Analysis of the electrochemical experiments of the synthesized materials in oxygen-argon mixtures revealed that average oxygen reduction reaction (ORR) orders at 800 °C in the oxygen partial pressure range from 0.02 to 1 (for NBFCC 0.01–1) are equal to 0.17, 0.20, 0.26, and 0.26 for NBCC1, NBFCC, NBCC2, and NBFC, respectively, whereas at 700 °C they are equal to 0.09, 0.14, 0.30, and 0.19 for NBCC1, NBFCC, NBCC2, and NBFC, respectively.

The NBCC1 cathode material showed high electrical conductivity combined with sufficient oxygen vacancies and the lowest polarization resistance values in ESI tests. Therefore, we distinguished this material as the most effective in catalyzing the ORR reaction in the intermediate temperature (IT) (500–800 °C) range among the studied layered perovskites. All synthesized materials can be recommended as potential cathode materials.



Fig. 1. Microstructure of NBCC1 (a), NFCC2 (b) electrodes – top view

Physicochemical properties of functional nanocarriers based on dendrimers and proteins

(Professor Barbara Jachimska)

Purpose of the task

The aim of the task was to verify the effectiveness of the PAMAM dendrimer system as carrier of oncological drugs. The research was carried out for complexes of poly (amidoamine) (PAMAM) dendrimers with 5-fluorouracil (5FU) and doxorubicin (DOX), drugs used in the treatment of gastrointestinal cancer and breast cancer.

Scientific and practical effects:

The effectiveness of the drug immobilization in the dendrimer structure was monitored using dynamic light scattering (DLS), zeta potential and UV-Vis, SAXS, NMR, FTIR spectroscopy. Spectroscopic methods confirmed the stability of the obtained complex. Release tests revealed a crucial role of environmental conditions (pH, ionic strength) on the drug release kinetics from the carrier structure. Complex activity tests against five cell lines: malignant melanoma (A375), ovarian cancer (MDAH), glioblastoma (SNB-19), prostate cancer (Du-145) and colon adenocarcinoma (HT-29) showed an increase in the effectiveness of the drug through immobilization in the structure dendrimer and the correct operation of the system up to 7 days after application.

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., Marcin Strojecki PhD, Arkadiusz Janas PhD)

As part of the research task, work was carried out on the further development of software for the quantitative assessment of the physical threat to historic buildings due to climatic fluctuations -HERIe. The platform's development plan includes enriching the database of types of historic objects, which so far includes pictures on boards, trapped wooden elements and parchment, with new examples of objects included in museum collections, as well as increasing the limit values of temperature and relative humidity (RH) for which calculations to reflect conditions in museums in other climatic zones.

The introduction of the above-mentioned modifications required considering the applicability of the superposition principle - the basis of HERIe's operations to date - to describe changes in the parameter determining the risk under the influence of climate fluctuations for each of the research problems. In the case of pictures on a board and trapped wooden elements, this parameter is the dimensional response of the object. The principle of superposition allows to perform a Fourier transformation on climatic data and obtain a series of periodic functions for which the calculated responses can be collected and, with the help of the transform, be assembled into a real object response. The principle of superposition can only be applied when the change in the hazard determining parameter depends linearly on the changes in RH.

One of the new types of historical objects to be analyzed is massive wooden objects. In the research on the development of cracks in this type of objects, the rate of energy release, G, was adopted as a parameter determining the risk of damage to the cultural object - a wooden sculpture. The critical value for the material, GIc, is the hazard criterion, the exceeding of which results in the increase of the crack depth in the relief. Based on the numerical simulations performed, it was shown that for each discrete initial crack depth, the maximum achieved G increases with the amplitude of the RH decrease in a non-linear manner.

In the case of pictures on a board, the loss of the linear dependence of the dimensional response of the object to RH fluctuations is characteristic of the support layer in the pictures on the board, the so-called gesso, under the influence of high temperature and high humidity, which determines the deformation of the object under the mentioned conditions.

After the analysis, it was concluded that the only solution to avoid the existing problem and thus enable users such as conservators, curators and owners of historic objects to estimate the risk for collections is to build a tool for full numerical simulation using the finite element method. Currently, analyzes are continued with the software provider COMSOL Multiphysics in order to choose the form of the license that allows for the development of the HERIe platform in this direction.

As part of the task, a manuscript of the publication was also prepared presenting the results of numerical simulations of the G value achieved for a massive pine wood object in conditions of dynamic climate change "Risk of fracture in massive wooden cultural heritage objects due to dynamic environmental variations" (currently under review).

Development grant

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

ICSC PAS development project (Anna Pajor-Świerzy PhD)

Due to the highest electrical and thermal conductivity, silver has been the most frequently used material for the production of protective coatings of power contacts. However, its disadvantage is the high friction coefficient and significant plasticity, therefore it is easily damaged and deformed, which provides losses in the layers and corrosion of the substrates. These phenomena lead to the destruction of power contacts, which results in an increase in their resistance and operating temperature. These phenomena significantly reduce the "life" of power contacts. Therefore, the main objective of the research project was to develop new materials (inks or pastes) based on metallic nanoparticles (NPs) such as nickel-silver with a core-shell structure, and their use for the preparation of coatings protecting power contacts.

During the research carried out in 2021, the process of obtaining conductive coatings based on metallic nanoparticles was optimized to enhance their conductive properties and/or lower their sintering temperature. The effect of the addition of noble metals NPs (silver or gold) to the previously used pastes based on nickel-silver core-shell nanoparticles was studied. The effect of the concentration of noble metal NPs (silver and gold) as well as their sintering temperature on the conductivity of deposited coatings were investigated. The obtained results, presented in Fig. 1, show that the addition of both types of nanoparticles enhances the conductive properties of coatings compared to layers containing only nickel-silver nanoparticles. The conductivity of the sintered coatings increases with increasing sintering temperature. However, the most promising results were obtained for coatings dopped with silver nanoparticles at a concentration of 0.5%. Regarding the economic point of view, the coating with the most promising conductivity (44% of bulk nickel) was obtained after the sintering at 200 °C, while the layers with the highest conductivity values (61%) were obtained after the sintering process at 300 °C.



Fig. 1. The effect of temperature and concentration of silver (A) and gold (B) nanoparticles on conductive properties of coatings based on nickel-silver core-shell nanoparticles.

FAU-type zeolites as modifiers of ANFO

ICSC PAS development project no. 2/GR/2020 [2021-2023] (*Łukasz Kuterasiński PhD Eng.*)

Explosives are currently widely used both in the military industry and in civil works, including mining, demolition works or macro-leveling. One of the most commonly used explosives (especially in mining) is ANFO (Ammonium Nitrate Fuel Oil) due to a relatively easy and cheap procedure of the production of ANFO as well as its good blasting properties.

ANFO is manufactured by the blending of ammonium nitrate (AN) (oxygen-bearing component) with fuel oil (FO) (combustible component) in an appropriate mass ratio (usually 94.5: 5.5). The ratio of 94.5:5.5 (AN:FO) provides a zero oxygen balance, i.e. no excess or deficiency of oxygen in the balance of the composition of the explosive, which is responsible for the formation of a maximal detonation energy with simultaneous low toxicity of the post-blast fumes (a minimal content of NO_x and CO_x).

So far, in the present works dedicated to ANFO, only results concerning physicochemical and blasting properties of the systems consisting of AN mixed with oils as well as with other organic and inorganic modifiers mainly in the form of dust and inorganic salts were reported. However, the use of additives acting a carrier for inorganic modifiers has not been published. An example of this type of additives could be zeolite due to the presence of, among others, silicon and aluminum in zeolite framework and due to the possibility of introducing a wide range of other elements to this group of minerals.

In the undertaken research, we investigate zeolite Y due to its low silicon to aluminum ratio (2<Si/Al<5), that means that the zeolite with this topology contains a lot of aluminum and therefore is characterized by a high ion exchange capacity in comparison with the majority of zeolites of another structures. Relative high aluminum content (and automatically introduced metals to the zeolite) allows the use of this mineral as a representative support for inorganic ANFO modifiers. The introduced metal into zeolite Y will be magnesium due to a beneficial effect of this element on the blasting properties of ANFO, which has been published in one of our previous works. All investigated physicochemical properties of prepared ANFO-based explosives were compared with the ANFO without zeolite Y (being a reference sample).

Analysis of either X-ray diffraction (XRD) patterns or infrared spectroscopy (IR) spectra revealed no changes in the structure of ANFO as a result of the addition to zeolite Y (both with and without Mg) to bare ANFO material. In turn, the addition of variously prepared zeolite Y influenced slightly thermal properties of such synthesized ANFO explosives.

Much interesting effects were found for the morphology and the status of external surface of the studied ANFO-based materials. Scanning Electron Microscopy (SEM) micrographs showed that the modification of ANFO with zeolite Y caused the appearance of numerous grains of irregular shapes and size ca 1 μ m coming from zeolite phase. Similar conclusions were drawn from Atomic Force Microscopy (AFM) images, in which the presence of irregular zeolitic crystallites was found. Furthermore, the introduction of zeolite Y to ammonium nitrate resulted in the drop of the surface folding of the investigated ANFO material.

First results taken from blasting tests and the simulation of the detonation properties suggested that the addition of zeolite Y (either in Mg-free or Mg-Y form) had a beneficial effect on the detonation properties of prepared ANFO-type explosives. The application of zeolite Y led to the enhancement of the strength of explosion, higher heat of explosion and higher velocity of detonation.

"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)

a) In studies on new 3-ketosteroid dehydrogenases (KstD) from *Mycobacterium bovis*, the KstD enzymes were isolated from *M. bovis* BCG (vaccine strain) and *M. bovis* DNA isolated from a patient. In both cases the enzymes turned out to be the same variant of the known KstD characteristic of *M. tuberculosis*. Protein products turned out to be insoluble and showed no enzymatic activity. New approaches to developing an effective overexpression system are planned.

b) In research focused on the optimization of protein production and purification conditions (Rhlb, two homologues of DODA, EctC, DIOX4, DIOX5, DIOX6), finally in order to search for the conditions of their crystallization, it was possible to develop protocols for the production of *P. somniferum* DIOX, *E. coli* DODA and *B. vulgaris* DODA, wherein the DIOX and *B. vulgaris* DODA were produced as MBP fusion proteins. In all cases, a sufficient amount of pure protein sample was obtained to allow for the attempt to crystallize the proteins. All attempts to obtain the recombinant Rhlb protein in *E. coli* were unsuccessful - despite the successful overexpression in bacteria, it was not possible to obtain the Rhlb protein at the purification stage in any of the variants used (use of chaperone proteins, in combination with MBP protein increasing solubility, use of different strains of *E. coli*).

c) Crystallization tests of the studied proteins were successful for the following proteins: *E. coli* DODA, *B. vulgaris* DODA and *P. somniferum* CODM. For some of the crystals obtained, diffraction data sets have already been collected at the BESY II and PETRA III synchrotron beam lines, and for the remaining crystals the data will be collected at the end of March this year. Diffraction data allowed for the solution of crystal structures by the molecular replacement method, and the obtained models are now being refined. In the case of the DODA proteins from *E. coli* and *B. vulgaris*, further work is underway to co-crystallize the proteins in a complex with their ligands.

d) The aim of the computational research was to determine the structure of enzyme-substrate complexes and mechanisms of cyclization reactions catalyzed by EctC and CAS enzymes. The molecular dynamics simulations for enzyme-substrate complexes provided insight into possible low-energy conformations of the substrate and protein residues interacting with it. In the case of EctC, two models are investigated, differing in the geometry of the active site and the way iron interacts with ligands: in the first model, based on the available literature, iron is 4-coordinated, has a tetrahedral geometry; in the second model, iron is 6-coordinate and has octahedral geometry. The calculations so far suggest that model 1 should be rejected due to the high energy barrier accompanying the substrate cyclization. Research on the second model is ongoing. Two possible positions of the substrate (proclavamate) relative to the active site have been identified for CAS. In the first, the atoms between which the new bond is formed are presented to the active site, according to the typical predicted ODD-catalyzed cyclization mechanism. The second, on the other hand, requires the reorientation of the substrate molecule. The two complexes are the starting point for further modeling by QM/MM methods to determine if one of the positions is more favorable to the reaction and to describe the role of substrate reorientation in the selectivity of the reaction.

Molecular mechanics force field for structure, dynamics and conformation of carbohydrates involving furanoses

"Sonata Bis" research project NCN 2015/18/E/ST4/00234 [2016-2021] (Project leader: Professor Wojciech Plaziński)

Interaction of cyclodextrins with selected drugs

The final stages of the project were devoted to the study on the interaction of the drug (cefuroxime axetil) with a number of non-functionalized or alkylated cyclodextrins. In a series of molecular dynamics simulations, the structures of drug-cyclodextrin complexes were investigated, the mechanism of such complex formation was described and the affinity of the tested cyclodextrins for the drug molecule was estimated (by using enhanced-sampling simulations). The generated structural data were used to calculate the theoretical IR spectra and to interpret the experimental data.

In addition, a chapter was developed to be a part of a scientific monograph on fructans, i.e. polysaccharides composed of fructofuranose units. The data obtained during the earlier stages of the project were used for the preparation of this chapter.

Synergistic effects of mixed biosurfactants solutions in stability of liquid films under dynamic conditions - fundamental research with practical importance in flotation separation process

"Sonata Bis" research project NCN 2020/38/E/ST8/00173 [2021-2025] (*Project leader: Associate professor Jan Zawała*)

The project is related to fundamental research on determination of mechanism of synergistic effects in solutions of chosen mixed flotation reagents. The experiments planned to be carried out are aimed to describe the reasons and conditions of synergism in relations to formation and stability of liquid films formed at various interfaces under dynamic conditions. New amino acid based surfactants and their mixtures with simple non-ionic surface-active substances were chosen for this purpose.

