GDAŃSK UNIVERSITY OF TECHNOLOGY
FACULTY OF APPLIED PHYSICS AND MATHEMATICS

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EXCELLENCE INITIATIVE

dr hab. inż. Jacek Ryl, prof. PG
Institute of Nanotechnology and Materials Engineering
Faculty of Applied Physics and Mathematics
Gdańsk University of Technology

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Review of doctoral dissertation

Daniel Aguilar Ferrer, M.Sc.

entitled "Understanding the Interface between Polydopamine and Metal, Metal-oxide Nanoparticles toward Photocatalytic Applications"

This review was prepared based on the letter from the Dean of Chemistry Faculty, Prof. Dr hab. Maciej Kubicki (RPW/653/2025 N). The doctoral dissertation submitted for evaluation was carried out between the NanoBioMedical Center of Adam Mickiewicz University in Poznań and the European Institute for the Membranes at the University of Montpellier, France. The doctoral dissertation was supervised by Prof. Emerson Coy (AMU) and Prof. Mikhael Bechelany (IEM). The project was financed by OPUS grant 2019/35/B/ST5/00248.

The research undertaken within this doctoral dissertation is focused on fabricating and characterizing nanoparticles and microstructures with functionalities developed by the presence of polydopamine (PDA) thin film coverage. The Author aims to study the interfaces between the PDA and gold (a plasmonic structure) and ZnO (semiconductors selected for these studies). The axis that unites both thematic areas of scientific achievement is the use of polydopamine to modify functional properties, in particular, to impart photocatalytic properties and an attempt to understand the influence of PDA on the physicochemical properties of both types of materials. The reference organic compound used for photocatalytic decomposition in this study is Rh6G.

Heterogeneous photocatalysts represent a vital area of modern research, owing to their ability to harness light energy to drive chemical reactions, paving the way for sustainable and eco-friendly processes. These catalysts are extensively utilized in environmental remediation, where they break down pollutants in water and air and in solar energy conversion, aiding in producing solar fuels and hydrogen. Additionally, integrating plasmonic structures and phototherapy has expanded the range of properties and applications of these materials, further enhancing their efficiency and versatility. PDA has attracted considerable scientific interest due to its remarkable adhesive properties, biocompatibility, and ability to form coatings on virtually any surface, inspired by the adhesive proteins found in mussels. PDA has been shown to effectively create heterojunctions, reducing unfavourable recombination effects and significantly boosting photocatalytic performance. These unique characteristics make PDA a highly adaptable material for various applications, including energy harvesting, biomedical engineering, and surface modification. For this reason, the research

topic of the PhD dissertation of Mr. Daniel Aguilar Ferrer concerns a very current and essential problem for materials engineering, chemistry, physics and beyond.

The doctoral thesis is built in the traditional form of a manuscript, composed of nine chapters: Introduction, Objectives, Materials and methods, Experimental, Results and discussion, Conclusions and perspectives, Annexes, Supplementary information and References. The introduction is well constructed and provides vital information on the current state of the art of PDA formation, electronic structure, and a wide range of properties related to the studied materials. The Author introduces these data in subsequent subchapters. To the best of my knowledge, the references in the introduction constitute an accurate and complete description of the current state of knowledge in this field. Yet, the Author did not put enough care in considering several connectors to guide the reader to better understand why he chose these particular metal/metal oxides and geometries and structures. For example, why were gold nanorods selected from numerous forms and shapes of gold nanoparticles, why ZnO tetrapods were chosen, and why zinc oxide in the first place? Indeed, after reading the title of the dissertation, one could expect to find broader information on different metal and metal-oxide structures, at least in the introduction section. This explanation is even more needed, after reading the Author's own statement that the properties of the nanoparticles are highly dependent on their shape, size etc. The dissertation title may also be misleading, considering the size of the ZnO tetrapods, which cannot be considered nanoparticles by traditional definition.

The materials and methods section has all the required information regarding the reagents and equipment used. I believe a large part of this section could be excluded from the dissertation, though. Explanation of *modus operandi* for popular, commonly used techniques such as SEM, TEM, UV-Vis, XPS, FTIR or even ICP-MS may be easily found in numerous books and does not correspond in any way to the state of art tackled by this research. Instead, reading about specific challenges related to these experimental techniques would be interesting, i.e., the purity of the acids used to dissolve AuNRs for ICP-MS, pre-treatment before XPS, information about charge compensation protocol, etc.

