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Review of doctoral dissertation

Jakub Szewczyk, M.Sc. Eng.

entitled „Development and Characterization of Polydopamine/Semiconductor Laminar Heterostructures for Efficient Photocatalytic Applications"

The basis for this doctoral dissertation review is a letter from the Dean of the Faculty of Chemistry of Adam Mickiewicz University in Poznań, prof. Maciej Kubicki, dated April 25, 2024 (RPW/18200/2024 N). The doctoral dissertation submitted for evaluation was prepared 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 groundwork for the research thesis is the development of fabrication methodology for large-scale nanometer-thick polydopamine (PDA) films, their detailed photochemical, structural, and electrochemical characterization, and assessment of its utility for various photocatalytic applications by heterojunction formation by placing the PDA film on semiconductor substrates. Heterogeneous photocatalysts are a crucial area of research due to their potential to drive chemical reactions using light energy, which can lead to sustainable and environmentally friendly processes. They are widely applied in fields such as environmental remediation, where they degrade pollutants in water and air, and in solar energy conversion, contributing to the development of solar fuels and hydrogen production. Concurrently, PDA has garnered significant attention in the scientific community for its exceptional adhesive properties, biocompatibility, and ability to coat virtually any surface, inspired by the adhesive proteins of mussels. It was found to effectively form heterojunctions, limiting unfavorable recombination effects, and contributing to the enhancement of the photocatalytic effect. These unique attributes make PDA highly versatile for various applications and surface modification, from energy harvesting to biomedical engineering. However, scaling up and industrializing research on nanometer-sized structures, including the production and application of heterogeneous photocatalysts, presents substantial challenges, related to uniformity and stability of nanomaterials at a large scale, addressing the development of cost-effective manufacturing processes and potential health and environmental risks.

The doctoral thesis is built in the form of a guide to six scientific articles, published by the Ph.D. student in the renowned journals. In this context, it has a typical structure, where the articles are preceded by three chapters i.e. (i) introduction to the research topic, (ii) presentation of main goals of the research thesis, and (iii) detailed discussion of the research methodology. Importantly, the manuscript culminates with conclusions, future perspectives sections, and an impressive list of Mr Szewczyk's scientific achievements. Mr. Szewczyk forms three research theses (among four theses proposed, Thesis I should be considered as a perspective statement rather than scientific hypothesis), channeling his research to confirm that: (i) controllable synthesis of PDA films allows for scaling to macroscopic level and superior mechanical stability; (ii) effective PDA film ex-situ transfer capability directly from solution to TiO_2 or ZnO surfaces and heterojunction formation and (iii) ex-situ transferring films will enable formation of advanced architectures and large-scale multilayer laminar structures.

Two first scientific publications are review articles, presenting the current state of the art related to developing polydopamine (PDA)-based photocatalytic nanocomposites from the perspective of physicochemical and electrochemical characteristics and their applications. The first review article, published in Catalysis Today has 455 references, while the second article in European Polymer Journal has 150 citations. Moreover, the manuscript itself is supported by 117 references. Naturally, some of the references might be duplicated between these works. Yet, their richness and reference to the latest trends in the field of nanotechnology and its application, especially in photocatalysis, and more specifically, the development of PDA films, leaves no doubt that Mr. Szewczyk is fully familiarized with and moves freely in the research topics he undertakes.

The third manuscript is dedicated to the fabrication method of 2D PDA thin films, revealing the outstanding potential of scalability up to the centimeter range, which may be tuned by fabrication conditions. Authors manage to obtain continuous and homogeneous PDA films even without functional agents and at low dopamine concentrations compared to other available literature sources. Next manuscripts propose and discuss implementation of this research. The fourth reviewed document focuses on the utility of boric acid and Cu^{2+} ions during PDA film growth, exploring different organization pathways, covalent vs non-covalent self-assembly, and their effect on film mechanical properties. The manuscript offers a direct and real-time monitoring of film growth and an in-depth discussion on physical self-assembly vs covalent bonding of dopamine monomers, highlighting significantly higher mechanical resilience through the former route and using boric acid.

The last two manuscripts focus on the transferring of PDA films on semiconductor interfaces and the formation of organic-inorganic heterojunctions. In the fifth paper, PDA films were transferred from the air/water interface on the surface of Si(100), Si/TiO_2, and Si/ZnO, revealing important observations regarding different physicochemical properties between scooped and stamped PDA films on the substrate. Importantly, ZnO/PDA interfaces were found to be characterized by a smaller number of electron-donor interactions, negatively affecting electron charge transfer through the interface. Yet, the easily-transferrable PDA films were found to successfully enhance the photocatalytic properties. Given the superior characteristics of TiO_2/PDA in the previous experiment, these were further utilized to form sandwich-like multilayer nanocomposites in the sixth manuscript. The most important and original finding of this work is the new and unique type of TiO_2 doping through both substitutive and interstitial nitrogen atoms from PDA as it adheres to the TiO_2 surface via catechol and amino groups. This gradient nitrogen doping is highly interesting from the perspective of photocatalytic properties as it provides new energy levels inside the forbidden band, lowering semiconductor band gaps.