In the reporting period the adsorption behavior of five chosen amino acid surfactants (AASs), having hydrophilic amino acid "head" connected to the twelve carbon atom chain by the amide bond, were chosen. The surfactants were based on alanine (C12-ALA), valine (C12-VAL), leucine (C12-LEU), proline (C12-PRO) and phenylalanine (C12-PHE) amino acids. During experiments, the pKa values of each of the studied surfactants were determined. In addition, systematic determination of influence of solution concentrations on surface tension values was performed, in order to determined so-called adsorption isotherms, presented in Fig. 1. It was showed that studied the AASs behaves in the aqueous phase as weak acids, with pKa values ranging between 4.5 - 5.5, depending on the type of hydrophilic group. Moreover it was found that surface activity of the AASs correlates with degree of amino acid hydrophobicity (polar part) and can be ordered as follows: C12-PRO < C12-ALA < C12-VAL < C12-LEU < C12-PHE. It was revealed that the surface activity of the studied AASs in much higher than cationic surfactants od similar length of carbon atom chain. The theoretical description of AASs structure and adsorption performance by means of numerical calculations (including molecular dynamic simulations) allow for determining such important parameters as: surface activity of the surfactant being the measure of the standard free energy of adsorption, limiting surfactant surface concentration of the closely packed monolayer, surface interaction parameter approximating the attractive lateral interaction among the adsorbed surfactant hydrophobic tails or van der Waals volume and surface of hydrophilic head group of surfactants. The results indicates that the AASs can be used as a quite good "green" alternative to the synthetic surfactants - their functional properties are comparable to non-ionic surfactants while, simultaneously, their environmental impact is significantly reduced (due to the fact that the amide bond between aminoacid polar group and C12 hydrophobic chain can be hydrolyzed both in basic and acidic environment)



Fig. 1. Surface tension as a function of solution concentration for five chosen AASs.

"Sonata" Research Projects of the National Science Centre

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 ethanol (EtOH) decomposition reaction was performed for CuZr (CuO/ZrO₂) and CuZrZn (CuO/ZrO₂/ZnO) catalysts modified with Ni and for pure CuO. The reaction progress was monitored by FTIR spectrometer and mass spectrometer (EtOH-TPD).

According to obtained results, it has been stated that ethanol adsorbed on CuO is oxidized to acetaldehyde and water. Since hydrogen was not formed, the dehydrogenation did not take place when reaction was carried out over CuO. In the case of Cu/Zr, acetaldehyde was also formed by the oxidation (together with water), but contrary to CuO some amounts of hydrogen was produced indicating that parallel with oxidation some amount of acetaldehyde is produce via dehydrogenation of ethanol. At temperatures above 513 K, acetaldehyde is further oxidized to acetic acid, and above 583 K acetic acid is transformed to acetone. At higher temperatures organic molecules were oxidized to CO and CO₂. The addition of ZnO to CuO/ZrO₂ lowers the temperature of acetone formation whereas addition of NiO causes that acetaldehyde decomposes to CH_4 and CO.

The DFT calculation was performed in order to investigate the interaction of ethanol molecule with both Cu7 cluster of D5h symmetry and with selected models of Cu7/m-ZrO₂. The calculations were done in Turbomol software. First, the adduct structures of Cu7-EtOH were optimised and ethanol energy adsorption was calculated. The obtained results showed that the most stable adduct is formed when ethanol is bonded via O atom to one of Cu atoms located in the plane of pentagonal five-member ring. The DFT studies on possible ethanol reaction pathway over Cu7-EtOH complex revealed that four main routs are possible: two routs leading to ethanol dehydrogenation to acetaldehyde and two routs leading to ethanol dehydration to ethylene. Among these four chemical routs, the dehydrogenation pathways exhibited the lower energy barrier.

The catalytic experiments of steam reforming of ethanol over Cu/Zr and Cu/Zr/Zn catalysts confirmed that the main carbon-containing product is acetaldehyde. Based on that, it was concluded that hydrogen is formed via dehydrogenation of ethanol over copper-based catalysts. The presence of acetaldehyde in outlet stream is related with the basicity of the synthesised catalysts, which was investigated with CO₂-TPD. On the other hand, the formation of ethylene was not recorded during steam reforming of ethanol, which proves that synthesised catalysts possess low acidity.

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

"Sonata" research project NCN 2018/31/D/ST5/01866 [2019-2023] (*Project leader: Piotr Batys DSc Eng.*)

In order to better understand the polypeptide complexation processes at molecular level and the effect of pH on this process, an extensive theoretical calculation of the complexation of poly-L-lysine (PLL) and polyglutamic acid (PGA) were performed using the molecular dynamics method (MD) at various ionization degrees of molecules. The changes in the hydrogen bonding, conformation, effective charge and secondary structure as a function of pH were analyzed. The results suggest, that the secondary structure of the resulting complex changes upon assembly and depends on the pH. Additionally, it was shown that assembly pH determines the number of intrinsic ion pairs formed between polyelectrolytes. The results were validated experimentally via zeta potential and circular dichroism measurements.

The effect of the assembly pH was also studied for complexes based on model weak polyelectrolytes, poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA). In particular, it was shown how thermal and mechanical properties are affected by the assembly pH. Extensive experimental characteristic, via dynamic mechanical analysis, differential scanning calorimetry, Fourier transform infrared spectroscopy, and proton nuclear magnetic resonance spectroscopy, was complemented with all-atom MD simulations. The results suggest that the relaxation times (τ) of polyelectrolyte complexes at different water contents and pH values collapsed into a single line (see Fig. 1), following the relationship: $ln(\tau) \sim n_i/n_w$, where n_i and n_w are number of intrinsic ion pairs and water molecules, respectively. This result highlights the role of water at the intrinsic ion pair in mediating the relaxation of hydrated complexes. The application of time–temperature–water–pH superpositioning indicated that complexation pH (number of intrinsic ion pairs) affects the material properties but does not change the relaxation mechanism.



Fig. 1. (a) Representative snapshot of a PAH/PAA complex containing 31.7 wt % of water at 20 °C, derived from MD simulations. The backbone and side-chain carbons of polyelectrolytes are shown in cyan, while oxygen and nitrogen atoms are marked in red and blue, respectively. (b) Dynamic mechanical data of PAH/PAA complexes at pH values of 4.5, 5.5, and 7.0. (c) Natural log of relaxation time vs the ratio of the number of intrinsic ion pairs to the number of water molecules for PAH/PAA complexes obtained at pH values of 4.5, 5.5, and 7.0.

Improving the conductivity of printed patterns by optimizing the synthesis process and physicochemical properties of metal nanoparticles.

"Sonata" research project NCN 2020/39/D/ST5/01937 [2021-2024] (*Project leader: Anna Pajor-Świerzy PhD*)

Printed electronics using nanomaterials open up new perspectives for the electronics industry. Until now, due to the highest electrical and thermal conductivity, silver has been the most frequently used material for the production of conductive electronic circuits. However, its disadvantage is high price and tendency to mechanical damage. Accordingly, alternative materials are being desired. In this context, copper, tin, and nickel nanoparticles can be used as substitutes for Ag NPs due to their lower price, better mechanical properties, and high electrical conductivity. However, their disadvantage is their tendency to oxidize under atmospheric conditions. The stability of metallic NPs (Cu, Ni, Sn) regarding the oxidation process can be achieved by the formation of thin protective coatings of noble metals (Ag or Au) on their surface, which results in the preparation of bimetallic particles with a core-shell structure. Therefore, the main goal of the "Sonata" project is to develop a method of synthesis various types of bimetallic core-shell nanoparticles, optimizing their physicochemical properties (size, shape, stability against the oxidation and aggregation process) and then their use in the process of obtaining conductive inks and pastes for producing printed conductive tracks.

During the research carried out in 2021, a method of synthesis of copper nanoparticles as the core of core-shell NPs was developed. Cu nanoparticles with optimal properties were obtained by reducing Cu ions with sodium borohydride as a reducing agent, in the presence of glycolic acid acting complexing agent and polymer (PSS, polystyrene as a a sulfonate) as a stabilizer, which protects nanoparticles against the process of aggregation and sedimentation. The obtained nanoparticles were characterized by a size of about 80 nm and zeta potential of about -40 mV, as shown in Fig. 1A, B, respectively. These nanoparticles show promising properties (size, stability regarding the aggregation process) for their use in the next stage of the synthesis of "coreshell" nanoparticles, i.e. formation of a protective shell. The obtained copper nanoparticles show great potential as the main component of inks or pastes for the production of conductive coatings or circuits by using various printing methods (screen, spray, or ink-jet printing).



Fig. 1. Size (A) and zeta potential (B) distribution of copper nanoparticles obtained in the optimal synthesis conditions.

"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)

The project research focused on ferromagnetic metal/ oxide epitaxial films and heterostructures, which are the starting point for systems with potential spintronic applications, including epitaxial iron oxides with a specific atomic, electronic and magnetic structure, i.e. magnetite (Fe₃O₄) with the orientation (111) and hematite (α -Fe2O3) with (0001) orientation, characterized by the occurrence of periodic modulations of the surface structure, known in the literature as biphase superstructures.

In the last year of the project implementation (2 months), the conducted research was summarized and it was stated that the most important achievements of the project include:

- 1. Obtaining repetitive and homogeneous biphase superstructures on the surface of Fe₃O₄ (111) magnetite and explaining their structure on the atomic scale based on high-resolution STM images and adsorption properties
- 2. Precise control and periodicity, size and density of self-assembled metal nanoparticles (in particular Au, Fe and Co) on bi-Fe₃O₄ surfaces (111)
- 3. Control of distributions of bimetallic Au-Fe nanoparticles on a monocrystalline rutile TiO₂ substrate (110)
- 4. Modelling of reversible oxidation and reduction processes of magnetite-hematite in epitaxial thin-film systems on Pt (111)
- 5. Development of epitaxial iron oxide technology directly on oxide substrates, MgO (001) and MgO (111), or with the use of a metallic Pt buffer layer
- 6. Investigation of the electronic and magnetic structure of boundary layers in epitaxial Co / magnetite and Co / hematite systems
- 7. Characterization of the magnetic properties of an artificial oxide ferromagnetic with FeO stoichiometry stabilized on Pt (111)
- 8. Stabilization of perpendicular anisotropy in a model TMR junction based on Fe / MgO / Fe₃O₄ trilayers (001).
- 9. Electrical switching of the Néel antiferromagnetic vector in epitaxial hematite layers in contact with platinum using a spin orbit torque (SOT).

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 the 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. The developed surface layers will also be tested for bacteriostatic and cytotoxicity properties. In order to achieve this goal, the project conducted research activities related to two thematic areas of the project during 2021:

- The surface properties of a synthetic surfactant called ethyl lauroyl arginate, LEA or Miranet were investigated. LAE is an amino acid-based cationic surfactant with low toxicity and antimicrobial activity. It is widely used as a food preservative and component for food packaging. When stored, LAE decomposes by hydrolysis into surface-active components N α -lauroyl–l-arginine (LAS) or dodecanoic (lauric) acid. We analysed the surface tension isotherm of LAE with standard analytical purity in relation to LAE after prolonged storage. We used quantum mechanical density functional theory (DFT) computations to determine the preferred hydrolysis path and discuss the possibility of forming highly surface-active heterodimers, LAE-dodecanoate anion, or LAE-LAS. We applied molecular dynamics simulations to determine the stability of those dimers linked by electrostatic interactions and hydrogen bonds. We used the adsorption model of surfactant mixtures to describe the experimental surface tension isotherms successfully. The real part surface dilational modulus determined by the oscillation drop method follows a diffusional transport mechanism. However, the nonlinear response of the surface tension could be observed for LAE concentration close to and above Critical Micelle Concentration (CMC). Nonlinearity originates from the presence of micelles and the reorganisation of the interfacial layer.
- In addition, solid surface films based on natural resources starch, chitosan, hyaluronic acid containing additions of graphene, solid particles or generated quantum dots of zinc sulphide and cadmium sulphide were developed. Due to their unique properties resulting from the presence of nanoparticles, the produced films can be used for the development of advanced sensors and biosensors, e.g. for various harmful substances, heavy metals, the growth of microorganisms, and environmental changes in food products.

In 2021 one online poster related to the work carried out in the project at the PtChem 2021 conference was presented. The developed results were published in four ISI / JCR publications issued in 2021. Due to the limitations related to the pandemic, the project was extended until January 2022. After more than four years of the project, 12 ISI / JCR publications have been published, and in the first half of 2022, 3 more publications will be submitted.

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, Sterolibecterium denitrificans, and belongs to the FAD-dependent 3-ketosteroid dehydrogenases. It catalyzed 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 focus on the elucidation of the enzyme's structure together with the characterization of its catalytic properties with theoretical modelling.

The last 6 months of the project enabled consolidation of theoretical modelling with kinetics resulting in the description of the catalytic mechanism of steroid dehydrogenations by KSTD enzymes. In particular, the results of pre-steady state kinetics for KSTD1 and AmcB were analyzed yielding kinetic constants of formation and dissociation of ES complex as well as constants for a chemical step for 17-methyltestosterone dehydrogenation. Furthermore, the experiments demonstrated a lack of pH influence of kinetics of AcmB reduction. The follow-up tests with a stopped-flow technique for AcmB showed, that the kinetic constant for FAD reduction is higher than 500 s⁻¹ which together with results of pH dependence indicates, that in the steady-state experiments it is the enzyme reoxidation that mostly controls the apparent kinetics. Too fast a rate of reduction, unfortunately, prevented the determination of the kinetic isotope effect for FAD reduction. However, it was determined with competition method for pH 6.5 and 8.0 yielding values of KIE 1.21 and 1.28 for C2 substituted and 1.5 and 1.23 for C1 substituted substrates, respectively.

The obtained kinetic results were combined with modelling. The QM:MM MD modelling for AmcB showed, that the enzyme catalyzes dehydrogenation according to the mechanism proposed in the literature i.e., unimolecular elimination with conjugate base (E1cB), even at higher pH. These results are in agreement with the lack of pH optimum below 7.0 in the pre-steady state kinetics of FAD reduction. Furthermore, based on the same model the energy profiles for mutated variants of AcmB were obtained. These results provided information on the role of individual hydrogen bonds in the stabilization of the subsequent reaction steps. The obtained barrier heights correlate with the experimentally measured activities of mutant versions of AcmB. The only exception deviating from the experimental results corresponds to the Y536F mutation for which the largest deviations in geometry were observed compared to the original structure of the enzyme. Finally, it should be noted that the refinement of the structure of AcmB has been completed and it has been shown that the additional "loop" near the entrance to the active site, characteristic for this subclass of KSTD, has in fact α -helical structure.

The obtained results were published in ACS Catalysis and Microbial Cell Factories while the refined structure of AcmB was deposited in PDB (code 7P18).

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.

