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Evaluation of the Ph.D. thesis of M.Sc. Daniel Aguilar Ferrer Entitled „Development and Characterization of Polydopamine/Semiconductor Laminar Heterostructures for Efficient Photocatalytic Applications"

Today's environmental challenges and growing demand for renewable energy sources are making heterogeneous photocatalysis increasingly important in science and industry. These processes, which use semiconductors to initiate chemical reactions with the action of photons (light), are promising technologies in a wide range of fields - from water and air purification to the production of alternative fuels (e.g., hydrogen as a clean fuel).

The development of technologies related to heterogeneous photocatalysis is focused on improving the efficiency of catalytic materials and their adaptation to visible light absorption (including, the design of new photoreactors, especially in flow). Research into new nanostructures and composite semiconductor materials can make these technologies even more efficient and widely used in everyday life.

The submitted Ph.D. thesis for evaluation covers the above-mentioned science and technology topics, more specifically:

1. Photocatalytic water purification.
2. Sustainability - photocatalysis is an environmentally friendly process, as it does not require additional reactants (only light) and the use of common metals on earth (e.g., Zn) to synthesize these photocatalysts.

This doctoral thesis was executed thanks to the research collaboration between two research institutions, NanoBioMedical Center Adam Mickiewicz University in Poznań (Poland), and European Institute for the Membranes at the University of Montpellier (France) under the direct supervision of Dr hab. inż. Emerson Coy, and Dr (HDr) Mikhael Bechelany, respectively from those institutions.

This collaborative thesis contains in total: 158 pages, 186 references, 77 figures and 9 tables. The dissertation follows the standard structure for such a scientific documents. The whole thesis is written in English with abstracts in Polish and French. There are some typos to be corrected (for instance, page 29: it should be "Scanning Electron Microscopy", the unit for frequency must be written as "kHz").

On pages 25 and 26 the objectives of this dissertation are perfectly defined for AuNRs/PDA and ZnO/PDA. For the former objective, gold is chosen as plasmonic material, while PDA is selected as the organic semiconductor for testing in dye degradation (nice studies giving a lot of information trough PDA shell thickness influence, the changes of the temperature (using a thermal camera), scavengers to detect ROS species). Very remarkable as a part of this thesis, it is the study of AuNRs/PDA with femtosecond transient absorption (fs-TAS) spectroscopy, and the complementary support of experimental results with theoretical calculations using COMSOL Multiphysics. The second part of the thesis is focused on ZnO/PDA where ZnO is in tetrapod shape. Here, Zinc Oxide Tetrapods/polydopamine (ZnOT/PDA) composites were synthesized, and the interface semiconductor/PDA was broadly characterized including testing the materials in (sono)photocatalytic degradation of Rh6G (organic dye).

Having carefully read the received dissertation, the following revealing and innovative elements can be extracted from it:

- Nicely optimized 6 different AuNRs/PDA with AuNRs/PDA6 presenting the best performance and reproducibility. Inside, full information comes from the kinetics of the reaction of degradation, which came out with discarding the hypotheses of a thermal mechanism of photodegradation. In this part of the Thesis, the author combined experimental results with theoretical results calculated by using COMSOL Multiphysics, demonstrating the behavior of the hot electrons at the interface.

- The Reactive Oxygen Species (ROS) production was measured by scavengers, investigating their influence on the degradation mechanism (I would recommend to use Electron Paramagnetic Resonance (EPR) spectroscopy as a strong complementary technique supporting the scavengers outcomes). The author found out that in AuNRs/PDA6, PDA gives a strong photo-thermal effect where the PDA provides slow thermalization, enhancing the charge carrier transfer and reducing the recombination rate by allowing the electrons generated in Au to be rapidly transferred to the PDA, where they underwent several reactions of photodegradation of the organic dye.

- Photo(sono)catalysis experiments were carried out under a range of low frequencies and power giving interesting results supported by perfectly done kinetic studies.

Below, I would like to highlight some minor comments, questions, and/or doubts that do not, in any way, detract from my positive assessment of the work of M.Sc. Daniel Aguilar Ferrer, and I hope to get answers to them during the dissertation defense, namely:

1. If you had the opportunity (the only opportunity) to choose one more technique/method to definitively prove (or improve) the mechanism of the formation of PDA-metal/semiconductor heterojunctions, what method/technique would it be?.
2. Does the author believe that conducting Life Cycle Assessment (LCA) and Techno-Economic Analysis type studies is possible and valid for the type of research included in this dissertation?.
3. What were the reasons for assuming that the kinetics of the reaction (Rh6G degradation) is based on the Langmuir-Hinshelwood (L-H) model?. Did the author check other models?. For this reaction, What is the reason for using an intense light NIR laser (808 nm)?.
4. Which evidence has the author for the strong photo-thermal effect detected due to the combination between the plasmonic properties of Au with the properties of PDA?.
5. Is it really degradation of Rh6G? or, Could it be the decolorization of the solution?. What about the grade of toxicity of the solution (water) after the photo(sono)catalytic test?.
6. How do you explain the blocking effect of PDA against sonication?. Could be PDA transparent to sonication?. According to the author statement (in the "abstract"): "PDA layer blocks the effect of the sonication waves in the ZnOT (Zinc Oxide tetrapods)". Did the author have some measurements supporting that?. As far as I am aware of, polydopamine (PDA) is generally considered to be acoustically transparent or at least not highly attenuative to ultrasound acoustic impedance (of course, its transparency to ultrasound waves depends on various factors, for instance, the thickness and density of PDA).
7. For ZnO/PDA (and for any (photo)catalyst), three consecutive photocatalytic rounds are not far enough. In the open literature, at least five runs are recommendable. What do you think?.
8. On page 26: What do you mean by "yield of the photocatalytic reaction"? Quantum yield?.
9. May I ask the author to give more details on the piezoelectric properties (measured by himself) of ZnOT and ZnOT/PDA1?.

10. According to the author (page 116) statement: "These results suggest that sonication indeed facilitates the charge carrier separation induced by the irradiation and decreases the recombination rate, thereby increasing photodegradation". Is sonication the responsible, or the piezoelectric effect of the material by absorbing the mechanical energy of sound waves?.

I see all of the above as a sign of arduous work and the ability of the candidate to collaborate with the supervisors and collaborators. This is a proxy of the candidate's maturity as a scientist and the potential to become a leading researcher in the future. Besides, ample discussion, rational interpretation of the results, and proposed exploratory future possibilities are commendable efforts. Apart from that, the scientific output of Daniel Aguilar Ferrer, MSc, is very good with 5 publications (among them two as a first author) achieved during his doctorate studies.

In conclusion, I find that the doctoral dissertation of Daniel Aguilar Ferrer, M.Sc., presented for evaluation, meets the standards of the Act of July 20, 2018. Law on Higher Education and Science (Journal of Laws of 2024, item 1571) in Poland, and therefore, it is requested that the Council of the Faculty of Chemistry of the Adam Mickiewicz University in Poznań admit the doctoral candidate to the next stage of the doctoral defense.

Sincerely yours,

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