ACADEMIA ROMÂNĂ
SCOSAAR

Anexa nr.6

ABSTRACT OF THE HABILITATION THESIS*

TITLE : **Pickering Emulsion Polymerization and Janus Nanoparticles: a Versatile Platform for Advanced Materials in Environmental Remediation and Electronic Applications**

Habilitation domain: **Chemistry**

Author: **Dr. Andrei Honciuc**

This habilitation thesis explores the synthesis, characterization, and applications of amphiphilic and pseudoamphiphilic nanoparticles, in the development of advanced functional materials for environmental and organic electronics applications. The thesis covers four fundamental research directions: (i) synthesis and applications of amphiphilic Janus nanoparticles and pseudoamphiphilic silica nanoparticles; (ii) Pickering emulsions stabilized by the amphiphilic nanoparticles; (iii) nanostructured microspheres obtained via Pickering emulsion polymerization technology; (iv) advanced composite materials and their applications, obtained from nanoparticles and nanostructured microspheres.

In the beginning chapters, a significant focus is placed on polymeric Janus nanoparticles (JNPs), with two lobes, where each lobe possesses distinct and contrasting physical or chemical properties. From this contrast in properties of the two lobes, the nanoparticles are intrinsically amphiphilic, which enables them to perform multiple functions simultaneously and making them exceptionally versatile in stabilizing emulsions. Additionally, the thesis gives an introduction into the design, synthesis and functionalization of pseudoamphiphilic silica nanoparticles to also be utilized as stabilizers of

Pickering emulsions.

The research results demonstrate that amphiphilicity is scalable from the molecular scale to larger structures, allowing JNPs to self-assemble into a variety of supra-structures such as micelles, capsules, vesicles, and double-layered membranes. Due to this JNPs are capable of stabilizing Pickering emulsions and foams, and their activity can be finely tuned. By adjusting the relative size of the Janus lobes—one hydrophilic and one hydrophobic or one conductive and the other insulating—the overall physical and chemical properties of the nanoparticles can be gradually modified. The thesis also introduces the concept of pseudoamphiphilicity, for example in silica nanoparticles, which functionalized on their surface with a combination of hydrophilic and hydrophobic groups, such that they are mixed at the molecular level and not spatially seggregated resulting in materials that efficiently stabilize oil-water interfaces. The pseudoamphiphilic nanoparticles show exceptional interfacial activity and are employed as stabilizers in Pickering emulsions. These emulsions, provide a feasable platform for generating advanced materials for utilizing in applications ranging from encapsulation and controlled release to environmental remediation. Based on this platforms stimuli-responsive Pickering emulsions were developed. For example, the pH-responsive behavior of JNPs allows for reversible phase transitions in Pickering emulsions, an important step towards the development of environmentally aware materials.

Another important feature of the JNPs is the fact that the asymetric architecture allows for asymmetric surface modification. This enabled us to chemically modify independently only one of the Janus lobes. In this way we have constructed semiconducting-electrically insulating nanocouples by attaching on one of the lobes a semiconducting polymer. In this way we can obtian series of JNPs of variable conductivity by simply adjusting the relative size-ratio between the semiconducting and the electrically insulating lobe. This feature is especially valuable in applications such as organic electronics, where JNPs can used as pigments for conductive inks of variable conductivity, changing in this way the properties without modifying their chemical composition. Such tunability, achieved through morphological rather than chemical modifications, has significant implications for the design of advanced electronic devices, construction of electronic elements such as diodes, printed circuits, organic fillers, and adaptive sensor technologies.

The thesis also highlights the development of Pickering Emulsion Polymerization Technology (PEmPTech), a green, water-based synthesis method that allows for the production of polymer microspheres with nanostructured surfaces. The microspheres generated through PEmPTech have nanostructured surface, trapping during the polymerization a monolayer of self-assembled nanopaticles. The PEmPTech method is highly versatile allowing for the synthesis of a variety of microspheres, whereas their chemical composition, size, morphology, porosity can be finely tuned and controlled.

We have utilized PEmPTech for the synthesis of metal-ion adsorbtion. Several homologous series have been specifically engineered for the adsorption of heavy metals and organic pollutants from aqueous environments. The integration of pseudoamphiphilic silica nanoparticles into these microspheres results in materials with customizable surface chemistry and good adsorption capacity. An important aspect of the thesis is the analysis of how nanostructuring and surface functionalization influence the overall properties of these materials. For instance, the PEmPTech microspheres exhibit enhanced water wettability due to the self-assembled monolayer of silica nanoparticles on their surfaces. This modification significantly improves their dispersion in aqueous solutions and hydrophilic hydrogel precursors, enabling their use in complex matrices.

The PEmPTech microspheres have also been incorporated into hydrogel matrices, forming Hydrogel Polymer Microsphere (HPM) composites with unique properties, including the ability to float on water surfaces. This floating capability addresses the need for imporving the energy consumption associated with traditional water-pumping methods, providing a scalable and eco-friendly solution for wastewater treatment and hydrological mining. Such materials could be deployed for environmental cleanup, and can be realeased as floating adsorbents for heavy metal ions in lakes, rivers, and industrial effluents. Additionally, the thesis presents comparative analyses showing how the morphology and composition of these composites influence their adsorption efficiency, providing insights into optimizing material design for specific applications.

A further application of HPMs is their potential to function as flexible displays that can be written and erased with the help of an electrode stylus or stylus with a ink containing a reducing agent. The application potential of these HPM is also explored towards their potential use as fluorescence detectors for CN^- ions. Also in this thesis we investigate the electro-mechanic properties of the HPMs containg semiconducting Janus nanoparticles or semiconducting polymers, and their potential use as „robotic skins". In the same time we have also explored their potential to function as humidity sensors with significant potential towards development of specific gas sensors.

In conclusion, this thesis presents a comprehensive study of amphiphilic and pseudoamphiphilic nanoparticles, from their synthesis to their application in environmental and technological fields. The research underscores the potential of these materials in creating sustainable solutions for water purification, energy-efficient pollutant removal, and the development of advanced electronic and adaptive systems. By harnessing the unique properties of JNPs and pseudoamphiphilic nanoparticles, this work opens new paths for material science innovations, addressing pressing global challenges and paving the way for future advancements.

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