The tests of the vanadium catalysts which differ by the type of zeolitic support (FAU, BEA, and their hierarchical forms) and the amount of vanadium (1-7 wt%) were tested in the ODH of etane. The catalytic tests were run in a fixed-bed gas flow reactor with a gas chromatograph to detect subtracts and reaction products at a temperature range from 400-500 °C, with varying contact times. The catalysts were ranged according to their activity in ODH of etane (at 500 °C):

• for the FAU-based systems:

 $V_{3.0}FAU_{\text{des}} > V_{6.0}FAU > V_{3.0}FAU > V_{6.0}FAU_{\text{des}} > V_{1.0}FAU > V_{1.0}FAU_{\text{des}}$

• for the BEA-based systems:

 $V_{4.0}SiBEA > V_{7.0}SiBEA > V_{3.0}SiBEA > V_{2.0}SiBEA$

The analysis of the obtained results allowed for the general observations regarding the activity of the studied catalysts in the ODH reactions. The BEA-based catalysts exhibited lower conversions (maximum C_3H_8 conversion of 38.6 % was enregistered for $V_{5.0}SiBEA$) than the FAU-based ones (maximum C_3H_8 conversion of 40.4 % was reached for $V_{6.0}FAU$). The hierarchized systems had higher selectivities than their pristine forms (in T = 450 °C for 5% iso-conversion of propane the selectivity to C_3H_6 was in the range 26.7 – 39.8 % for the V_xSiBEA series, in comparison to 12.7 – 27.6 % for the V_xBEA series; in T = 450 °C for 10% iso-conversion of propane the selectivity to C_3H_6 was in the range 41.2 – 65.0 % for the V_xFAU_{des} series, in comparison to 18.9 – 31.7 % for the V_xFAU series).

Based on the DFT(PBE/def2-TZVP) calculations the propane ODH mechanism was proposed for the most probable models of vanadium active centers present in T2 and T3 positions of the BEA zeolite. The first H atom abstraction is the rate determining step. For the T2 site it is done over the (-SiO)₃-V=O center: the H atom is abstracted by the V=O group, the V-OH is formed, and the step is accompanied by the energy barrier (E_{TS}) of 42.0 kcal/mol. For the T3 site the reaction proceeds over the (-SiO)₄-V-OH center ($E_{TS} = 42.9$ kcal/mol) – the H atom is abstracted by the V-OH group, the H₂O molecule is formed. The second hydrogen abstraction is done with the participation of the oxygen which links the vanadium phase with the zeolite matrix (Si-O-V) and preferentially is done on the other vanadium center than participated in the first H atom abstraction. For the T2 site it is the (-SiO)₃-V=O center, where the energy barrier of the process equals to 19.5 kcal/mol (as compared to 32.3 kcal/mol when H is abstracted by V=O). For the T3 site on the (-SiO)₃-V=O site the activation energy of the second H abstraction equals to 21.6 kcal/mol (the reactivity of the (-SiO)₄-V-OH group in the T3 site is lower in the second reaction stage: E_{TS} equals to 33.3 kcal/mol when the oxygen from the Si-O-V group is involved, while it is equal to 40 kcal/mol when the reaction proceeds on the V-OH group).

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)

To investigate the dependence of selected ions from the Hofmeister series on the structure and properties of polyelectrolyte multilayers is the scientific goal of the project. 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^- , CI^- , Br^- , NO_3^- , CIO_4^- on the formation of PAH/PSS and PDADMAC/PSS multilayer polyelectrolyte films. The ellipsometry was used to study the thickness of the multilayers deposited in the presence of selected basic electrolytes: NaCH₃COO, NaCl, NaBr, NaNO₃, NaClO₄ at ionic strength I = 0.15 M. The results were compared with previously obtained mass from QCM studies.



Fig. 1 Thickness (1a) and mass (1b) of polyelectrolyte films as a function of adsorbed layers for the PDADMAC/PSS systems.

The thickness adsorbed in the case of the PDADMAC/PSS system is bigger than for films with an analogous number of layers but made of PAH/PSS polyelectrolytes, which is consistent with our previous research. In the case of the PDADMAC/PSS multilayers, the better indicated effect of the counterion on the adsorbed film is observed. For 10-layer PDADMAC/PSS systems, the lowest thickness is for a film with Cl⁻ counterion while the highest is for films adsorbed in the presence of NO₃⁻. PAH/PSS films show analogous dependency on counteranions, except that films with ClO₄⁻ 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 1mM K₃Fe(CN)₆ / K₄Fe(CN)₆ in 0.15 M NaCl was 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)

The physicochemical properties of nanocarriers are fundamental parameters in drug delivery system (DDS) design. The conducted research concerned the characteristics of G5.5 PAMAM dendrimers and the formation of complexes with bovine serum albumin (BSA). Measurements of electrophoretic mobility showed that the charge of the dendrimer in the range of pH 3-5 is positive due to the protonation of the tertiary amine groups. Above pH 5, the dendrimer has a negative charge induced by surface carboxyl groups. The isoelectric point for G5.5 occurs at pH 5. The particle size in the low pH range is 3.5 nm, but above pH 7.5 it increases as a result of the protonation of the carboxyl group. The formation of a stable dendrimer-protein complex was monitored by the UVvis method and zeta potential measurements. The presence in the UV-Vis spectrum of the peak at 278 nm, derived from tryptophan in the BSA molecule, confirms the immobilization of protein molecules on the surface of the dendrimer. Moreover, the decrease in surface potential also means that the protein molecules bind to the surface of the dendrimer. The properties and stability of the obtained complexes were monitored under dynamic conditions using the QCM-D method. The complexes were found to adsorb irreversibly to the Au surface, contrary to the dendrimer, which tends to desorb at high pH when negatively charged. No significant differences are observed during the bilayer formation, only the wettability of the surface changes with the change of the outer adsorption layer. The contact angle is lower when the BSA layer is the last layer that is adsorbed on the sensor. CD measurements confirm that the secondary structure of BSA is altered by interaction with G5.5 dendrimers, with the most significant changes being seen with a large excess of dendrimers relative to protein. BSA binds to the G5.5 surface of PAMAM via the positively charged domain III, forming a protein envelope or crown on the carrier surface. This is advantageous for the potential use of the system as a DDS. It inhibits the adsorption of plasma proteins to the dendrimer surface, reduces system toxicity, and prevents rapid clearance from the blood, prolonging circulation time. The biological properties and bioavailability are also improved when a stable protein-dendrimer complex is formed.

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 Zawała*)

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 influence of kinetics of formation of the dynamic adsorption layer at a rising bubble surface on stability of single foam films formed in solutions of BSA (bovine serum albumin), was studied. The systematic profiles of velocities of a rising bubble were determined and compared with those measured in solutions of simple anionic surfactant SDS (sodium dodecyl sulfate). Next, the kinetics of a single bubble coalescence at solutions surface were determined in order to calculate so-called bubble lifetimes (τ), whose values depend on kinetics of drainage of liquid films to the critical thickness of rupture. For both studied surfactants the solution pH was native (not adjusted by base or acid addition). The range of concentration of both surfactants solutions was chosen in such a way to cover all the range of rising bubble velocity variations, i.e. to reflect gradual immobilization of the liquid/gas interface (changes of the hydrodynamic boundary conditions from slip to no-slip). It was found that for both studied compounds, the trends in profiles of the bubble velocities were similar – depending on the solution concentration the velocity was gradually decreased, passing through the maximum. These trends indicated that structure of the DAL is quite similar, independently on the surfactant type. Stability of the liquid films (kinetics of a bubble coalescence), however, was completely different. For SDS solution, the bubble lifetimes were constant and practically independent on the solution concentration (in the studied concentration range) - see Fig. 1. For BSA solutions gradual increase of the bubble lifetime with increasing concentration was revealed. The obtained results suggest that the structure of the DAL at the rising bubble surface in protein solutions can be quite different comparing to this induced in solutions of "classical", simple surfactants. Further experiments, where the evolution of the liquid film thickness in time will be determined, should provide the results helping in verification of this hypothesis.



Fig. 1. Single bubble lifetimes at surface of the BSA and SDS solutions of different concentrations.

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%. By measuring the surface and interfacial tension (water / decane interface) by the drop shape analysis method, we found significant differences depending on the linker used. Hydrophobized polyelectrolytes with an ester linker were characterized by a lower surface activity than ones with an amide linkage. On the basis of the molecular dynamics simulations, we explained that the reason for the observed differences may be hydrophobic domains formed along the polyelectrolyte chain by hydrophobic moieties. In the case of amide linkers, due to intermolecular hydrogen bonds between the amide and carboxyl groups of the maleic acid segments, it is energetically more advantageous to transfer the hydrophobic segments from the interior of the solution to the surfaces than in the case of ester linkers.

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. In the case of adsorption on a solid substrate, we found no significant differences in the dependence of the linkage used between the polyelectrolyte chain and the hydrophobic groups.

Research was also carried out on the use of hydrophobized cationic polyelectrolytes to stabilize the emulsions and on the antibacterial properties of anionic polyelectrolytes functionalized with quaternary amine groups.

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*)

We performed calculations in order to investigate the stabilization effect of the non-canonical structure iM as a result of the interaction with single-walled carbon nanotubes. The results obtained so far in relation to the research on the influence of the spatial structure of the SWCNT on the stability of the iM and the influence of the functional groups attached to the SWCNT did not explain this effect. Therefore, the proton transfer processes from carboxyl groups located in the SWCNT structure to the cytosine triads present in the telomeric fragment of dsDNA were analyzed in detail. The research consisted of two stages; determination of geometric and energetic 'availability' of cytosine triads by carboxyl groups using steered classical molecular dynamics and quantum-chemical investigation of proton transfer processes for systems in which, due to geometric availability, such a process was physically probable. It turned out that the cytosine triads are quite well accessible both for nanotubes with carboxyl groups located at the ends of the SWCNT and on the side walls. For both situations, systems were selected for which the enforced proton transfer analysis was carried out with the use of the EGO (enforced geometry optimization) method. As a result, it was found that the direct proton transfer is not possible in any of the tested systems and the presence of water as a proton carrier or catalyst is necessary.

In the next task, the drug carrier model was analyzed, in which the covalent attachment of the iM to the tips of the SWCNT was used and the ability of the iM to perform reversible changes of the spatial structure was used to control the binding/release of DOX from such a structure. It has been shown that DOX can play a twofold role in the structure of a carrier: it can be an activator and an active molecule. The carrier activation is where DOX molecules intercalate in the iM structure at neutral pH and block other DOX particles inside the nanotube. On the other hand, at acidic pH, DOX molecules are weakly bound to the i-motif structure and undergo spontaneous desorption from the carrier structure. This leads to the unlocking of other DOX molecules encapsulated inside the SWCNT. This effect is very important in the construction of DOX carriers based on the use of iM and it does not require very complex mechanisms of action as proposed in the literature.

In a further step, the effect of DOX intercalation within the iM bundles at neutral pH was used to study the transport and controlled release of another molecule, namely carmustine. This molecule is highly hydrophobic and, at the same time, very unstable in contact with water. The conducted research led to interesting and useful conclusions. Namely, it has been shown that encapulating the carmustine inside the nanotube and introducing a certain amount of DOX as an activator leads to a system in which the access of water to the carmustine molecules can be regulated by the pH of the environment. In addition, it has been shown that as a result of the decay of carmustine, only the real DNA alkylating agent can escape spontaneously from the inside of the nanotube, while the most undesirable component, i.e. the protein carbamylating agent, is retained inside the nanotube. This means that the use of CNTs can lead to significant reduction of side effects in carmustine therapy.

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).

In the reported work two routes enabling the preparation of finely crystalline Mg-Al HT materials were compared: (1) the inverse microemulsion technique, requiring the use of surfactants, and (2) co-precipitation in the presence of starch biotemplate. Both methods yielded HT materials less crystalline than the conventionally co-precipitated reference (Fig. 1). Carbonate, chloride and bromide forms of HT were prepared, examined with X-ray diffraction, scanning electron microscopy/energy dispersive X-ray spectroscopy and infrared spectroscopy, and used as catalysts in the Baeyer–Villiger oxidation of cyclohexanone to ε -caprolactone with a H₂O₂/acetonitrile system. The bromide forms proved significantly less active than the chlorides and carbonates, as they promoted nonselective consumption of H₂O₂. The fine crystalline materials were more active than the more crystalline HT references obtained by conventional co-precipitation. Catalysts prepared by inverse microemulsion were less crystalline and more active than the starch-templated ones, but suffered stronger deactivation in the acidic reaction environment. Alkalization of the reaction medium with NaHCO₃ stabilized the HT materials and increased the ε -caprolactone yield, which became comparable for both types of fine crystalline catalysts. In view of this, the cheaper and easier synthesis based on the use of starch template is the procedure of choice for the preparation of fine crystalline Mg-Al HT catalysts.



Fig. 1. Powder XRD patterns of synthesized carbonate forms of HT.

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*)

Description of the formation and stability of biocompatible macroion films and explaining the mechanisms of the fibroblast growth factor binding to the films are the main goals of the project.

The biocompatible macroions (polysaccharides) such as: carrageenan, chitosan, heparin were thoroughly characterized in bulk. The hydrodynamic diameters, the zeta potentials and the electrokinetic charges of the polysaccharides were determined in various electrolytes and ionic strengths at broad pH range. The dynamic viscosity measurements for dilute carrageenan solutions were carried out. This enabled to determine of its intrinsic viscosity for various ionic strengths. The viscosity attained 50000 for dilute electrolyte solutions compared to the Einstein value for spheres equal to 2.5. It was confirmed that the molecules assumed extended conformations in accordance with theoretical modelling. The theoretical calculations allowed to obtain the chain conformations, the end-to-end distance, the gyration radius and the density of carrageenan molecules.

The kinetics of the carrageenan adsorption/desorption on/from anchoring layers under diffusion- and convection-controlled transport conditions were also investigated.



Fig. 1 The dependence of dissipation shift (ΔD) on frequency changes (ΔFq) determined for the formation of dendrimer (PAMAMD)/ carrageenan (λ -car) (black curve) and polyethyleneimine (bPEI)/ λ -car (blue curve) bilayers, respectively. The arrows show the start of injection of PAMAMD (black), bPEI (blue) and λ -car solution (green). The bulk mass concentration of the macroions was equal to 1 mg L⁻¹, ionic strength of 0.01 M, pH 5.8. Numbers: 1st, 2nd and 3rd indicate stages of bilayer formation process.