Mr Szewczyk's role as the first and corresponding author in all but one of the review articles, as well as the author statement from contributors leave no shade of a doubt, that he took the leading and dominant role in conceptualization, investigation, and preparation of the discussed manuscripts.

The editorial layer is presented with great detail, yet the Author's oversight is the failure to include supplementary information files together with the articles, which makes it difficult for the reader to get acquainted with the series of performed experiments without reference to external sources. All of the experimental works are characterized by attention to detail and the use of multiple and complementary microscopic and spectroscopic tools, including AFM, SEM, TEM, XPS, XRD, Raman spectroscopy, Brillouin light scattering, DLS, UV-Vis, FTIR, photoluminescence and more. The Author and his group also proposed and developed a tool dedicated to measuring the thickness of very thin layers - spectroscopic reflectometry. Also, the way of measurement data presentation is consistent throughout different manuscripts, which facilitates effective comparison of results and tracking of observed relationships.

The review of a publication guide is both more simple, yet also more demanding for the reviewer because the presented documents were subjected to rigorous review before publication in prestigious journals. Guided by the reviewer's duty to look for loopholes, and encouraged by the dimensionality of the presented research I invite the Author of the dissertation to expand the already presented discussion in the following aspects:

1. What is the origin of the loss in uniformity of the PDA film thickness reported in the third manuscript? It appears that dopamine concentration, pH, and even stirring speed influence uniformity. In particular, the stirring speed increase shows no logical trend, both 200 and 300 rpm reveal higher uniformity compared with 250 rpm. Eventually, the Author optimized the procedure to obtain PDA film uniformity but without proposing any mechanism. Perhaps it was related to errors related to PDA film synthesis methodology or film thickness methodology (scan direction or other factors). Did you perform XPS analyses for different distances from the center of the PDA film?
2. In the same manuscript, Authors discuss a small, 0.5 eV shift in the R_2-NH *N 1s* peak on XPS data, connecting it with the presence of $(dopamine)_2$/DHI 5,6-(dihydroxyindole) complex and more homogeneous surfaces. Such peak shifts may easily originate from differences in the electronic properties of materials. The only spectra correction applied here is spectra correction by the "spurious carbon method". Please explain this approach. It is calibration by adventitious carbon? Why the flood gun was not used in this case? Low-energy electrons and ions bombardment should not lead to changes in surface oxidation states.
3. Did the Author or other group members use spectroscopic reflectometry in other studies on different materials and processes i.e. adsorption, and biosensing? I assume that the accuracy of measurements strongly depends on the film thickness. What is the applicable thickness range? Please briefly discuss SR's strengths and limitations.
4. Given that the Author mentions the PDA film utility toward electrochemical sensing or membrane technology I wonder how the Author perceives the Cu^{2+} and boric acid effect on the transport properties of different species through the PDA films.
5. The efficacy of methylene blue photocatalytic decomposition presented in Article 5 is debatable. First, the scale of C/C_0 (Y axis) should start from 0, not 55%. While covering TiO_2 with PDA indeed increases the decomposition efficacy and retention over a few cycles, I wouldn't call it remarkable

as the Authors did, since many photocatalysts offer even over 95% removal in similar timeframes. Moreover, the Authors do not present the data regarding MB adsorption in the dark, thus the proof for the photocatalytic action is not demonstrated.

6. In the same work, when analyzing the EIS results authors use constant phase elements. Its use instead of capacitance should be linked to heterogeneity, either with surface or normal distribution. Please discuss differences in CPE values (in particular CPE exponent n) between studied samples.
7. Finally, given the different hydrophilicity and roughness of scooped and stamped PDA films in the fifth manuscript did you consider the performance of the XPS depth profile?
8. How would the Author comment on the possibility of TiO_2 doping during multilayer nanocomposite formation by other heteroatoms introduced to the PDA film structure, i.e. through physical entrapment or covalent bonding, such as presented in Manuscript 3?

The comments and questions listed above do not undermine the scientific quality of the presented studies and do not lower my very positive assessment of the reviewed documentation. I say firmly, that the cognitive value and originality of the proposed solutions are at a high, world-class level, demonstrating the scientific maturity of the candidate for the Ph.D. degree. Apart from the quality of conducted research, Mr Szewczyk's research is characterized by thoughtful and often innovative nature, well-built research hypotheses, and properly selected experimental techniques.

