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SUMMIT
SOFIA UNIVERSITY MARKING MOMENTUM FOR INNOVATION AND TECHNOLOGICAL TRANSFER

National Recovery and Resilience Plan
OF THE REPUBLIC OF BULGARIA

Sofia University - Marking Momentum for Innovation and Technological Transfer

Functional nanostructured materials for green energy and environment

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Contract BG-RRP-2.004-0008 for the financing of project "Sofia University - Marking Momentum for Innovation and Technological Transfer“ under pillar 2 "Establishing a network of research higher education institutions in Bulgaria", component "Innovative Bulgaria" from National Recovery and Resilience Plan part of the program to accelerate economic recovery and transformation through science and innovation

General aims of the project

- **Preparation of new functional materials on metallic, inorganic and organic basis using various synthetic methods: wet chemistry, metallurgical, solid-phase, sol-gel.**
- **Complex characterization of the microstructure and functional properties of the obtained materials.**
- **Study of the relationship between microstructure and properties of the synthesized materials and their applications (focus on clean energy and environment).**

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Specific aims of project:

- Synthesis and characterization of amorphous and nanocrystalline alloys based on selected metals such as Ni, Co, and Mo by rapid melt quenching and mechanochemistry revealing attractive catalytic activity towards hydrogen evolution reaction (HER) or oxygen evolution reaction (OER). Optimization of their composition and microstructure in terms of high catalytic activity and corrosion resistance in alkaline electrolytes.
- Formation of porous metal structures by selective chemical or electrochemical dissolution of amorphous and nanocrystalline alloys, thereby providing additional 'opening' of catalytically active sites for HER/OER.
- Develop materials (including nanostructured and nanoporous alloys and composites) demonstrating high hydrogen sorption capacity with appropriate thermodynamics and kinetics of hydrogen charge/discharge reactions.
- Development of a hydrogen storage tank based on newly developed materials.
- Development of a technology for production of micropolymer beads and membranes incorporating functionalized nano- and microparticles and their subsequent characterization.

- Investigation of the potential of newly developed functionalized polymer-aerogel composites for selective separation of heavy metals (e.g. Cd, Zn), rare earth and toxic anions (e.g. thiocyanate, cyanide) from environmental waters and industrial wastewaters
- Develop, optimize and characterize polymer inclusion membranes and granules incorporating existing and novel extractants (deep eutectics, macrocyclic cavitands) for selective separation of heavy metals (e.g. Cd, Zn), rare earth metals and toxic anions (e.g. thiocyanate, cyanide) from environmental waters and industrial wastewaters
- Modeling the interactions between modified conventional solvent extractants and a series of macrocyclic molecules (cyclodextrins and cucurbiturils) on the one hand, and heavy metal ions (e.g., Cd, Zn) and rare earths on the other, to elucidate the factors controlling the selectivity of these interactions
- Engineered extractants with enhanced selectivity towards target metal cations of heavy metals and rare earths

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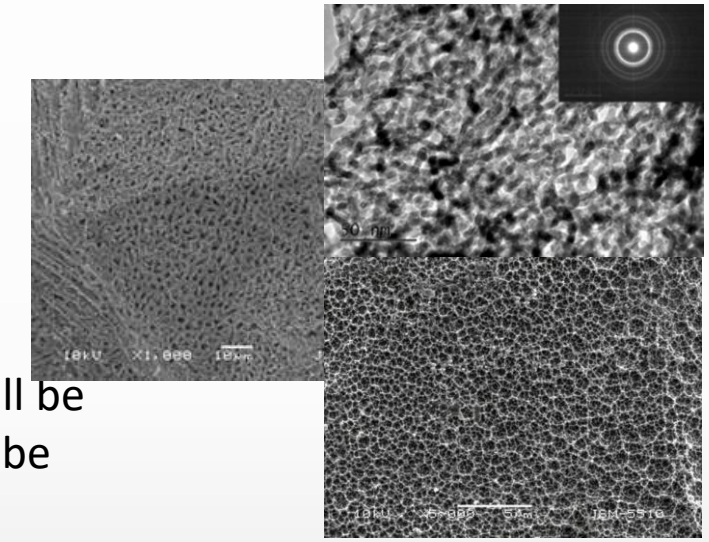
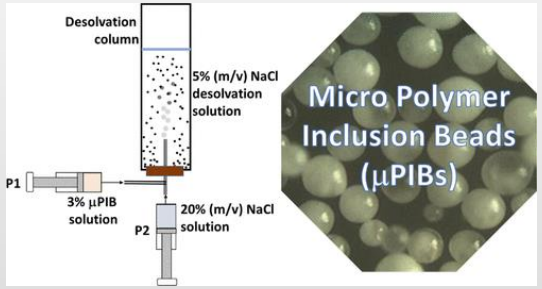
Expected results