The combination of the employed techniques (QCM-D, AFM, OWLS) enabled detailed insights into the mechanism of the polysaccharide adsorption mainly controlled by electrostatic interactions. The results show that the macroion adsorption efficiency is strictly correlated with the value of the final zeta potentials of the anchoring layers, the transport type, and the initial bulk concentration of the macroions. The high hydration (reaching 60%) of the dendrimer, dendrimer/ carrageenan, and polyethyleneimine /carrageenan layers and the low hydration of the carrageenan monolayer were found. For low initial bulk concentrations of carrageenan, their chains tend to adsorb in the "side-on" conformation, whereas for high bulk concentration of the polysaccharide "end-on" conformation is preferred and the adsorbed carrageenan chains formed highly hydrated quasi "polymeric brushes". It was found the dendrimer/ carrageenan bilayers are heavier and more viscous/soft than the one built on the polyethyleneimine layer.

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 $TiO_2/clay$ composites according to a novel design based on the synthetic procedure employing exfoliated organoclays and inverse microemulsion of TiO_2 -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 naoparticles 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 TiO_2 nanoparticles.

Ti pillaring solution from TiCl₄ precursor was used for preparation of inverse Ti-microemulsion, using 1-hexanol as an oil phase and cetyltrimethylammonium bromide as a surfactant. The microemulsion was added to the organomontmorillonite dispersion in 1-hexanol, and neutralized by addition of NaOH or NH₃ (aq). The recovered precipitates were divided into two parts. One was calcined at 600°C straight after synthesis (Ti-IMEC), the other was subjected to additional hydrothermal treatment at 90°C in sealed vessels under autogenic pressure (Ti-IMEC_{hydr}). For comparison, conventionally pillared montmorillonite, referred to as Ti-PILC, was also obtained. The composites were characterized with XRD, SEM/EDS, TG/DSC and N₂ adsorption/desorption isotherms and subjected to photocatalytic experiments of Rhodamine B degradation. In all samples titania component was present as anatase modification, of highest crystallinity in the hydrothermally treated composites obtained by inverse microemulsion method. These samples displayed also the highest activity in the photocatalytic decomposition of Rhodamine B, a model contaminant of water bodies. The observed order of catalytic activity was: Ti-IMEC_{hydr} > Ti-IMEC > Ti-PILC.

Coarse-grained modeling of carbohydrates Conformation of glycosaminoglycans and the MARTINI 3 force field parameterization for polymers of glucose

"Opus" research project NCN 2019/35/B/ST4/01149 [2020-2024] (*Project leader: Associate Professor Wojciech Plaziński*)

The results of a series of simulations aimed at examining the conformation of glycosaminoglycans at the level of accuracy of all-atom simulations and in the context of their building blocks were analyzed. A limited dependence of the glycosidic bond conformation on the type of functionalization (sulfonation or N-acetylation) was found. The topology of the glycosidic bond almost always plays a dominant role in this context. The contribution of hydrogen bonds between the disaccharide units as well as the distortion of the iduronate ring are relatively small. The types of sulfonation patterns with the greatest potential effect on the kinks in the glycosaminoglycan chain were identified. It has been proven that the data generated at the disaccharide level translate well into the properties of longer chains, composed of the same disaccharide units.

In the second stage of the research, the procedure of parameterization of sugars at the coarsegrained level was initiated. A newly developed set of non-bonded parameters MARTINI 3 was used, ensuring compatibility with numerous other types of molecules (solvents, lipid membranes, proteins), independently parameterized by other research teams. Our work began with monomers and polymers of glucopyranose. Among others, parameters for glucose monomers and polymers with linkages of the type of $\beta(1-4)$ (cellulose), $\alpha(1-4)$ (amylose) and $\beta(1-3)$ (curdlan) were developed and validated. Parameterization and validation were performed based on the all-atom simulations (CHARMM force field, in the context of bonded interactions and polymer properties, such as gyration radius) and the experimental data (e.g. the log P values and structural data related to carbohydrate complexes and their interaction with lipid bilayers).

External stimuli-assisted Molecular Beam Epitaxy of functional layers and nanostructures

"Opus" research project NCN 2020/39/B/ST5/01838 [2021-2024] (*Project leader: Professor Józef Korecki*)

In the first months (6 months of 2021) of the project implementation, the tasks related to the modernization of the vacuum system for the deposition and characterization of epitaxial films were undertaken. The new and modified components of the ultra-high vacuum (UHV) equipment were designed, and their installation as well as operational functionality was simulated and optimized. The original elements of the vacuum equipment, such as chambers, sample holder transfers and manipulators, which require adaptation to the new holder system, were disassembled and sent for modification.

A magnetron sputtering source was purchased and tested under vacuum. The need to use a high partial pressure of argon to generate plasma in the magnetron and the deposition of the sputtered material on a significant area of the vacuum chamber led to conclusion that the magnetron should be installed in a separate vacuum chamber. For this purpose, it is planned to use the existing preparation chamber (which is to be replaced by a new one) and separate it from the entire vacuum system. Samples, after the sputtering process, will be transferred to the main UHV system using the vacuum transportable chamber that is planned for purchase.

The project task is to design, manufacture and test new sample holders, for which the process of the molecular beam epitaxy can be assisted by magnetic and electric fields, as well as mechanical stresses. At the initial stage of this task, prototypes of sample holder with a magnetic field generated by permanent magnets were made, which will allow for the application of the field both in the plane of the sample and along the normal, as well as prototypes of holders with the field generated by the electromagnet, which will enable work with a regulated field along the sample normal. The first attempts of in situ bending of a flexible substrate (mica) were also carried out as an initial step for the use of the strained substrates.

New generation teranostatic nanocarriers for detection, diagnosis and neuroprotective treatment of ischemic stroke brain damage

"Opus" research project NCN 2020/39/B/NZ7/01913 [2021-2025] (*Project leader: Professor Piotr Warszyński*)

Ischemic stroke is one of the major causes of death or long-term disabilities worldwide; thus, detection and treatment of ischemic-related damage, being still largely unresolved problems of contemporary medicine, require new technologies for diagnostics and therapeutics. Moreover, referring to the present pandemic, there is mounting evidence that also patients affected by COVID-19 may develop clinically significant complications, including ischemic stroke. The main limitation of current ischemia/reperfusion injury treatment is an inefficient delivery of neuroprotective drugs to the affected part of the brain due to the blood-brain barrier (BBB) permeable only by small, lipophilic molecules. Additionally, some neuroprotective drugs may influence the body, causing peripheral toxicity and numerous adverse reactions. The term "theranostic" describes the integration of therapeutic and diagnostic functions in one modality. The theranostic drug carriers are not only able to deliver their therapeutic cargo to the desired organ, but simultaneously, the delivery can be monitored by some imaging technique for optimizing targeting and dosage. The diagnostic agents used for imaging are magnetic resonance imaging (MRI) or computed tomography contrast agents. Theranostic drug carriers combine the ability to load lipophilic drugs with high efficiency with their detectability with some imaging technique. Moreover, they should transport the drug to the targeted place in the organism without its loss and release it in the place of action without imparting the therapeutic effect.

The main project objective, realized by the consortium of four research groups from Jerzy Haber Institute of Catalysis and Surface Chemistry of the Polish Academy of Sciences, Jerzy Maj Institute of Pharmacology PAS, Henryk Niewodniczański Institute of Nuclear Physics PAS and Collegium Medicum Jagiellonian University is to develop the new strategy of delivery of selected neuroprotectants by theranostic nanocarriers that can cross BBB without side effects on its normal function. We will concentrate on the methodology of encapsulation of neuroprotectants and fluorescent or MRI contrast agents in nanocarriers with the size below 150 nm and surfaces functionalized for targeted delivery. In the first stage of the project two neuroprotective drugs, cyclosporine A (CsA) and tacrolimus (FK506) were selected as the candidates for the encapsulation, while superparamagnetic iron oxide nanoparticles (SPIONS) and Gadolinium-PLL (poly-L-lysine) complexes will be used as MRI contrast agents. As the encapsulation method the sequential deposition of charged nanobjects (polyelectrolytes or nanoparticles) on the biocompatible nanoemulsion or polymer cores will be applied. The hydrophobic drugs will be placed in the cores. The MRI contrast agents will be mainly located in the carrier shells.

At the next stages of the project, the effects of the neuroprotectants in the theranostic formulations on the viability of the human neuronal-like SH-SY5Y cell line and on the organotypic hippocampal slice culture exposed to oxygen-glucose deprivation (OGD) will be examined. Moreover, the impact of theranostic formulations on the harmful factors related with OGD will be measured. In vivo experiments will determine the biodistribution of nanocarriers and the efficiency of transport to the brain. At the final stage of the project, the effect of the nanocarriers containing neuroprotectants will be tested in the middle cerebral artery occlusion (MCAO) animal ischemic stroke model.

Exploring metal ion cooperation in binuclear transition metal sites

"Opus LAP" research project NCN nr 2020/39/I/ST4/02559 [2021-2024] (*Project leader: Associate Professor Dorota Rutkowska-Żbik*)

In the current project we aim at the exploration of the reactivity of the binuclear divalent transition metal ion (TMI) sites (TMI = Fe, Co, Mn, Ni) stabilized into the zeolitic matrices as models of the binuclear sites in enzymes. In particular, the following research questions are to be solved by the interplay of various experimental approaches and theoretical calculations:

- 1. what affects the mechanism of O_2 and N_2O splitting and formation of the active oxygen centers for selective oxidation?
- 2. what affects the properties of α -oxygens which can be formed on the binuclear TMI sites?
- 3. what role is played by the confinement?
- 4. is catalytic activity in selective oxidation of C2–C4 hydrocarbons by zeolites bearing binuclear metal sites changed / improved in comparison to the systems containing typical monometallic sites?

Our project aims to address these questions by a controlled synthesis of the selected binuclear transition metal sites in zeolitic matrices of various types (we propose FER, MOR, *BEA, or SSZ-13). The resulting systems will be further tested in selective oxidations of light saturated and unsaturated hydrocarbons (ethane, propane, ethylene, and propylene) to explore their ability to activate inert C-H bonds. The planed studies will combine experiments and theoretical approach employing comparison of real systems in zeolite matrices and enzyme centers mimics (modelled by porphyrin moiety).

In 2021, the Fe-FER samples were prepared by methodology leading to maximum fraction of Fe binuclear transition metal ion (TMI) sites in the zeolite matrix. Samples were then characterized by FTIR spectroscopy of antisymmetric T-O-T vibrations of the zeolite framework to quantify concentration of Fe ions in the ferrierite β -sites (forming binuclear Fe sites) and by UV-Vis spectroscopy to monitor formation of Fe(III) ions and Fe-oxo species. These samples were employed by ICSC to study the reactivity in ODH of propane by air and oxygen. To compare reactivity of binuclear iron sites in ODH with the reactivity of other Fe species in this reaction, Fe-ZSM-5 samples (topology of which prevents the formation of binuclear metal ion sites) were prepared and characterized by FTIR and UV-Vis.

Because an Al organization in the zeolite matrix is a decisive parameter controlling the nature of the TMI sites (isolated and paired ones) in the zeolite, characterization of Al distribution in selected matrices (mordenite, chabasite, and USY zeolites) was started to select suitable matrices for controlled preparation of isolated and paired TMI sites at various geometric arrangements.

The set of theoretical models of the binuclear centers composed of Co, Mn, Fe, and Ni porphyrin analogues are proposed. The distance between the metal ions is varying in the range between 6-9 Å (with the step of 0.5 Å). Their electronic structure is being calculated.

"Sonatina" Research Projects of the National Science Centre

Multifunctional chitosan-based composite coatings for biodegradable Mg alloys

"Sonatina" research project NCN 2021/40/C/ST5/00266 [2021-2024] (*Project leader: Dzmitry Kharytonau PhD*)

Metallic orthopedic implants are well-established in medical practice for bone repairing, with hundreds of thousands of operations performed annually. The traditional concept of metallic biomaterials requires metals with improved corrosion resistance in the body. The typical lifetime of the titanium implant is around 15 years, thus, a majority of the patients require at least one revision or replacement surgery. After decades of developing strategies to minimize the corrosion of metallic biomaterials, there is now an increasing interest in using corrodible metals emerging as an alternative for biomedical implants. These biodegradable metals are expected to corrode gradually in vivo, releasing corrosion products metabolized by the human body. Such implants will assist tissue healing and then dissolve completely with no implant residues. The recently developed Mg-based biodegradable alloys corrode too fast, which results in a dramatic decrease in the implant stiffness before the completion of the tissue-healing process and generating high volumes of hydrogen gas. Lack of surface modification approaches for biodegradable metallic materials is chiefly one of the main barriers limiting further development of that technology. One of the possible ways to modify the surface of materials to increase their corrosion resistance is to cover them with a suitable polymeric protective layer, Chitosan is a natural polymer, which is increasingly used in biomedical applications due to its nontoxicity, excellent biocompatibility, biodegradability, antibacterial activity, film-forming ability, mechanical properties, and low cost.

The present project focuses on the development of the scientific background for the process of electrodeposition of a new type of multifunctional chitosan-based composite coatings on the surface of magnesium alloys with enhanced corrosion resistance and antibacterial functionality. In this regard, the main aim is to develop new electrochemical deposition approaches, optimize the key process parameters, which are deposition regime, bath composition, substrate pre-treatment, and systematically characterize coatings' properties. A full set of in vitro corrosion experiments in the solutions mimicking physiological conditions will be performed. Along with corrosion resistance, the in vitro antibacterial performance of the developed coatings towards common implant-related Grampositive bacteria, such as Staphylococcus aureus and Staphylococcus epidermidis will be examined.

The synthesized materials will be characterized by improved surface morphology, adhesion, mechanical, in vitro corrosion, and antibacterial properties. The new scientific information obtained in this project will allow evaluating the applicability of chitosan-based composite coatings as components of biodegradable implants. Materials for implants coatings developed within this project are expected to have a crucial impact on the development of biodegradable implants, thereby resulting in decreasing implant rejection and, ultimately, increasing the life span and life quality and of a patient.

"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 [2018-2021] (PhD student: Agata Wiertel-Pochopień MSc; supervisor: Associate Professor Jan Zawała)

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.