As Mr. Daniel Aguilar Ferrar stated, the PDA structure is still unknown, same as its polymerization process, and requires numerous further investigations. Thus, among the leading research goals, the Author emphasizes the synthesis of AuNR and AuNR/PDA with controlled characteristics and fabrication of PDA-covered ZnO tetrapods. In both cases, the Author has the ambition of controlling the fabrication protocol to obtain reproducible structures and identify the mechanism and kinetics of Rh6G degradation. The Author does not outline and specify a research hypothesis directly, yet few of them are defined and verified in the subsequent stages of the manuscript.

The results and discussion chapters follow the above-described path and are divided into two areas, i.e. devoted to AuNR and ZnO. The research on AuNR synthesis and subsequent functionalization with PDA are undertaken and described in Chapter 5.1. I consider the level of control on the synthesis protocol and, as a consequence, on AuNR's properties to be one of the most valuable achievements of the PhD student and a testimony to his skill in chemical synthesis. The use of CTABr is indeed necessary for the formation of specific shapes of gold nanoparticles. However, this compound significantly hinders further surface functionalization (in this case by PDA), which is a significant scientific and technical challenge for many research teams, including my own. Using thiolated polyethylene glycol as the intermediate to PDA film formation was found to

be an effective solution. The PDA shell thickness was tunable by modifying the dopamine hydrochloride concentration or the reaction time. Shifts in localized surface plasmon resonance measurement monitored the outcome of this process. The Author also proposed a very interesting approach to measure the AuNR concentration in the solution employing ICP-MS.

Next, the photocatalytic experiments were carried out on Rh6G, revealing the dependence between the PDA thickness and the degradation efficiency. Regrettably, the overall Rh6G removal rates did not exceed the kinetics that would allow them to be in competition to other photoactive nanoparticles at this point. In particular, it considers loss in removal efficiency in subsequent photocatalysis cycles. After a series of well-structured thermal response experiments, the Author concluded that the main role of AuNRs in the degradation process is the transfer of excitons to PDA. Finally, using femtosecond transient absorption spectroscopy, the Author confirms his earlier hypothesis, revealing that the PDA layer can capture charges that gradually diffuse back to the Au and release heat.

Within Chapter 5.2, Mr. Daniel Aguilar Ferrer focuses on PDA covering and in-depth characterization of ZnO tetrapod. The Author skillfully utilizes the previously acquired know-how on PDA synthesis while simultaneously adapting the methodology to new challenges, such as the formation of PDA aggregates cage inside ZnO microstructures. Mr. Daniel Aguilar Ferrer notices that combining ZnO with catechol from the PDA binding with the hydroxyl group and decreasing ZnO surface oxygen vacancies may act as electron traps, affecting the recombination rate. Yet, the TEM findings reveal that ZnOT does not resist mechanical stirring and that the PDA film is easily torn off from the substrate. This raises a question on the adsorption mechanism of the PDA in this scenario and causes significant issues in data reliability, as honestly addressed by the Author.

Nevertheless, the ZnO/PDA offer significantly higher RhG6 removal rates, which, however, are related to the photocatalytic properties of ZnOT. A very interesting follow-up of this part of the manuscript is the approach to trigger the piezoelectric response from the ZnOT/PDA composites by sonication. While the improvement was negligible for the composite, the idea succeeded for bare ZnOT.

Finally, a short 2-page annexe at the end of the dissertation reveals results from a collaborative work by the Author on MXene/PDA synthesis. These structures are very interesting and might offer a promising range of applications. Regretfully, none of them were reported in the text.

In my opinion, one of the most noteworthy areas of the PhD dissertation is a very rich and innovative workshop of advanced and non-trivial research techniques, which the Author properly selects and efficiently uses. Consequently, expanded analysis using a wide range of research tools allows him to confirm or reject previously posed hypotheses. Moreover, the Author's sincerity should also be acknowledged, as he is able to admit the low reliability of some of the obtained data. This feature seems to be an obvious requirement from a scientist, yet, is not always observed. Another strong side of the research is its interdisciplinary and international nature. Indeed, the PhD thesis itself is the fruit of a very effective collaboration between high-profile research groups in Montpellier University in France and Adam Mickiewicz University in Poland. One should also emphasize that part of the samples were obtained from the University of South Denmark and Kiel University in Germany.