- Nanostructured/microstructured and nanoporous metal and materials for aqueous electrolysis will be fabricated and microstructurally characterized.
- Efficient electrocatalysts for water electrolysis (HER/OER) will be developed.
- New amorphous and nanocrystalline alloys and composites for hydrogen storage will be prepared by applying advanced methods such as RQ and RMA. The composites will be used to develop an efficient laboratory hydrogen storage tank.
- Advanced novel composites in the form of membranes and beads that are composed of polymers and extractants (polymer incorporated membranes and beads) or functionalized silica aerogels and capable of selectively separating toxic metallic and non-metallic chemical species from their aqueous solutions will be produced and characterized. These composites will be used to develop methods for cleaning natural waters and industrial wastewaters.



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Administrative - staffing, equipment, publications, patents

- Appointed 3 young researchers (one young left and one new young joined) and 5 established scientists and one administrative secretary.
- Development and design of automated apparatus for solid phase extraction studies of metal ions and anions by polymer membranes.
- Published 15 scientific publications (Web of Science) and 1 (Scopus). 2 publications are under print and 3 are prepared for publication.
- One participation with an invited paper at an international conference: Joint RQ and ISMANAM: 17th Rapidly Quenched and Metastable Materials (RQ 17) and 27th Internationals Symposium on Metastable, Amorphous and Nanostructured Materials (ISMANAM 27), 20 - 24 August 2023, Warsaw, Poland.
- No patent or utility model has been registered yet but is planned for the second year.
- Workshops were held regularly throughout the period to discuss progress towards project objectives. The scientific group consisted of 6 established and three young scientists.
- Visit of distinguished scientist from NC university (USA) – prof. Orlin Velev: preparation of chitosan/n-Ag composites for battery application.

Some more significant results achieved in the first year

- Novel hierarchically structured microparticles with high catalytic activity.

A simple method for the preparation of CuO micro/nanoplates was developed. First, copper hydroxide acetate (Cu2(OH)3(CH3COO)-H2O) micro/nanoplates were successfully fabricated by a simple and scalable precipitation method using urea, and the formed product was pseudomorphically transformed into CuO. The physicochemical characteristics of the oxide particles were analyzed, and finally, the effects of CuO micro/nanolayers, H2O2, and visible LED irradiation on the degradation kinetics of sulfathiazole were evaluated for the first time. Sulfathiazole is a sulfonamide antibiotic that is commonly found in aqueous media and can affect human health. 100 % degradation of sulfathiazole and 87.3 % TOC removal were achieved within 90 min.

- Synthesis and physicochemical characterization of functional sol-gel composites

SiO2-based sol-gel composites doped with AuNPs gold nanoparticles and doped with dodecanethiol (DDT) - SiO2:AuNPs@DDT - were prepared for the first time. The preparation conditions of the hybrid composites were refined, and their UV/Vis optical spectra were investigated.