Analysis of the influence of the length of the hydrocarbon chain of alkyltrimethylammonium bromides (dodecyltrimethyloammonium bromide - $C_{12}TAB$, hexadecyltrimethyloammonium bromide - $C_{16}TAB$, octadecyltrimethyloammonium bromide - $C_{18}TAB$) on the kinetics of three-phase contact (TPC) formation by colliding bubble with quartz surface in solution of surface-active substances with identical hydrophilic group was performed. Concentrations of C_nTAB solutions were chosen based on the measurements of the contact angles (Fig. 1A) of the quartz surface in C_nTAB solutions. When contact angles do not increase it means that hydrophobization of the solid surface does not significantly affects the kinetics of TPC formation and the liquid film formed between bubble and quartz surfaces ruptures as a result of electrostatic interactions. The second parameter influencing the choice of surfactant concentrations was the same value of adsorption coverage with CnTAB molecules on the gas/liquid interface. Adsorption coverage was calculated on the basis of the Ward-Tordai equation, using the dependence of the surface tension of the solutions of C_nTAB as a function of their concentration. During the experiments the quartz sample was located at distance L=3mm from capillary orifice to eliminate the influence of dynamic adsorption layer (DAL) on time of threephase contact formation (t_{TPC}). It was shown that with increasing the value of adsorption coverage the three-phase contact was formed faster (Fig. 1B). It was found that there is no correlation between the length of the hydrocarbon chain of C_nTAB and time of the three phase-contact formation by air bubble colliding with quartz surface.



Fig. 1. (A) Contact angles of quartz surface and (B) dependence of time of three-phase contact formation by colliding bubble with quartz surface on adsorption coverage at gas/liquid interface in solutions of $C_{12}TAB$, $C_{16}TAB$ and $C_{18}TAB$.

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 from *Aromatoleum aromaticum* (AOR_{Aa}) is characterized by the lowest sensitivity to oxygen.

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.

As a result of enzyme activity tests, it was discovered that AOR_{Aa} is able to catalyse the reduction of carboxylic acids in presence of hydrogen as sole electron donor. This is a new activity for tungsten enzymes that do not contain a subunit with characteristic hygrogenase cofactor. The enzyme was shown to reduce benzoic, p-hydroxybenzoic, transcinnamic and nicotinic acid. The activity with hydrogen was also shown in reduction of NAD⁺ to NADH, which is a reaction of great application potential. The enzyme of hydrogenase activity provides a NADH regeneration system that may be used in biotechnological reactors with hydrogen as a clean electron (without production of additional side-products).

In cooperation with SYNMIKRO Center, University of Marburg, Germany, the AOR_{*Aa*} enzyme was subjected to single-particle cryo-electron microscopy and the analysis of obtained images resulted in resolving a structure of 3.3 Å resolution. The structure shows, that enzyme consists of subunits in ratio $(\alpha\gamma)_2\beta$, where the α subunit contains one iron-sulfur cluster and a tungsten cofactor of structure very similair to cofactor from AOR from *Pyrococcus furiosus*. Unlike the AOR of the archaea, AOR_{*Aa*} has an additional γ subunit containing 4 iron-sulfur clusters and a β subunit containing FAD cofactor. Resolving the enzyme structure confirmed the remarkably high structural similarity of the α subunit from AOR from *Pyrococcus furiosus*. The determined protein structure will also provide the necessary information for studying the reaction mechanism by testing the enzyme activity with amino acid mutations in the active site.
The analysis of the influence of selected factors on changes in α -synuclein structure

"Preludium" research project NCN 2020/37/N/ST4/02132 [2021-2023] (PhD student: Paulina Komorek MSc, supervisor: Professor Barbara Jachimska)

Parkinson's Disease is a neurodegenerative disorder, affecting about 2% of the population after the age of 60. It is characterized mainly by motor system disorders and is principally manifested through bradykinesia, tremor muscular rigidity, and loss of coordination. The hallmark of the disease is associated with the appearance of Lewy bodies characterized by abnormal protein aggregation that develops in nerve cells. Studies on the composition of the Levy bodies have shown that they contain mainly α -synuclein, which occurs in misfolded forms and can cause neuronal death. Although a lot of research has been performed in the area of α -synuclein, there are still many issues regarding changes in the II structure of this protein and the causes of its toxicity that are still not fully understood. Misfolding of α -synuclein can be initiated by perturbation of long-range interactions between domains of the protein. The research aims to investigate the key factors that play a role in changes in α -synuclein structure as a result of protein adsorption on the solid surface. The protein structure changes are investigated using several physicochemical methods, including characterization of the protein in bulk solution and adsorbed state. In addition, performing a wide range of spectroscopic studies allows monitoring the influence of selected factors in the context of changes in structure at the molecular level. It significantly contributes to the formation of abnormal forms of protein.

Development of evidence-based environmental specifications for short religious, cultural and commercial events in historic buildings

"Preludium" research project NCN 2020/37/N/HS2/01727 [2021-2023] (PhD student: Magdalena Soboń PhD Eng., supervisor: Professor Łukasz Bratasz)

As part of the project, work was carried out on the development of rational, evidence-based guidelines for climate control in historic interiors, which will allow curators and owners of similar buildings to make decisions to protect the cultural heritage remaining in their custody, mainly constituted by the massive wooden objects, i.e., sculptures and decorative elements. In particular, the project aims to define a safe strategy for heating historic interiors for religious, cultural, and commercial short-term events.

For the purposes of the research, a two-dimensional model of a massive wooden element was developed to analyze the crack propagation process under the influence of climate fluctuations in lime wood. The model was created in COMSOL Multiphysics and allows for solving physical problems using the finite element method. In the preliminary tests, the parameters of lime wood determined in the previous measurements carried out by the Cultural Heritage Research group were used, which will be updated with the material properties measured in the frame of PRELUDIUM-19 project.

In the analysis of crack development in massive objects made of lime wood, the energy release rate (G) was adopted as a parameter determining the risk of damage. The critical value, G_{Ic}, of lime wood was considered a risk criterion, the exceeding of which causes an increase in the depth of the crack in the sculpture. Preliminary numerical simulations of G changes as a result of a sudden decrease in relative humidity (RH) and as a result of cyclical changes reflecting the actual climate variability of historic interiors were carried out. This allowed the determination of the safe amplitude and time of the RH drop associated with the heating episode, below which the existing crack will not deepen.

In the next step, an analysis of the case of several cracks in the sculpture was carried out. The existence of two cracks was initially considered and the change in G due to the sudden drop in RH was calculated. The performed analysis showed that for deep cracks the G values obtained for two cracks are lower than for a single crack. It is planned to extend the simulation for more fractures.

The obtained results of computer simulations were presented at the CollectionCare conference and the Imaging Cultural Heritage: technologies, methods, models and risk assessment workshop.

In the initial analysis of the crack propagation risk, the G_{Ic} value used was estimated from the literature. For its experimental determination, lime wood samples with appropriate geometry were obtained. Also, "dog-bone" samples were obtained, which will be used to determine the remaining mechanical properties of the lime wood.

"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 the ultrathin magnetic ultrathin films (deposited by sputtering techniques and molecular beam epitaxy) in which the Dzyaloshinskii-Moriya interaction (DMI) is expected were studied.

One of them were layers with unsymmetrical type of interfaces was trilayers NiO/Co/Ir and NiO/Co/Pt where ferromagnetic layers is in contact with nonmagnetic layer (Ir or Pt) and antiferromagnetic layer (NiO). Brillouin Light Scattering spectroscopy studies revealed existence one of the biggest value of DMI (mainly in the case of NiO and Pt surrounding). Magnetooptical microscopy allow to visualize magnetic domain structure with asymmetrical magnetic domain wall movement induced by magnetic field applied simultaneously perpendicular and in the sample plane. It was also planned new samples for temperature studies induced: (i) magnetic domain structure demagnetization process, (ii) changes of magnetic anisotropy and magnetooptical properties, (iii) creation of magnetic domain structure like bubble/skyrmion.

It was also performed test studies on W/Co/Pt and Pt/Co/W ultrathin films to check existence of DMI. It turned out such kind of layers have very interesting properties, DMI is quite big and their amplitude/value depend on W layers thickness. It was also observed untypical magnetic domain structure behavior especially in the range of very thin Co layer thickness. There are also planned complementary studies on such kind of layers.

It was also studied multilayered sample like Pt/Co/Ir and Ir/Co/Pt. this type of samples showed strong dependence of DMI depending on order of the layers, Co and Pt/Ir layers thicknesses and number of layers repetitions. It was also observed interesting effect of magnetic resonance probably coming from magnetic domain walls – strengths of the resonances was dependent on number of layers repetitions and strength of DMI. More studies of this phenomena are planned using e.g. BLS technique.

Additionally micromagnetic simulations of magnetization distribution were performed taking into account variation of magnetic anisotropy and DMI value in the simulated layers. This simulations allowed to analyze changes of magnetic domain structure in layers with DMI and magnetization process in such kind of layers.

In the frame of visit at University of Kiel (partner of the Beethoven project) it was performed test studies on W/Co/Pt ultrathin films using magnetooptical microscopy combined with synchronized technique of light pulse and image acquisition. It was also performed visualization of magnetic domain movement induced by electric field – continuation of such studies are planned during next visit.

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: Professor Maciej Szaleniec, German leader: Professor 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)-bezylsuccinate.

During the second year of the project, we focused on the development of homology models for several FAE enzymes i.e., BSS from Aromatoleum toluolicum strain T, A. aromaticum strain EbN1, Tauera aromatica strain K172 as well as 2-methylnaphthylsuccinate synthases (NMS) from strains NaphS2 and NaphS6 and T. aromatica K172. We also continued the MD simulations for the BSS from T. aromatica strain T1 and its mutants (I617V, R508K) with different substrates (especially xylenes and 3-acetylacrylate). The analysis of the distance between the methyl group and sulphur atom of cysteine allowed the estimation of the probability of substrate activation. It also allowed identification of the residues responsible for imposing substrate selectivity of the BSS from T1. Part of those results was published in ACS Catalysis. Furthermore, we finished modelling of reaction mechanism using the QM-only cluster model and fully deprotonated fumarate. The obtained energy profile indicates, that C-C bond formation (TS2) is a rate-limiting step. For this step, we also observed kinetic preference of an attack on distal (Fig. 1, TS2a – 60.9 kJ/mol) vs proximal in relation to Cys (TS2b – 85.8 kJ/mol) C atom of the fumarate double bond. The preference of attack on distal C atom together with enzyme preference for binding fumarate in proR position ensures R-chirality of the product. Furthermore, pathway B is characterized by a prohibitively high energy barrier associated with quenching of the radical intermediate (TS3b – 240.0 kJ/mol).



Fig. 1. TS2a obtained for the QM-only cluster model. Attack on distal C atom of a double bond in fumarate; green lines – H bonds

The calculated intrinsic kinetic isotope effect (iKIE) was 7.7 for TS1 (toluene activation) and 2.0 or 2.2 for C-C bond formation at distal or proximal C atoms, respectively. The experiments were conducted either at ICSC PAS or in Marburg, in a group of prof. J. Heider. The analytical procedures were developed enabling quantitative analysis of benzylsuccinate (i.e. LLE or SPE, synthesis detection of benzylsuccinate or fumaric acid with LC-ESI(-)-MS/MS, chiral chromatography in normal-phase) as well as methods for BSS mutant preparation and FPLC Strep-Tag[®] purification of BSS under anaerobic conditions. The BSS activity was confirmed for wild-type BSS and Gln707Glu mutant cell extract. The LC-MS based analysis confirmed that the mutation is not detrimental to enzyme activity.

"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*)

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. The team from the ICSC PAS is responsible for theoretical studies in the project, in particular to propose models for the photocatalytic systems and elucidation of their electronic structure as well as the determination of the reaction mechanism.

In 2021 the following research tasks were undertaken:

- 1) The structure of the $Ag^+@TiO_2$ system was determined. Ag^+ ion was placed in 12 structurally different positions at the surface of TiO_2 nanocrystal of tetragonal bipyramid geometry. For each of the structures the geometry was optimized and the electronic structure was calculated with the DFT:PBE+D3/def2-TZVP method. It was found that the Ag^+ is best stabilized while at the edge of the nanocrystal. Ag^+ orbitals are located near the valence band of TiO_2. The introduction of the Ag^+ ion leads to the material band gap narrowing from 2.41 eV for the adopted model of pure TiO_2 to 0.68 1.30 eV for the $Ag^+@TiO_2$ system.
- 2) The experimental groups proposed the new system, Au@TiO₂, as the effective catalyst for methane coupling in the presence of oxygen. The DFT calculations enabled to identify the most probable site for methane activation. To do this, theoretical models of various fragments of the catalysts were proposed: the Au₆ cluster, the Au₆⁻ cluster (which is created as a result of the electron transfer from TiO₂ upon light irradiation), the TiO₂ fragment, and the model of the interface between two phases Au₆@TiO₂. Methane adsorption energies were computed (see Table below). It was concluded that methane is preferentially bound at the interface of gold and titanium dioxide.

Table. Methane adsorption energies on different fragments of the Au@TiO₂ system. DFT:BP/def2-TZVP calculations.

System:	Au ₆	Au ₆ -	TiO ₂	Au ₆ @TiO ₂
Adsorption energy [kJ/mol]	-23.7	-22.5	-20.2	-35.1

"GRIEG" Research Projects of the National Science Centre

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, Sergii Antropov PhD, Noemi Zabari PhD, Katarzyna Poznańska MSc Eng., Marcin Strojecki PhD)

In 2021, the institute's research team implementing the GRIEG Craquelure project focused on developing a database of historical properties of artistic materials used in paintings, and contemporary materials used to consolidate paint layers. For this purpose, representative materials were selected for laboratory tests together with Dr. Aleksandra Hola, the conservator of painting at the Academy of Fine Arts in Krakow, which covered three types of yolk tempera with lead white, yellow ochre and azurite as pigments, glue tempera with azurite as pigment. For each pigment, the proportions previously developed were optimized on the basis of mechanical criteria and visual assessment of samples after several months of natural aging. Then, the obtained raw material was subjected to mechanical machining to obtain samples of a given size, enabling the mechanical tests to be carried out in a universal testing machine. Based on the samples made, the water vapor sorption isotherms, the swelling and shrinkage isotherms as well as the stiffness moduli, the critical deformation at which the samples broke for four ranges of relative humidity (30%, 50%, 75% and 90%) were determined. young moduli and the tanDelta parameter were determined for some samples using a dynamic mechanical analyzer. Additionally, samples of natural and synthetic conservation materials were made - Lascaux 4176 and BEVA 371b consolidants, and Regalrez 1094 and damar varnishes.

