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Report on the PhD thesis manuscript of Mr. Daniel Aguilar Ferrer

The PhD thesis manuscript submitted by Mr. Daniel Aguilar Ferrer to obtain the grade of Doctor of Philosophy of the Adam Mickiewicz University (UAM, Poznan, Poland), and of the University of Montpellier (France) is entitled "*Understanding the Interface between Polydopamine and Metal, Metal-oxide Nanoparticles toward Photocatalytic Applications*".

This research work has been jointly conducted at the NanoBioMedical Centre of UAM and at the European Institute of Membranes of Montpellier, under the co-supervision of Dr. hab. Inz Emerson Coy and Dr. Mikhael Bechelany.

The main objective of this thesis is to explore the role of polydopamine (PDA) in improving the photocatalytic performance of gold and zinc oxide (ZnO) nanostructures. More specifically, the aim is to study how the interaction between PDA and these materials affects the photodegradation of rhodamine 6G (Rh6G).

The thesis manuscript is well organized and concise, it is divided into five main chapters.

The Chapter 1 introduces the state of the art and the challenges using nanosciences and nanostructuring of materials and presents the materials that were synthesized and characterized during this piece of work. The structure of polydopamine and related polymerisation process are described. Materials exhibiting plasmonic properties, in particular metals in the form of nanoparticles of gold, copper, silver, etc... as well as the density of states and metal/semiconductor interface theories are introduced. Gold/PDA combination and the creation of hybrid nanostructures are explored for different applications related to environment, nanomedicine, photocatalysis and their photothermal properties. This chapter is clearly written however one could have expected a more detailed overview regarding the targeted application, photocatalysis, including a comparative study in terms of performance with composite materials from the literature.

In the Chapter 2, the main objectives of the thesis work are introduced. From a methodological viewpoint, two main systems have been studied.
Firstly, the author reports on the study of nanocomposites based on gold nanorods and polydopamine (AuNRs/PDA), including the synthesis of different sizes and shapes of gold nanorods (AuNRs) followed by a polydopamine coating of various thicknesses, the analysis of the influence of PDA on the plasmon resonance and photocatalytic degradation of Rh6G. Experiments were carried out under UV-VIS and near infrared (NIR) irradiation to examine the thermal effect and the role of charge carriers.

Secondly, composite materials based on ZnO tetrapods and polydopamine (ZnOT/PDA) were investigated, including the synthesis of PDA-coated ZnOT structures with variations in roughness and morphology, the photodegradation tests on Rh6G under simulated solar irradiation and the photo(sono)catalysis experiments at different sonication frequencies and powers.
Complementary modelling aspects are also reported within the frame of this thesis work which brings a real added value to the discussion of the experimental results. Overall the objectives are clearly explained.

The Chapter 3 describes the materials and the methods that have been used during this research work, as well as the different characterization techniques, including the type of equipment and the experimental conditions that have been implemented by the author. Among the numerous and well-employed physico-chemical characterization techniques, one can mention transmission and scanning electron microscopies, UV-vis spectroscopy, inductively coupled plasma mass spectroscopy, Fourier transform infrared spectroscopy, thermal camera, femtosecond transient absorption spectroscopy (fsTAS) and X-ray photoelectron spectroscopy that are briefly described.

Chapter 4 presents the different synthesis and functionalization methodologies and protocols including Au nanorods and corresponding AuNRs/PDA composites, the use of electropinning to generate polymeric fibers in order to encapsulate the catalysts, and ends with the synthesis method for preparing ZnO-based composite materials. The experimental protocols to carry out the photocatalysis and photo(sono)catalysis measurements are described as well.

The Chapter 5, which constitutes the heart of this manuscript, focuses on the results and discussion. Regarding AuNRs/PDA nanocomposites, the experiments showed that combining the plasmonic properties of gold with PDA resulted in a strong photothermal effect, enhancing charge transfer and reducing carrier recombination. The photodegradation, combined with temperature increment were systematically measured. Analyses using femtosecond transient absorption spectroscopy (fs-TAS) and COMSOL modelling confirmed the role of hot electrons in the degradation of Rh6G. In particular, it was proven that temperature increment was not the main driving force triggering the photodegradation and the generation of reactive oxygen species were studied using scavengers. The recovering of the catalysts as well as their stability are discussed. A strategy consisting of encapsulating the catalysts in polymeric nanofibers generated by electrospinning is proposed. Even if the performance is quite limited, the idea is original and opens interesting perspectives.
Regarding ZnOT/PDA composites, the PDA layer improved photocatalytic activity, degrading up to 97% of Rh6G in 30 minutes. However, sonocatalysis experiments showed that the PDA could limit the effect of ultrasound waves on ZnO, opening up a new field of research. The band gap of the materials under study has been determined using absorbance spectra and Tauc plot. The study of the stability of the composite revealed no yield decay after several cycles that make this system a good candidate for photocatalysis application. Most of these results correspond to preliminary experiments which are very encouraging and opens very interesting perspectives.

In conclusion, through his thesis work, Mr. Daniel Aguilar Ferrer demonstrated that polydopamine plays a key role in improving the photocatalytic performance of metallic and semiconducting nanoparticles. He also proposes research prospects including the optimization of the thickness of the PDA layer to maximize plasmonic and photocatalytic effects, the exploration of new hybrid PDA/semiconductor material systems and finally an in-depth study of the interactions between PDA and ultrasound waves to improve sonocatalysis.

Overall, this work addresses major issues in the context of the use of nanomaterials for photocatalytic applications. The scientific contribution made by Mr. Daniel Aguilar Ferrer is of a high standard, as is the writing of the manuscript. The candidate was also able to draw on the recognized expertise and quality of the host teams in the field of nanomaterials synthesis and characterization for photocatalytic applications.

For all these reasons, I highly recommend the thesis of Mr. Daniel Aguilar Ferrer to be accepted for defense in order to obtain the degree of Doctor of the Adam Mickiewicz University (Poznan, Poland) and of the University of Montpellier.

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