- Preparation and characterization of polymer-infused membranes and microspheres for solid state extraction

- Polymer inclusion membranes with crosslinking for rare earth ion extraction were developed.
- A system for the preparation of polymer inclusion hollow fibres was developed.
- Extraction experiments with PIMs with crosslinking were performed for the extraction of lanthanide ions
- Extraction experiments with PIMs containing as extractant a deep eutectic solvent consisting of decanoic acid and dodecanol were conducted.

- Electrocatalytic materials for aqueous electrolysis and Hydrogen storage materials

- Synthesis and microstructural characterization of Ni-Co-Fe-Cu based electrocatalytic alloys, and characterization of hydrogen absorption properties of AB5 and AB alloys.
- Promising characteristics of the metal hydride electrode LaNi4.5Co0.4Al0.1 prepared by induction melting followed by hydrogen-induced decrepitation were demonstrated.
- Synthesis and microstructural characterization of electrocatalytic amorphous zirconium-based alloys.

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- Storage of gases in porous molecules

➢ The incorporation of various "beneficial" and "harmful" gases into beta-cyclodextrins has been investigated - a topic aimed at both the storage and utilization of beneficial and the removal of harmful substances.

➢ The molecular modeling methods were used to investigate the binding processes of gases of practical interest (guest molecule, N_2O, CO_2, HCN, NO_2, SO_2, CH_4 and $CH_3CH_2CH_3$) with beta-cyclodextrin (host molecule). The key factors controlling the affinity of the "guest" molecule for the macrocyclic "host" were determined

➢ Combining experimental and theoretical studies, a new method was proposed for the incorporation of dinitrogen oxide into cyclodextrins. The thermal stability and capacity of the formed complexes to store N_2O and CO_2 were determined.

- Studies were conducted on the complexes of beta-cyclodextrin with citric acid. The complexes formed will be used to bind gas molecules as well as larger organic molecules

➢ Experimental characterization of the type of complexes and the efficiency of their formation under different conditions, and determination of their structure and thermal stability. The thermodynamic parameters of the complexation process of the respective complexes were also calculated, which showed agreement with the experimental observations.

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What's next

Research tasks are to be carried out under each of the Work Packages, depending on both the results achieved so far and the development of the research being carried out. A brief summary of the next tasks:

- Synthesis and characterization of hydrogen storage alloys based on AB and AB5 type compounds with improved sorption characteristics is to be carried out.
- High-entropy alloys with applications for both hydrogen production by electrolysis and hydrogen storage will be synthesized and investigated.
- Experimental and theoretical work will continue on the investigation of systems (including host-guest complexes) for the storage of useful and harmful gases and larger molecules.
- Synthesis and characterization of sol-gel composites with catalytic and optical applications.

  Preparation and characterization of SiO2-based sol-gel composites doped with gold nanoparticles AuNPs and doped with dodecanethiol (DDT) - SiO2:AuNPs@DDT and other substances. Dependence of optical properties and thermal conductivity of the synthesized composites on heating conditions.

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- Development of new chemical sensors for heavy metals. Investigation of the properties of N,N'-bis(salicylidene)-o-phenylenediamine - CAS: 3946-91-6 as a complexing agent for heavy metal detection. Incorporation of complexes based on Zn, Ni, Cu and other metals into silicate materials and use of the resulting composites as heavy metal indicators.
- Preparation and characterization of polymer-inclusion membranes and microspheres.
- Characterization of the mechanical properties of a wide range of polymer inclusion membranes (PIMs) (123 different membranes) containing glass fibers of different fiber concentration and length.
- Continuing extraction experiments with crosslinking PIMs for lanthanide ion extraction.
- Continuation of experiments with newly developed PIM transport systems via 3D printing. Experiments include zinc transport through PIMs incorporating diethylhexylphosphoric acid as an extractant and lanthanide transport through PIMs incorporating as an extractant deep eutectic solvents consisting of decanoic acid and dodecanol as well as TOPO and BTA.
- Experimentation with the system to produce polymer inclusion hollow fibres.

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