In parallel, a three-dimensional model of panel painting with an developed network of rectangular cracks to simulate the formation of new cracks under moisture loads was tested and refined. Two typical load modes were adopted in the model. One, uniaxial, generated by the moisture response of the wooden support, the other isotropic due to annealing shrinkage of the ground/paint system. A mixed mode in which both modes are present was also considered. The optimized 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 images and their superposition. However, the model did not explain the cracks perpendicular to the wood grain.

The project is also developing image processing algorithms to isolate cracks from selected image fragments. Among others, binarization, thinning methods and filtering algorithms were used to search for sets of neighbouring pixels, for which the intensity is local extremes towards the main curvature, allowing for the separation of the crack lines on a homogeneous background. The developed algorithms were used to characterize the pattern of cracks in the mockup of panel painting resulting from the humidity cycles in the climatic chamber. The algorithms also allowed for the statistical characterisation of the developed cracks, i.e. the average length of the cracks, the 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 mesh of cracks.

Theranostic nanocarriers for drug delivery in central nervous system disorders

"GRIEG" research project NCN 2019/34/H/ST5/00578 [2021-2024] (*Project leader: Professor Piotr Warszyński*)

Prevention and treatment of neurodegenerative diseases and stroke-related brain damage are major and unresolved problems of contemporary medicine. Despite the progress in understanding of molecular mechanisms of neuronal injury and preventing them, only few neuroprotective substances are used in the clinic and their efficiency in the treatment of stroke and neurodegenerations is not satisfactory. One of the major limitations to current neurodegenerative disease treatment is an inefficient delivery of neuroprotective drugs to the affected part of the brain and difficulties in the diagnosis if the drug is well addressed, i.e., if it reaches the targeted organ. Theranostics is a new branch of medicine based on joining of therapeutic and diagnostic function in one entity. Application of nanotechnology in theranostics will allow engineering of drug carriers simultaneously delivering therapeutic components and possessing a diagnostic function. The main objective of the project is to develop a new strategy to deliver neuroprotectants by applying theranostic nanocarriers for neuroprotective drugs, which are able to cross the blood-brain barrier without imposing side effects on its normal function, and can be detected in a given part of a brain by Nuclear Resonance Imaging (MRI). Three Polish scientific institutions, Jerzy Haber Institute of Catalysis and Surface Chemistry of the Polish Academy of Sciences, Jerzy Maj Institute of Pharmacology PAS, Henryk Niewodniczański Institute of Nuclear Physics PAS and two Norwegians SINTEF Oslo and Oslo University Hospital participate in the project consortium.

In the project we aim to apply various methodologies of encapsulation of neuroprotective drugs together with fluorescent or MRI contrasting agents. The size of nanocarrier should not exceed 150 nm, they should be non-toxic, invisible to the immune system, able to cross the blood-brainbarrier and can be precisely localized in the organism. Fluorescently labelled nanocarriers will be used in the in vitro cell tests of neuroprotective activity of encapsulated drugs and ex vivo test of their localization in the brain, whereas nanocarriers with MRI contrasts will be used in the in vivo tests on animal models. The ultimate aim of the project is the development new drug carriers that can be used in future in therapies for neurodegenerative diseases, like Parkinson, Alzheimer or schizophrenia. "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 was the identification of a physiological role for potential FADdependent 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 2021 a final report of the project has been prepared. The major result of the project was obtaining a functional protein AcmB2 from *Sterolibacterium denitrificans* Chol-1S, for which an initial biochemical characterization together with answers to above questions was prepared. An unexpected result was revealing that the enzyme was active with five-ring system substrates. Unfortunately, despite many trial and approaches, for another potential KstD enzyme from *Sterolibacterium denitrificans* Chol-1S it was not possible to clone the vector containing gene encoding the enzyme to the bacterium. Thus, no results were obtained for this potential enzyme. Whereas for another three potential KstDs from *Pseudomonas putida* KT2440 there were difficulties with obtaining an efficient overexpression system. As a result received proteins were insoluble and therefore inactive. For three KstDs from *Pseudomonas putida* KT2440 only in one experiment the activity towards 1,2-dehydrogenation was confirmed. The product of the reaction was present for all three enzymes from *Pseudomonas putida* KT2440 when androstendione nor the cholest-4-en-3-one was applied.

Results of the project were a base for polish patent application, scientific paper and an introduction to another scientific project for further investigations.

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: Łukasz 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 the prepared FAU-type zeolites demonstrated that the addition of ultrasounds during the aging of a precursor gel allowed the preparation of mesoporous zeolites without the application of post-synthesis modification. It was also discovered that exposing the aged gel to ultrasonic irradiation for an extended period of time resulted in a gradual increase in mesopore volume and average pore diameter.

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.

For the prepared zeolites with faujasite structure, catalytic tests in the decarbonylation of furfural into furan reaction were performed. All studied samples were inactive in the tested reaction, which was probably related to the low acid strength of protonic acid sites existing in the investigated catalysts. For comparison, a commercial zeolite with a faujasite structure of Si/Al=31 and containing bridged Si-OH-Al Brønsted acid sites of a high acid strength (355 cm⁻¹) was investigated. At 300 °C, the furfural conversion was 33%, whereas, the furan yield was 16%. All tested catalysts underwent coking.

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*)

The main goal of the project was to investigate the influence of the microstructure of magnesium alloys doped with rare earth metals (QE22, ZRE1, and WE43) on the mechanisms of corrosion inhibition by anionic (vanadates, molybdates) and cationic (rare earth metal salts) inhibitors on the macro and micro scale.

In 2021, cationic inhibitors were tested. Cerium (III) nitrate $Ce(NO_3)_3$ has been tested as a cationic inhibitor. During electrochemical tests, it was found that the protective layer of the inhibitor on the surface of Mg alloys was formed too slowly, which did not allow for effective corrosion protection. In order to accelerate the process, the H₂O₂ oxidant (10 mL 30% H₂O₂/L) was used, which allowed to achieve the degree of corrosion inhibition at the level of 70–80%. The study of the mechanism of action of cerium compounds has also shown the presence of a similar mechanism. The protective layer consists of Ce(III)/Ce(IV) compounds.

In summary, the structure of Mg QE22, ZRE1, and WE43 alloys, corrosion mechanisms and the process of its inhibition by inorganic inhibitors were investigated during the preliminary tests carried out in the project. These results are important for understanding the mechanisms of action of oxidative inhibitors and further development of corrosion protection for Mg alloys.

'Confinement effect' - 5-fluorouracyl in mesopores

"Miniatura" research project NCN 2019/03/X/ST5/01756 [2019-2021] (Project leader: Mariusz Gackowski PhD)

Many mesoporous silica-based materials were used to carry out the scientific activity: SBA-15, MCM-41 and mesoporous zeolites of various topologies (ZSM-5, Y, BEA). The effect of the presence of aluminum in the materials was also tested by using the MCM-41 preparation after alumination (Al-MCM-41) and mesoporous zeolites prepared from materials with different Si / Al ratios (zeolite ZSM-5 with Si / Al = 11 and Si / Al = 40). After establishing the optimal application conditions, 5-fluorouracil was incorporated into all carriers. The samples were characterized by the following methods: porosimetry (N₂ BET), infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), thermogravimetry (TG), X-ray diffraction (XRD), solid-state NMR spectroscopy (MAS NMR). For selected samples, drug elution into SBF (simulated body fluid) tests were carried out at 37 °C, controlling the drug concentration in SBF using UV-VIS spectroscopy. Distilled water as a solvent and a concentration of 10 mg/ml of 5-fluorouracil were used to introduce the drug. SEM pictures of the starting porous materials show that they are characterized by a different morphology and size of the crystallites. In XRD studies, only 2 samples (SBA-15 and mesoporous zeolite BEA) show a characteristic reflex originating from 5-flurouracil crystals at 28.6 [2 theta]. This means that in most cases the drug is present in the material in a non-crystalline form. TG shows the presence of an organic phase, but only in amounts ranging from a few to a dozen or so wt%. FT-IR spectra show weak signals characteristic for 5-fluorouracil, visible especially in the range 1650 - 1800 cm⁻¹, where there are vibrations from the groups C = C and C = O. C = C stretching vibrations are shifted in relation to pure 5-fluorouracil not introduced into mesoporous materials by more than 30 cm⁻¹. N₂ BET studies show that the specific surface area, the volume of the mesopores, and the surface area of micropores decrease after the introduction of 5-fluorouracil into porous materials. This means that the drug molecules are present in both the micropores and mesopores of the tested materials. The ¹³C CP MAS NMR spectra show 4 characteristic signals in the range 120-170 ppm. For the mesoporous zeolite ZSM-5, the ¹³C CP MAS spectra show the signals from the C = O and C = C carbons are shifted compared to the spectra recorded for pure 5-fluorouracil. The two-dimensional ¹H-¹H NOESY spectrum showed the coherence between the protons from 5-fluorouracil and the Si-OH-Al groups in the zeolite, which confirms the introduction of the active substance into the micropores. ¹H MAS NMR spectra show characteristic signals from the organic phase at 7 and 10 ppm. However, in most cases, they are of low intensity and overlap with the intense water signal. In some cases (SBA-15, mesoporous Y zeolite) narrow signals from 5-FU were observed. This could mean the high mobility of these molecules, possibly due to the presence of water in the materials. Experiments were carried out to determine the effect of water on the 5-FU spectra in mesopores. ¹H MAS NMR spectra of degassed preparations show wider signals of 5-FU than in the hydrated form. Hydration of these preparations was also performed by keeping in a desiccator with saturated $Mg(NO_3)_2$ for 18 hours. Such hydrated formulations show even narrower signals than the organic phase for the SBA-15 and mesoporous Y zeolite formulations. This may indicate that the water present in the materials affects the mobility of the organic phase in the mesopores.

Selected samples (based on SBA-15 and MCM-41 and mesoporous zeolites ZSM-5 and Y) were subjected to drug washout experiments from the carrier. The tested samples are characterized by a very fast elution, i.e. the plateau of 5-fluorouracil concentration in SBF is reached after just 15 minutes of elution.

Research Projects of the National Centre for Research and Development

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

"EIG CONCERT-JAPAN" research project NCBiR EIG CONCERT-JAPAN/1/2019 [2019-2023] (*Principle investigator: Aleksandra Pacula D.Sc. Eng.*)

The aim of the research was to characterize of physicochemical properties by means of XPS, TEM, XRD and to evaluate photocatalytic performance of metal-TiO₂-zeolite composites. A series of samples (Ag-TiO₂, Ag-TiO₂-ZY, Pd-TiO₂, Pd-TiO₂-ZY) were obtained via deposition of metal nanoparticles (NPs) (Ag or Pd) on commercial TiO₂ (Sigma-Aldrich, "aeroxide® P25") or on a physical mixture of TiO₂ with commercial zeolite Y (WAKO) containing 5 wt. % zeolite Y – sodium form. The nominal concentration of metal (Ag or Pd) deposited in the form of NPs was 0.05 wt. % in the case of Ag or 1 wt. % in the case of Pd.

Analysis of the surface composition of the composites by XPS confirmed the presence of Ag, i.e. 0.08 and 0.15 wt. % in Ag-TiO₂ and Ag-TiO₂-ZY, and in the case of samples: Pd-TiO₂ and Pd-TiO₂-ZY, the presence of Pd, i.e. 0.4 and 1.2 wt. %.

Analysis of TEM images allowed to describe the morphology of grains of composite components and their mutual distribution. Micrometric sized zeolite Y grains (~ 6 μ m) were coated with TiO₂ nanoparticles (~ 21 nm). Using TEM imaging and EDX analysis, it was possible to confirm the presence of Pd nanoparticles in the samples: Pd-TiO₂ and Pd-TiO₂-ZY, which preferentially located on TiO₂ grains and formed smaller or larger clusters. However, due to the low concentration of Ag in Ag-TiO₂ and Ag-TiO₂-ZY, it was not possible to detect and locate Ag NPs.

Analysis of XRD diffraction patterns of TiO₂ (Sigma-Aldrich) and TiO₂ (Evonik) by the Rietveld method using TOPAS software allowed to estimate the phase composition of both TiO₂, i.e. TiO₂ (Sigma-Aldrich): anatase (79 %) and rutile (21 %), TiO₂ (Evonik): anatase (76 %) and rutile (21 %). Commercial TiO₂ had similar phase compositions and thus were characterized by similar photocatalytic properties confirmed in the degradation reaction of the dye: methyl orange (using a UV lamp with emission of radiation in the wavelength range: 365 - 367.5 nm). The degree of degradation of the dye in the presence of TiO₂ was: 36 - 40 % after 1 h of exposure, 70 - 71 % and after 2 h of exposure. The degree of adsorption of the dye (after 2 h of mixing in the dark) on both TiO₂ was similar (34 - 37 %).

Photocatalytic properties of the composites was examined in degradation reaction (using 4 UV-A lamps with the emission of radiation with a maximum wavelength: 365 nm) of the surfactant - dodecylbenzenesulfonate (SDBS) and dichloroacetic acid (DCA) in the presence of Ag-TiO₂, Ag-TiO₂-ZY, Pd-TiO₂-ZY, Pd-TiO₂-ZY, TiO₂ and TiO₂-ZY. SDBS degradation in the presence of TiO₂ or TiO₂-ZY was 80 and 72 % after 3 h of exposure. The addition of Ag to TiO₂ or TiO₂-ZY resulted in a reduction in degradation that was 60 % for Ag-TiO₂ and Ag-TiO₂-ZY. A higher concentration of Pd in Pd-TiO₂ or Pd-TiO₂-ZY resulted in a greater reduction in degradation, which was 40 or 35 %, respectively. DCA degradation in the presence of Ag-TiO₂ or Ag-TiO₂-ZY or TiO₂-ZY was comparable to that in the presence of TiO₂ and was 100 % after 1 ½ h of exposure. In the presence of Pd-TiO₂ and Pd-TiO₂-ZY, the degree of DCA degradation was lower after the same exposure time, i.e. 1 ½ h until finally (after 2 h) it reached 100 % for Pd-TiO₂ and 85 % for Pd-TiO₂-ZY. The degree of adsorption of SDBS or DCA (after ½ h of mixing in the dark) on all the samples was similar and small (< 10 %).

