Faculty of Materials Science
and Engineering

WARSAW UNIVERSITY OF TECHNOLOGY

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DISSERTATION REVIEW REPORT

The report was prepared in response to the letter of Professor Maciej Kubicki, PhD, DSc, Dean of the Faculty of Chemistry, Adam Mickiewicz University, Poznań, from 28.06.2023.

Thesis title: *Synthesis and functionalization of low-dimensional materials towards high-performance supercapacitors*

PhD Candidate: Włodzimierz Czepa

Supervisor: Prof. Artur Ciesielski

GENERAL EVALUATION

Originality of dissertation topic, relevance to the field, and possible applications

A doctoral dissertation prepared by Włodzimierz Czepa was submitted in the form of a thematically coherent series of four scientific articles, numbered P1-P4, published in scientific journals such as *Chemical Society Reviews*, *Nanoscale*, *Small Science* and *Journal of Materials Chemistry C*. It was correctly assigned to the discipline of chemical sciences (according to the Regulation of the Minister of Education and Science of 11 Oct. 2022 on the fields of science and scientific disciplines and artistic disciplines, Journal of Laws of 2022, pos. 2202, from 11 Oct. 2022).

The dissertation is devoted to functionalizing novel low-dimensional and two-dimensional materials (coined by the PhD candidate as 2DMs) and investigating their electrochemical properties. The fields of interest include sensing and energy storage, while he has obtained key results in the sub-field of supercapacitors. 2DMs are novel structures that provide unprecedented flexibility in designing various functionalization approaches and facile processability toward verifying their electrochemical behavior.

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In this sense, I would position this work in the group of timely topics for chemical and material sciences disciplines. The matter of high-performance supercapacitors is convenient and impactful. The PhD candidate contributes by a better understanding 2DMs' functionalization on electrode performance. He has developed a series of facile chemical functionalization approaches for his 2DMs (taking graphene oxide as model 2DM), performed their thorough characterization, careful electrode preparation, and detailed multiparameter electrochemical testing. Furthermore, the PhD candidate extends his synthetic approaches into other low-dimensional materials (by taking copper nanowires, CuNWs, as a model case). Altogether, the doctoral dissertation, prepared by Włodzimierz Czepa, is timely, original, relevant to the assumed research goals and considerable in applying to modern electrochemical devices.

Technical quality, consistency of theory and experimental work, completeness

The doctoral dissertation is of high technical quality and is well structured. The description part (a guide to a series of P1-P4 papers) covers 42 pages in total and is accompanied by a list of abbreviations, an abstract, and a description of scientific achievements. I consider nine key figures relevant to the descriptions of a thematically coherent series of scientific articles. I am also glad to see a schematic representation of research objectives presented in the dissertation (Fig. 1). It is a well-structured informative schematic that helps in understanding the concept. The descriptions of the introduction, results and discussion parts were validated with 76 carefully chosen references.

The dissertation consists of four main sections. The "General introduction and motivation" presents a literature overview of low-dimensional materials, emphasizing various 2DMs, their *top-down* and *bottom-up* synthesis, and functionalization. The functionalization part further extends into specific techniques that could be applicable to GO, guiding the reader into the reasons behind chosen synthetic approaches. The characterization techniques are also placed here and described one by one. In the future, I would recommend placing the methodology in a separate section. The combined descriptions are difficult to follow. Notably, the PhD candidate carefully studied the research subject matter with a critical review and used appropriate resources to define the goals. It is also evident that he gained a deep understanding of the theory behind electrochemical processes and supercapacitors in general. He also acquired relevant problem-solving skills regarding low-dimensional materials functionalization and appropriate characterization.

The "Research objectives of dissertation" section coherently presents the doctoral dissertation's aims and motivation. The aim was to fabricate new hybrid materials based on low-dimensional nanomaterials, multiscale characterization of prepared hybrids, electrochemical investigation of synthesized materials, and their further application in supercapacitors as electrodes. It was assumed reasonably and correctly augmented by the PhD candidate.

The "Results and discussion" section nicely guides the reader through the most important findings presented in works P2-P4. Note that publication P1 is a review paper that inspired the PhD candidate to further studies, as was mentioned in the Abstract. However, no more details are provided in the Results and discussion section, which could clarify what was an inspiration. It is clear to me that the PhD candidate widely analyzed the data about 2D materials, their functionalization approaches, electrochemical properties, etc. But what problems and challenges were found, and why the supercapacitor application was finally chosen instead of electrochemical sensors? Apart from this point for a discussion, the experimental results are very good or excellent. Two bottom-up functionalization techniques (protocols) were chosen for GO. To obtain rGO-POSS, the PhD candidate chose octaammonium POSS (octa(3-aminopropyl)silsesquioxane hydrochloride) and applied a nucleophilic ring-opening reaction to bond POSS molecules covalently to GO surface. The hydrazine (NH_2NH_2) reduction was further applied to obtain rGO-POSS and remove the excess of electrostatically anchored POSS. The second protocol involved thioamide polymer (THA) and was more complex. The Hoffman's rearrangement reaction was first applied to obtain a dithiocarbamid salt, which was further transformed into diisothiocyanate due to enable a condensation reaction with 2,2'-(ethylenedioxy)bis(ethylamine). Final GO-THA, as well as rGO-POSS were incorporated into the supercapacitor electrdes and thoroughly tested. Additionally, the CuNW were synthesized by reducing copper(II) chloride with glucose in presence of octadecylamine. They were further surface-functionalized with THA and applied as above GO-based materials. This idea allowed the Author to verify the approaches as universal and applicable to other types of low-dimensional structures, meaning not only 2D materials. Obtained hybrids were characterized with a series of advanced techniques, which allowed the PhD candidate to investigate their material-structure-property relationship in model electrode systems.