On the other hand, I have mixed feelings regarding the editorial layer of the dissertation. It must be highlighted, that the document is well edited, the cause-effect chain is preserved, and the reader has no problems following Mr. Daniel Aguilar Ferrer's train of thought while conducting new and numerous experiments. The figures are also well structured and prepared to allow data analysis to be followed properly throughout the manuscript. Yet, I feel that the manuscript part dedicated to AuNR and ZnO could be connected more efficiently; some subchapters are overextended, as previously mentioned. What is the point of chapter 4.1.4 if MXenes were not used in the manuscript? The Author did not pay enough attention to small grammar, punctuation and similar errors, such as eaten spacebars, upper/lower indices not always used for chemical formulas, K instead of k for *kilo* prefix, etc. Finally, reading the small scale on axes or legends of some graphs (i.e. Fig. 16, 18, 21, 22 etc.) is challenging.

Below, I would like to list a few questions and comments, inviting the dissertation Author to offer a more detailed insight on several aspects of his research thesis:

1. Why were AuNRs chosen over other, different types of gold nanoparticles?
2. Is the adsorption of Ag+ ions during AuNR formation a factor affecting nanorod properties and PDA interactions, or is the silver removed in the post-treatment processes? Did you try to analyze ICP-MS for silver?
3. Would the PDA film formation route developed by the Author be transferable to other metal and metal oxide structures?
4. What is determined as success indicators to prepare a mixture for electrospinning? The Author mentioned about the preparation of different polymer mixtures, but not all of them are studied in detail in the manuscript
5. Given that the TEM reveal the undamaged structure of AuNR/PDA after photodegradation events, what is the suggested mechanism behind retention loss? The "non-straightforward recovery process" statement is vague and needs further explanation.
6. As the results of photodegradation with ZnO/PDA are indeed less representative or reliable, did the Author try to perform several repetitions to verify the possibility of minimizing the obtained errors?
7. What is the expected error of ICP-MS estimation, considering the possible presence of Au ions in the electrolyte (i.e. from $HAuCl_4$) and the most certain presence of Zn^{2+} from different sources?
8. In the XPS analysis, please provide the reference to attribute C1s peaks (at 284.8, 286.1, 287.3, 288.8 and 290.2 eV) with aromatic polymer (Fig. 62c). Was there any pre-treatment used before the XPS analysis, such as Ar-etching?

Neither the questions listed above nor the comments presented in the earlier part of my revision do not undermine the scientific quality of the presented studies and do not lower my very positive assessment of its Author, Mr. Daniel Aguilar-Ferrer. I believe the studies presented in the manuscript and provided analyses and interpretations offer new and unique value to the field. The proposed experimental path is deeply explained and expanded upon receiving subsequent experimental results, adequately determined, and often unique. The research workshop and interdisciplinary approach to the undertaken research problem all demonstrate the scientific maturity of the candidate for the Ph.D. degree.

Mr. Daniel Aguilar Ferrer is the Author of five articles, the most notable of which is published in the very prestigious *Advanced Functional Materials*. This manuscript strictly corresponds to the Ph.D. dissertation, and Mr. Aguilar-Ferrer is the first Author. Moreover, he is co-author of two research papers and two review papers (once as first Author) in other very reputable journals related to PDA films. The five articles were cited 145 times (Scopus, 08.02.2025), which is very high considering recent publication. These numbers testify that Mr. Aguilar-Ferrer is a well-established young researcher, experienced in nanoparticle synthesis and modifications.

Summarizing my review, I state that the research goals set by Mr. Daniel Agilar Ferrer have been fully achieved, and the results obtained by him are characterized by high innovativeness, allowing to exceed the existing state of knowledge in particular in the fields of chemical sciences, nanotechnology and materials engineering. The submitted doctoral dissertation, entitled: "Understanding the Interface between Polydopamine and Metal, Metal-oxide Nanoparticles toward Photocatalytic Applications" is, in my opinion, a significant scientific achievement. Thus, the study meets the formal requirements for doctoral dissertations in accordance with the Act of 20 July 2018 - the Law on Higher Education and Science, Republic of Poland (Journal of Laws item 1668, as amended). In view of the above, I request the Scientific Council of the Chemical Science Discipline of Adam Mickiewicz University to accept the doctoral dissertation and admit Mr. Daniel Agular Ferrer to the next stages of her doctoral studies.

Signed by / Podpisano przez:

Jacek Ryl
Politechnika Gdańska

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