The obtained composites have ability for photocatalytic degradation of methyl orange. The addition of zeolite Y and the deposition of metal NPs on TiO_2 reduces the efficiency of photocatalytic degradation of SDBS and DCA in comparison to pure TiO_2 .

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. Fermentations leading to aPHA

The objective of this task is to produce the amorphous polymer mclPHA produced by the bacteria Psedomonas putida CA3. During the reporting period the process was successfully scaled up to 30L and then to 200L scale. Cultures were carried out to produce significant quantities of polymer, which were transferred to the Consortium to enable planned research.

2. Fermentations leading to PHB

The objective of this task is to produce the crystalline polymer PHB produced by the bacteria Z. denitirficans MW1. During the reporting period the process was successfully scaled up to 30L and then to 200L scale. Cultures were carried out to produce significant quantities of the polymer, which were transferred to the Consortium to enable planned research.

3. Development of wet-spun polymer-composite materials

During the reporting period, a methodology was developed for wet spinning of foams obtained by precipitation of a chloroform PHB solution in a methanol bath. Methodologies were developed for the synthesis of foams containing active substances - diclofenac, as well as the addition of ceramic dust based on calcium triphosphates.

4. Management of waste streams

In the reporting period, the development of a method for chemical hydrolysis of postfermentation biomass was completed. Pilot studies were initiated in which the hydrolysates are tested for their use as fertilisers for cultivation of useful plants.

Task 2

In the reporting period, a hall at 100 Balicka Street in Krakow was adapted for the purposes of the project and equipped with an appropriate process line. Movable elements of the prototype biorefinery line have been installed. The construction of the target housing for the prototype has started on the premises of the Institute.

CULDIGI - Integrated digitalization, filing and documentation system for cultural heritage

"Program operacyjny Inteligentny Rozwój" research project NCBiR POIR.04.01.04-00-0145/19 [2021-2023]

(Project leader: Jakub Barbasz D.Sc. Eng., Leszek Krzemień PhD)

The main goal:

The aim of this project is development of a full surface scanner, a device that scans big art artefacts like painting drawings and documents with microscopic resolution.

In 2021, all planned work was completed.

The possibility of photographing historical objects with a moving camera was tested. Tests were carried out by moving the camera in the XY plane and along the Z axis.

It was demonstrated that it is possible to capture sharp and high quality images.

Requirements and necessary documentation for the implementation of the prototype were developed. Existing IKIFP equipment was adapted to perform the necessary tests.

Two illumination methods were designated for testing, both based on led lighting. Preliminary results suggest no significant effect of lighting method on the results obtained.

During the tests, MOS scale image parameters were determined as described in the submitted application. TLR 6 was achieved in this regard.

Appropriate test datasets were prepared to work on the development of image assembly algorithms.

An analysis of the performance needs of the computers used to assemble the images was prepared.

Work was carried out on the analysis of known algorithms with functionality similar to that required for the final product.

Work has been carried out on the development of systems for finding so-called "control points" or "common points" for positioning in two-dimensional space sequentially collected images.

As part of the design work, simulations of motor drivers used for camera positioning were performed. There were also simulations of lighting controllers used to shorten the exposure time.

Work on the documentation of the implementation of individual electronic components was completed.

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 [2019-2023] (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 recurring pandemic waves, a large part of the planned trips and arrivals could not be implemented so far. In 2020 only 2 internships for foreign workers at ICSC PAS were carried out. In 2021:

- two PhD students from IKiFP PAN took part in a scientific conference abroad;
- one representative of the research staff of IKIFP PAN has completed a research internship at a foreign research unit;
- one female and one male PhD student from foreign research units completed a research internship at IKIFP PAN in Krakow;
- one representative of foreign research staff completed a research internship at IKiFP PAN.

The contract with NAWA for the implementation of the project was extended till the end of March 2023.

"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 aim of the "Polish Returns" program, 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 financial resources obtained from external sources and conducting other research in the area of cultural heritage preservation. Therefore, the third year of the project was devoted to the further submission of applications for research funding. During this period, several applications for external financing were submitted to:

- European Commission "Data Science for Preventive Conservation Doctoral Network" call HORIZON-MSCA-DN-2021,
- European Commission "Sustainable conservation and climate control strategies for cellulosebased cultural heritage" call HORIZON-CL2-2021-HERITAGE-01-01,
- Polish Academy of Sciences, "Time-dependent behavior of historical wooden constructions and panel paintings" programme Pasific 1,
- Polish Academy of Sciences, "Time-dependent behavior of historical wooden constructions and panel paintings" programme Pasific 2.

At the beginning of 2021, Eng. Łukasz Berger, an IT specialist whose task was to develop the HERIe tool. As part of the work, a chemical degradation module was developed that allows the calculation of the relative lifetime of objects vulnerable to chemical degradation, such as paper, wood, textile and plastics, which is calculated in relation to the reference conditions, 20 ° C and 50% relative humidity. The module is based on three degradation functions developed for acid paper, cellulose acetate and the general material. In addition, the module allows you to calculate the lifetime of vulnerable materials expressed in years for cellulose acetate and acid paper. The next implemented module is the "fire" module that allows to calculate the predicted loss of value of the collection due to risk of fire depending on the type and structure of the building in which collection is stored, the material's vulnerability to water and combustion and the number of objects stored in display cases. A module for calculating the concentration of gaseous pollutants in a room was also implemented. It is calculated using the concentration of these pollutants outside depending on the type of material the room is made of and air exchange rate. All modules have been tested, thoroughly checked and their operation optimized.

In parallel, a three-dimensional model of panel painting was tested and refined with an developed network of cracks to simulate the formation of new cracks under moisture loads. Two typical load modes were adopted in the model. One, uniaxial, generated by the moisture response of the wooden underpainting, the other isotropic due to annealing shrinkage. A mixed mode in which both modes are present was also considered. The optimized 3D model was used to determine the critical distances between the cracks along and across the wood grain below, which will not form new cracks. The model explained the cracks parallel to the wood grain and the square-shaped cracks observed in real images as well as their superposition. However, the model did not explain the cracks perpendicular to the wood grain.

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 catalytic tests of the studied systems in the oxidative dehydrogenation of propane in temperature range 100-300 °C were continued.

The series of iron and manganese zeolite *BEA catalysts were prepared and characterized by various physico-chemical methods. Characterization of the obtained iron and manganese catalysts confirmed that for various metal loadings, different speciation of metal species is observed. Moreover, comparison of catalytic results revealed that catalytic performance in alkane oxidation of the studied Fe and Mn catalysts strongly depends on the zeolite matrix. Among the studied samples the Fe- or Mn- FER exhibited higher catalytic activity in comparison with *BEA. FTIR study performed under in-situ reaction conditions enabled monitoring the reaction pathways of oxidation process occurred in metallozeolites with various types of metal species.

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 the project, we have investigated a new class of photo-active surfactants, which create twodimensional structures at the liquid / gas interface, making the individual interfaces, as well as the entire macroscopic foam, react to light radiation. This opens up new possibilities for foams, such as the ability to heal itself or the ability to adjust the properties of the foam by "turning on" and "off" the high surface activity of photo-surfactants (light stimulus as a switch).

The use of such molecules provides an opportunity to reconstruct the phase boundaries of soft matter in response to a light stimulus. This is possible because light-induced reversible changes (cistrans transformation) in molecules adsorbed at the interface cause the entire system to be brought out of equilibrium. On the other hand, the return to the state of equilibrium is associated with new physicochemical properties, which are a consequence of the changed molecular structure under the influence of light irradiation of a specific wavelength.

During the project, a series of studies on the surface and foam-forming properties of spiropyran sulfonate, synthesized in the laboratory of our German co-operator, was carried out (research task 1). In Munster / Germany, the surface activity and dilational elasticity by pendant drop was analyzed, and spectroscopic studies were carried out using the Sum Frequency Generation SFG method (research task 2). In Krakow, we performed complementary analyses of the surface activity of this compound, registering changes in the local velocities of the bubble discharged (research task 3). In both groups, the foam-forming capacity and stability of foams produced on the basis of the tested solutions were tested simultaneously (research task 4). The research was carried out so-called by the membrane method in a glass column equipped with a gas-permeable sinter at the base of the column.

Due to the fact that the tested compound exhibits the assumed by us features of "intelligent surfactant", in which the surface activity changes under the influence of changes in pH and light, all experiments were carried out at two selected pH 2.7 and 5.3, for each pH by taking measurements in the dark and under strong light blue light 440 nm. The obtained results confirmed the influence of pH and lighting on the examined person's surface activity and foaming abilities.

The research results have been published in the journal ACS Langmuir and presented at several scientific conferences
Understanding molecular aspects of the protein misfolding process: in situ spectroscopic and microscopic studies



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

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

Adsorbed protein films consist of essential building blocks of many biotechnological and biomedical devices. The electrostatic potential may significantly modulate the protein behaviour on surfaces, affecting their structure and biological activity. In this study, lysozyme was used to investigate the effects of applied electric potentials on adsorption and the protein structure. The pH and the surface charge determine the amount and secondary structure of adsorbed lysozyme on a gold surface. In-situ measurements using polarization modulation infrared reflection absorption spectroscopy indicated that the concentration of both the adsorbed anions and the lysozyme led to conformational changes in the protein film, which was demonstrated by a greater amount of aggregated β -sheets in films fabricated at net positive charges of the Au electrode (Eads > Epzc). The changes in secondary structure involved two parallel processes. One comprised changes in the hydration/hydrogen-bond network at helices, leading to diverse helical structures: α -, 310- and /or π -helices. In the second process β -turns, β -sheets, and random coils displayed an ability to form aggregated β -sheet structures. The study illuminates the understanding of electrical potential-dependent changes involved in the protein misfolding process.

Dynamic nanostructures at moving liquid/gas and liquid/liquid interfaces

Project NAWA PPN/BEK/2020/1/00025 [2021-2022] (Project leader: dr hab. Jan Zawała, prof. IKiFP PAN)





The main goal of the project was to use Dynamic Fluid-Film Interferometry (DFI) technique, elaborated at the Department of Chemical Engineering, Stanford University, to determine an influence of dynamic adsorption structures at a rising bubble surface on drainage kinetics of a single foam film. The rate of a film drainage was measured by video registration of thin liquid layer formed by a bubble colliding with solution surface in a liquid column. Registered images with color interferometric fringes were analyzed using elaborated software, allowing direct determination of thickness of the liquid film separating the bubble and solution interfaces. The experiments were carried out to check the influence of the stage of formation of so-called dynamic adsorption layer at the rising bubble surface. Solutions of cationic and non-ionic surfactants, namely dodecyl-trimethylammonium bromide (C₁₀TAB) and n-octanol, respectively, were used in all the experiments. The experiments were aimed to verify the following hypothesis: due to different state of adsorption layer at the rising bubble surface, the kinetics of drainage of a single foam film formed by a colliding bubble should depend significantly on distance covered by the bubble in the liquid column. To verify this hypothesis two liquid columns of different lengths were used, were the distance covered by the bubble before liquid film formation was equal to L = 3 and 25 cm.

For $C_{10}TAB$ solutions it was found that for L = 3 cm there is positive correlation between solutions concentration and single bubble lifetime at the top solution surface - higher was the concentration, higher was the lifetime of the bubble before coalescence. For L = 25 cm similar trend was revealed only for concentrations $< 1 \times 10^{-3}$ mol/dm³. For higher concentrations the observed effect was opposite. For n-octanol, positive correlation between solution concentration and the bubble lifetime was observed both for L = 3 and 25 cm. However, above some characteristic threshold concentration, the bubble lifetime was shorter for L = 25 cm comparing to L = 3 cm and this effect was observed for both studied surfactants. For C₁₀TAB the threshold concentration was equal to 5×10^{-4} mol/dm³, while for n-octanol to 1×10^{-4} mol/dm³. These results suggested that research hypothesis, formulated at the beginning of the experiments, is very probable. On the basis of these qualitative observations, however, it was not possible to verify if the shorter bubble lifetime for L = 25 cm is caused by increased rate of liquid film drainage or by its higher rupture thickness. To check which mechanism is responsible for observed trends, the DFI technique was used. Using the DFI method it was possible to directly observe the liquid films and measure time evolution of their thickness in time. For the lowest concentrations of $C_{10}TAB$ (5×10⁻⁵ and 1×10⁻⁴ mol/dm³) the measured critical rupture thicknesses were practically identical for both liquid columns lengths. For higher concentrations, however, significant differences in rupture thickness for different L were revealed. The average value of this difference was equal to ca. 150 nm. It was found that for L = 25 cm the rupture thickness of the liquid films was higher comparing to L = 3 cm. Moreover, rupture thicknesses for L = 25 cm in all solution concentrations were very similar. It suggests that shorter bubble lifetime observed for L = 25 cm was a caused by increase in the rupture thickness, not by modification of the liquid film drainage rate.

Horizon 2020 Programme

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 started in previous years aimed at determining the mechanical properties depending on the relative humidity of canvas, canvas sized with animal glue, and sized canvas covered with a layer of animal glue ground (gesso) was continued. The measurements were carried out with the use of a universal testing machine and optical methods in climatic chamber. The aim of the research was to extend the previously conducted research to other types of canvas, to obtain more reliable experimental statistics and to repeat measurements that weren't consistent. In the research, the canvases of the Italian manufacturer CTS were used, with a close and open weave. Various types of glue used for sizing, i.e. rabbit skin glue and cow hide glue, were also tested, as well as two methods of glue application: so-called cold method, in which the glue in the form of a gel is applied with a knife and the so-called the warm method, where the glue in a liquid form is applied with a brush. The obtained results showed that in the tested samples there is a strong anisotropy of mechanical properties depending on the direction of the canvas as in the case of the measurements previously made for the canvas of the Polish manufacturer. The stiffness modulus of the canvases in the weft direction is an order of magnitude larger (~ 100 MPa) than the warp direction and the bias direction (~ 10 MPa). Covering the canvas with a layer of animal glue significantly increases the stiffness modulus (~ 400 MPa in the direction of the weft and ~ 100 MPa in the direction of the warp). In spite of that the sized canvas maintain anisotropic mechanical properties. This observation cannot be explained by assuming a laminar system of glue and canvas. Hence, the canvas covered with a layer of animal glue should be considered as a composite material. The tests were carried out in a wide range of relative humidity, from 30% to 90%. An increase in relative humidity above the value of 75% causes a decrease in the stiffness modes of the glued canvas. However, no significant influence of the type of canvas, the amount of glue, the type of glue or the method of its application on the mechanical properties of the sized canvases was found. Moreover, the moisture expansion coefficients of the tested canvases were determined. These coefficients depend primarily on the direction of the canvas and are largest in the warp direction. These coefficients is about two times lower in the weft direction. There was no significant dependence of the coefficient on the type of canvas, the amount of glue, the type of glue or the method of its application. Additionally, the annealing shrinkage of the sized canvases due to repeated relative humidity cycles between dry and humid conditions was determined. It has been found that this shrinkage is predominant in less stiff directions – warp and bias - and can be up to 1%, while in the longitudinal direction it is up to 0.4%. The value of the drying shrinkage does not depend on the type of the canvas, the amount of glue, the type of glue or the method of its application. The conducted research allowed to obtain basic data for the development of a computer model of an painting on canvas and to verify its predictions.