Mr Szewczyk was offered excellent conditions for development within the research group of Prof. Coy, which he took full advantage of. Moreover, he expanded his experimental workshop through multiple internships and international cooperations, including a 12-month stay at the University of Montpellier, with Prof. Bechelany's group at IEM. In 2023, he also took two short internships at the Catalonia Institute for Energy Research (Barcelona, Spain) and the Technical Faculty of Christian Albrecht University (Kiel, Germany). As a capable young scientist, he managed to acquire funds for his research from the National Science Centre, entitled "*Development and chemical tuning of novel 2D-like polydopamine ultrathin membranes*" (2021/41/N/ST5/00211) under Preludium frame. He also took part in three different research projects. Mr Szewczyk gathered exceptional achievements, before and during the Ph.D. program, including scholarships from the Minister of Science and Higher Education in Poland (2019), the French Government Scholarship (2021), and the Scholarship for Doctoral Students of the AMU Foundation (2022).

To sum up my review, I can with full confidence testify that the dissertation presented by Mr. Jakub Szewczyk contains many original research results and significant elements of scientific novelty, reaching beyond the existing state of the art and contributing to the development in the fields of chemical sciences, materials engineering, nanotechnology, and physics. The author has managed to confirm all hypotheses and fulfill all the set goals. The assessed doctoral dissertation Mr Jakub Szewczyk, entitled: "*Development and Characterization of Polydopamine/Semiconductor Laminar Heterostructures for Efficient Photocatalytic Applications*" exceeds the formal requirements for doctoral dissertations under the Act of July 20, 2018 - Prawo o szkolnictwie wyższym i nauce (Dz. U. poz. 1668 z późn. zm.). Given the above, I recommend to the Chemical Sciences Discipline Council of the Adam Mickiewicz University in Poznań to accept the doctoral dissertation and admit Mr. Jakub Szewczyk to the next stages of the doctoral conduct.

Taking into consideration the outstanding quality of the research conducted by Mr Jakub Szewczyk, its potential significance in numerous fields, and its perspective practical utility I also recommend the Chemical Sciences Discipline Council of the Adam Mickiewicz University in Poznań to distinguish the doctoral thesis.

Mr Szewczyk's dissertation is characterized by an outstanding level, in-depth consideration and understanding of the researched area, correct and complete formulation of original research hypotheses, and their full proof. Thus, the publications submitted significantly go beyond the current state of knowledge in the fields of chemical sciences, nanotechnology, materials engineering, and related sciences.

The doctoral dissertation outcomes stand out due to its potential for enhancing sustainable and environmentally friendly processes through improved heterogeneous photocatalysts. This research is particularly noteworthy as PDA's unique adhesive properties and biocompatibility, combined with its ability to form effective heterojunctions and enhance photocatalytic effects, address significant challenges in scaling up nanotechnology while offering versatile applications from energy harvesting to environmental remediation. The most important, original findings of Mr Szewczyk's dissertation are the following:

- Successful control over the synthesis of PDA films at the air/water interface, while the free-standing films reach the centimeter scale.
- Designing and successfully utilizing a novel spectroscopic reflectometry tool to measure on-line the nanometer-scaled thicknesses of PDA films during their formation
- Understanding and controlling the mechanism of dopamine oxidation by boric acid and copper ions, the former allowing to obtain ultra-thin, below 20 nm film thicknesses, while maintaining excellent mechanical properties
- Successful transfer of the large-scale PDA films on semiconductor substrates, revealing a significant bandgap shift toward lower photon energies (TiO_2/PDA), which boosts the electron transfer at the interface and lowers local heating effects in TiO_2
- Discovering and providing a description for a new, previously undescribed mechanism for gradient-like N-doping of TiO_2 in multilayered nanocomposites, where nitrogen occupies both substitution and interstitial positions of the TiO_2 lattice, significantly reducing the band gap.

Most importantly, the centimeter-sized and nanometer-thick PDA films offer a great promise of scaling up the technology and material commercialization, offering not only scientific but also technological advancement. The capability for a simple, direct, and repeatable transition of PDA films formed at the air/water interface to other substrates, successfully boosting photocatalytic activity creates the opportunity to expand technologies of remediation systems, organic photovoltaics, and more. In the chapter devoted to research perspectives, Mr. Szewczyk reveals that the above-mentioned achievements are only an element of a broader research policy that he implements together with his supervisors, and within international research teams, among others from the European Institute for the Membranes, Southern Denmark University and Christian-Albrecht University in Kiel. Full understanding of the research being conducted, the ability to direct it, and find sources of financing (obtaining an NCN Preludium grant) is the domain of mature scientists and emphasizes the distinctive character of not only the dissertation itself but also the candidate for the doctoral degree.

The thesis meets the formal requirements given in Adam Mickiewicz University Faculty of Chemistry Dean's ordinance 3/2021. Among six articles in JCR-listed magazines discussed and strictly related to the dissertation, four present new experimental findings (two remaining ones are review documents). These were published twice in ACS Applied Materials and Interfaces (top 92% by Scopus, IF = 8.3), in European Polymer Journal (top 92%, IF = 5.8), and in Materials Today Chemistry: top 84%, IF = 6.7.