The "Conclusions" section summarizes the results and provides a future outlook. It begins with presenting the aims of this study and reveals the concluding remarks on the efficiency of performed surface functionalizations. The general conclusion states that the PhD candidate achieved high energy storage performance for tested electrodes and was considerably better than for conventional electrodes. In particular, for rGO-POSS, the achieved parameters are as follows: 174 F g^{-1} capacitance, 2.25 W cm^{-3} power density, 41.4 mW h cm^{-3} energy density, and 98% capacitance retention after 5000 cycles. GO-THA parameters are 221 F g^{-1} capacitance at 1A g^{-1} (1M H_2SO_4) but even 340 F g^{-1} in an organic media, 94.4 Wh kg^{-1} energy density. And for pseudocapacitive CuNW-THA (ionic liquid electrolyte) these are 324 F g^{-1} capacitance, 60.5 F cm^{-3} volumetric capacitance, and 70% stability after 5000 cycles. However, it is hard to generalize due to some variables in protocols chosen for electrode preparation and testing conditions. Apart from a general description, I would rather expect a comparison of the experiment outcomes with mentioned testing conditions. This could be organized, for instance, in a table and compared in the conclusions section with the conventional electrodes/materials and other 2D

materials. But as I mentioned, that would be an additional favorable advantage, not an issue. Altogether, the presented doctoral dissertation is complete and conclusive. The main objectives of the PhD works have been fulfilled and well-argumented. The work also exhibits very good theory and experimental work consistency.

Writing quality and clarity

The PhD thesis, in its whole matter, is written clearly and possesses high quality. There are almost no typing errors. The sentences are concise and readable. The figures and tables are also interestingly presented and adequately addressed. The introduction and state-of-the-art descriptions are based on valuable and actual literature. The arguments and resulting aims of the study are also well formulated. Presented conclusions are meritorious, consequent and essential. The explanations are based on in-depth studies and thorough analyses.

CONCLUDING REMARKS

The doctoral dissertation prepared by PhD candidate Włodzimierz Czepa is of very high quality. It reveals valuable results obtained with thorough experimental work. The well-designed objectives have been fulfilled and correctly argumented. This original work represents advancements in designing electrode materials for supercapacitor applications *via* facile and effective surface functionalization. It is relevant to the requirements of advanced materials and paves a solid foundation for potentially scaling up their synthesis processes.

Altogether, I asses the doctoral dissertation, prepared by Włodzimierz Czepa, a PhD candidate advised by Prof. Artur Ciesielski, as excellent. Therefore, I conclude that it **fulfills all the provisions**, specified in Act of 20 July 2018 "Law on higher education and science", Journal of Laws 2021, pos. 478, with further changes (Ustawa z dnia 20 lipca 2018 r "Prawo o szkolnictwie wyższym i nauce", Dziennik Ustaw 2021, poz. 478 z późniejszymi zmianami). Therefore, I favorably **recommend it for defense in front of the respective committee**.

In addition, I recommend this outstanding doctoral dissertation for the honor of a **distinction thesis recognition**. The specific reasons underlying my recommendations are as follows: completeness, high scientific novelty, an extensive range of research and advanced experimental set-up, good writing style, interpreting and concluding skills, as well as his outstanding scientific activity confirmed by papers published in highly ranked scientific journals, research stays and conferences.

The doctoral dissertation was clearly written with high technical quality. The writing manner is good, making the work readable by practitioners and the general audience. Introduction and discussion sections are consequently presented and essential. Experiments and measurement techniques were correctly arranged and applied. The designed experiment is convincing and supports the obtained results,

which were thoroughly described. The PhD candidate also gained experience in interpreting results from diverse methodologies. Presented descriptions and conclusions are meritorious, consequent and essential, based on valuable studies and thorough analyses performed at the highest scientific level.

The PhD candidate has already gained considerable scientific achievements. The doctoral dissertation was published in high-tier peer-reviewed journals with high-impact points, such as *Chemical Society Reviews* (P1, if=60.6), *Nanoscale* (P2, if=8.3), *Small Science* (P3, here no if), *Journal of Materials Chemistry C* (P4, if=8.1). All of these are relevant to the PhD topic. He was involved in a series of other works carried out in international collaboration with experts in the field of study. They were published on similar topics from 2016 to 2019. He also presented a list of scientific internships and stays in research labs in France and Italy in 2015, 2016, 2017, 2019, 2020. In addition, he was running his own "Preludium 17" NCN-funded project and participated in the other three. His works were presented at over ten scientific conferences. Such achievements strongly showcase the dynamic development of the scientific career of the PhD candidate and constitute a sound basis for the successful defense of his doctoral dissertation.

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