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 second year of the project implementation, tools supporting decision-making for practitioners, museologists and object owners were created and implemented. The first tool included was the HERIe tool estimating the risk of mechanical damage as a result of environmental variations. A chemical degradation module was developed that allows the calculation of the relative lifetime of objects vulnerable to chemical degradation, such as paper, wood, textile and plastics, which is calculated in relation to the reference conditions, 20 ° C and 50% relative humidity. The module is based on three degradation functions developed for acid paper, cellulose acetate and the general material. In addition, the module allows you to calculate the lifetime of vulnerable materials expressed in years for cellulose acetate and acid paper. The next implemented module is the "fire" module that allows to calculate the predicted loss of value of the collection due to risk of fire depending on the type and structure of the building in which collection is stored, the material's vulnerability to water and combustion and the number of objects stored in display cases. A module for calculating the concentration of gaseous pollutants in a room was also implemented. It is calculated using the concentration of these pollutants outside depending on the type of material the room is made of and air exchange rate. All modules have been tested, thoroughly checked and their operation optimized.

NanoPaInt - Dynamics of dense nanosuspensions: a pathway to novel functional materials (nanoPaInt)

Project H2020-MSCA-ITN-2020 nr 955612 (Project leader: prof. dr. hab. Piotr Warszyński)



Nanoparticles serve as additives for controlling the liquid properties. They are extensively applied in food industry and home care products, they are the essential part of ink and paint formulations and of coatings, they are used for manufacturing of functional materials and are very promising drug carriers. The presence of nanoparticles in air or in water can influence the Earth ecology and human health. Although dilute suspensions of nanoparticles which are close to equilibrium have been extensively studied, in many important applications, such as food industry and printing, the suspensions are dense, or strongly interacting, they experience significant external stress and are far from equilibrium. A fundamental understanding of interaction between nanoparticles in liquid bulk and at interfaces, allowing to effectively use particulate systems in these applications, has not yet been achieved. The aim of the nanoPaInt network is understanding, predictive modelling and application of the strongly interacting nanoparticle-laden systems out of equilibrium. The specific objectives are: understanding strong interactions between the nanoparticles and their effect on the rheological properties of suspensions; understanding the behavior of nanoparticles in complex interfacial flows under strong external forces and with wetting and dewetting; design and applications of smart capillary nanosuspensions; drying of nanosuspensions towards assembly and fabrication of functional superparticulate systems. The training aim of nanoPaInt network is to support the career development of young researchers both in academic and non-academic sectors and to train a new generation of creative, mobile, entrepreneurial and innovative early-stage researchers (ESRs) through the experience of independent and interdisciplinary research, participation at local and network-wide training activities and intersectorial and international secondments. In the network there are 14 participants representing European research institutions and industrial laboratories.

The aim of the ESR research project run in the Jerzy Haber Institute of Catalysis and Surface Chemistry PAS is to obtain core/shell bimetallic non-oxidizable nanoparticles with high stability against aggregation process for conductive inks and pastes formulations. The suthesized formulations will be used to the engineered process for fabrication of printed circuits and devices with high electrical conductivity. In the first year of the project the ESR was recruited and the review of the state-of-art and preliminary laboratory works of the synthesis of core/shell nanoparticles (Ni/Au, Sn/Ag, Sn/Au) and Cu/Ag nanowires.

EU COST Actions

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



EU COST Action no 18234 [2019-2021] (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 group from ICSC PAS was involved in the project "Extremely small nanocrystals". By employing Density Functional Method, with PBE functional and def2-TZVP basis set, the geometry structure of three TiO₂ nanocrystals was elucidated and their electronic structure was computed: bipiramid crystal (Figure a), truncated bipiramid crystal (Figure b), and spherical crystal (Figure c). The width of the HOMO-LUMO band gap was determined. It equals to 2.41 eV, 2.40 eV, and 2.21 eV, respectively.



Figure. Structures of TiO_2 nanocrystals of different geometries: a) bipiramid crystal, $(TiO_2)_{84}$, b) truncated bipiramid crystal, $(TiO_2)_{78}$, c) spherical crystal, $(TiO_2)_{78}$.

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 Strojecki PhD*)

The research activity conducted within the project was aimed both at experimental work and theoretical computer aided modeling. The experimental work covered controlled laboratory tests and long-term monitoring of microclimate impact of environmental conditions on risk of physical damage of moisture-sensitive wooden elements in two selected stave churches (Heddal and Ringebu). Both experimental results obtained in controlled laboratory conditions and results collected during on site monitoring provided from one hand a reliable information on ranges of fluctuations of environmental parameters (air temperature - T and relative humidity - RH). From the other hand, results provided an experimental verification of *proofed fluctuations* concept.

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. However creating the software as an additional module to HERIe tool developed by the partners' consortium turned out to be not feasible. It is caused by the non-linear dependence of the most important simulation parameter G (energy release rate in a wooden object due to fluctuations in RH) and the amplitude of the RH change, which makes Fourier transform not applicable to the studied problem. It was shown that full numerical simulation for each combination of object's diameter, crack depth and environmental parameters is not practical due to very time-consuming calculations. Therefore, risk maps (Fig. 1b) allowing to choose the crack depth and time of the RH variation arbitrarily and estimate the size of the crack's extension were proposed, with an emphasis on the variations typical of the stave churches interiors.

As an example the full finite element simulation in COMSOL software was performed for the crack of depth 22mm and the one year of climate data recorded in Heddal church. Climate data comprised both T and RH readings recorded by sensor every 5 minutes, but the sampling was reduced to one T and RH reading per hour. The depth of crack for simulation was chosen as the crack depth reaching the highest value of G in step RH change simulation and at the same time one of the critical depths in sinusoidal RH variations when T_{sin} longer than 30 days is considered. Results of simulation together with environmental parameters are presented in Fig. 1a). It can be observed that in this situation obtained *G* values were significantly below the critical value of $G_{Ic} = 250$ N/m.



Fig. 1 a) The full finite element simulation for 22mm crack depth and one year of climate data recorded in Heddal church. b) Two-parametric risk map for a sinusoidal RH change with constant $A_{sin}=30\%$, and sine period $T_{sin}=30$ days. Crack depth is plotted on *y* axis, time of the drying on *x* axis and corresponding energy release rate is plotted in the form of isolines. G_{Ic} is represented by the dashed line.

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 2021, 45 doctoral students (out of 50 accepted in two recruitments) continued their education. The education program in the 2020/2021 academic year included only the "Doctoral seminar", during which doctoral students presented their research results. Due to the epidemic situation, the classes were carried out on-line. Other elements of the framework program and additional activities resulting from the project implementation were organized, as planned, in theprevious years. All PhD students obtained the fourth year credit. In addition to curricular education, PhD students of the InterDokMed carry out their research on an ongoing basis, under the supervision of two tutors, from two different partner units, representing various scientific disciplines.

In the academic year 2020/2021, InterDokMed PhD students completed 10 internships abroad, participated in 14 courses / workshops, thematically related to the work they carried out. They co-authored 72 publications from the JCR list, 2 book chapters, and 2 popular science articles. They co-authored 61 oral presentations and 53 posters presented at national and international conferences. InterDokMed PhD students have won five awards, incl. for the best speech, popular science article. They received conference scholarships and finally scholarships for the best doctoral students in their home institutions and the President of the Polish Academy of Sciences scholarships.

2 people completed their studies after the fourth year, 43 doctoral students asked for the extension of their doctoral studies for the fifth year and received such consent. By the end of 2021, 6 people defended their doctoral dissertation, 5 of them received a distinction.



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. By the decision of NCBiR, the FCB project was extended until October 31, 2023. 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 four institutions; 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 (IFJ) of the Polish Academy of Sciences (IKiFP).

FCB doctoral studies are interdisciplinary. The interdisciplinary nature of FCB doctoral studies results from the participation of doctoral students in lectures and seminars in natural sciences in the discipline of chemical sciences and physical sciences. The assumptions of this project envisaged the education of 75 PhD students, currently 72 PhD students are studying under the project, including 3 students studying at IKiFP PAN. Until September 2021, there were 4 defences of a doctorates (from IFJ AGH and from WIMiC AGH), 2 of them were awarded. Additionally in 2021 three PhD students from IKiFP PAN started the procedure for the award of the doctoral degree.

In the 2019/2020 academic year the FCB schedule included 15 hours of doctoral seminar conducted in the summer semester. The doctoral seminar was held online via the *Skype* application. PhD students attended classes in 4 groups, including one group of 24 people led by the researcher from IKiFP PAN. Programme also included 30 hours of didactic lessons, PhD students made the instructional videos for laboratory for students of Faculty of Materials Science and Ceramics of the AGH University of Science and Technology in the field of qualitative analysis laboratories.

The scientific achievements of three PhD students from IKiFP PAN from the beginning of the FCB project include: 7 publications, 2 patents, 5 oral presentations. PhD students participated in 5 grants, including 2 Opus grants as contractor, 1 grant from the Solaris National Synchrotron Radiation Center, 1 European Union Soft Matter Infrastructure grant and 1 Preludium project (2018-2021), led by a doctoral student FCB.



Unia Europejska Europejski Fundusz Społeczny



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 the 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 become the basis of the cosmetic and dermatological composition for multiple use products in the near future. The application of other biologically active particles, like i.e. chitosan, silk fibroin or liposomes, will also be carefully studied. A 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. The skin will be simultaneously protected, lubricated, and regenerated thanks to them. 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 agricultural production in natural green pesticides. A similar application of the technology lets us soon reduce the number of synthetic surfactants incorporated into the natural environment.

During the project's second year, saponin-chitosan containing foam and emulsion systems were developed in parallel, with the emulsions based on Migoil MCT triglyceride oil. The research was carried out simultaneously using the equipment facilities of both institutes in Poland and Italy. It has been proven, using experimental techniques, i.e. nonlinear infrared spectroscopy, called Sum-Frequency Generation, and measurements of surface activity and elasticity, that saponin and chitosan interact with each other in solution, creating complex systems, thanks to which the inactive surface chitosan adsorbs to a significant excess in the surface layer, dramatically changing its flexibility and surface stability

Project funds also allowed for two-week research internships in Genoa for Dr. Marcel Krzan and Dr. Ewelina Jarek. The obtained results on emulsion systems were presented in an oral presentation at the international scientific conference ECIS 2021 European Colloid and Interface Society in Athens in September 2021. Two more project data publications are in preparation, which will be published in the first half of 2022 in ISI / JCR journals (the first project publication was published at the end of 2020).

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)

The project aims to develop a technology for producing and applying stable liquid foams and emulsions based on mixtures of hypoallergenic, non-toxic biological polymers, mainly the so-called biosurfactants. Furthermore, we want to enrich the developed formulations with additional nanoparticles, e.g. metallic silver or other nanoparticles of natural origin (e.g. chitosan, silk fibroin or liposomes). Surface films based on such naturally bioactive compositions would be the first line of defence against various pathogens.

During the project, measurements of dynamic and equilibrium surface activity and surface elasticity in solutions of one of the so-called "Green surfactants," i.e. n-dodecyl-ethyl-arginate enriched with colloidal silica nanoparticles (with different particle sizes - 6, 9 and 30nm). Based on the obtained results, the concentration ranges of the tested substances and mixtures necessary for forming a stable foam film were determined, which was verified by tests in an apparatus for measuring foam stability.

It was also found that the presence of particles influences the stability of surface layers made from n-dodecyl-ethyl-arginate much more than for films generated from BSA or methylcellulose. 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 from measurements of changes in dynamic surface tension. The obtained foam-forming and foam-stability tests showed that the foam-formation is closely correlated with the surface adsorption processes of the tested bio-surfactants and hybrid systems containing biosurfactants and solid particles.

The results obtained in the project were presented during scientific conferences and will be reported in a joint publication in the ISI / JCR journal in 2022. It was also used to prepare one review chapter in a scientific book.

Project ''Mobility for higher education students and staff" between Programme Countries



Program EU Erasmus+ [2014-2021] (koordynator programu: dr hab. inż. Aleksandra Pacuła)

In 2021, the following staff mobilities for training took place:

- Marcel Krzan National Research Council, Institute of Condensed Matter Chemistry of Technologies for Energy, Geneva (Italy)
- Marcel Krzan Institute of Chemical Process Fundamentals of the CAS, Prague (Czech Republic)
- Piotr Batys Aalto University, Aalto (Finland)
- Maria Morga Aalto University, Aalto (Finland)
- Maciej Guzik University College Dublin, Dublin (Ireland)
- Maciej Guzik University of Belgrade, Belgrade (Serbia)
- Małgorzata Ruggiero-Mikołajczyk Foundation for Research and Technology Hellas, Institute of Chemical Engineering Sciences, Patras (Greece)
- Małgorzata Ruggiero-Mikołajczyk Reykjavik University, Reykjavik (Iceland)
- Monika Wasilewska Institute of Technical Physics and Materials Science Centre for Energy Research, Budapest (Hungary)
- Magdalena Oćwieja University of Malaga, Malaga (Spain)
- Paweł Wolski University of Edinburgh, Edinburgh (UK)
- Magdalena Procner Philipps-University Marburg, Marburg (Germany)
- Maciej Szaleniec Philipps-University Marburg, Marburg (Germany)

The participation in the mobilities resulted in the collection of research data for articles in scientific journals of international scope and for conference contributions.

The project will continue in 2022 and another application for funding will be submitted for the 2022/2023 academic year.