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Review of the doctoral dissertation of Joanna Duch, M.Sc.

Title: Surface chemistry of carbon materials - from models to functional composites

The doctoral dissertation of Joanna Duch presented for review, under the supervision of Prof. Andrzej Kotarba, was prepared in the Materials and Surface Chemistry Group, Faculty of Chemistry, Jagiellonian University in Krakow. The dissertation is composed of an introduction, scope, experimental methods, results with a discussion, summary, conclusions and an extensive list (117 positions) of literature. The dissertation also includes a list of abbreviations and symbols used in the work, a summary (in Polish and English), a preface and a table of contents. The Author included a list of six articles related to the topic of the doctoral dissertation, published in reputable journals and her contribution to the letter ones. Moreover, summary of the PhD candidate scientific achievements, unrelated to the topic of the doctoral dissertation (three publications and one patent) was provided. A list of 12 conferences was also presented, during which the results obtained during the implementation of the doctoral dissertation were disseminated. The main part of the dissertation is contained on 57 pages of a carefully prepared manuscript, containing 30 high-quality drawings and 3 tables. The modern arrangement of the dissertation makes it interesting and easy to read. An important advantage, especially from the reviewer's point of view, is its transparency and clear presentation of all information needed for its evaluation. I would especially like to emphasize, that during the reading, I had no doubts about the contribution of the PhD candidate's to obtaining the presented results. It is especially valuable, because in typical designs of doctoral dissertations, which are presented as individual PhD student's achievement, the participation of other contractors is carefully hidden. In the case of the reviewed work, the PhD student clearly indicated, which parts of the study are her work, and yet the presented work is coherent, well planned, consistently implemented and allowed the Author to fully present her achievements and acquired experimental skills (plasma modification, X-ray diffraction XRD, Nanoparticle Tracking Analysis - NTA, work function and water contact angle measurements, Thermogravimetric/Differential Thermal Analysis TGA/DTA, Raman spectroscopy RS, in situ work function measurements, microbiological tests, zeta potential measurements) and publications (data acquisition, analysis and interpretation, drafting the first version of manuscript, proofing).

1. Topics of the doctoral dissertation

The subject of the dissertation is the functionalization of the surface of carbon materials using oxygen plasma. In the doctoral dissertation, systematic research was carried out on surface modification of various carbon materials (graphite, graphene materials, multiwalled carbon nanotubes) using a number of experimental methods (XRD, RS, TGA, scanning electron microscopy SEM, transmission electron microscopy TEM, transmission electron microscopy XPS, laser desorption/ionization mass spectroscopy LDI-MS, secondary-ion mass spectrometry SIMS, measurements of the work function and water contact angle). Interpretation of the experimental results was supported by molecular modeling (DFT). The practical use of the obtained results is presented on the example of biological and electrocatalytic applications. The PhD candidate showed that precise surface functionalization can be used to reduce the risk of bacterial colonizations, while in the case of electrocatalysts, the oxygen reduction reaction, which is the basis for the operation of fuel cells, allows to increase the surface activity and improve the quality of the prepared carbon films on the electrode surface. The subject of the presented work is important and current. It is worth emphasizing above all the holistic nature of the solution of the analyzed research problem - covering theoretical issues (molecular modeling), the synthesis and modification of the analyzed material, its comprehensive characterization and application diversity. This approach deserves recognition, because it requires courage and faith in your own abilities.

2. Scope of the doctoral dissertation

The doctoral dissertation has been divided into seven chapters. The introduction (Chapter 1) presents the background of the conducted research and ends with the presentation of the purpose of the dissertation and the strategy for its implementation (Chapter 2). The Author presented carbon materials in a very general way, paying attention to the unique diversity of their structure and the importance of surface properties. The description is brief, but precise, and contains all relevant information, including correctly selected references. I assess similarly of the fragments of the dissertation presenting the methods of functionalization, surface chemistry, and the issues of wettability and electronic properties. The presented description of the current state of knowledge in relation to surface properties, fully justifies the main goal of the work, as gaining general knowledge on changes in the electronic structure of the surface of carbon materials and determining the main correlations between these modifications and properties, especially wettability and electronic properties.

The experimental part (Chapter 3) describes the materials, synthesis and functionalization, methods and techniques used during the study. This part is very precisely written. Taking into account the number of research techniques presented, the correctness of the presented descriptions is appreciated.

Chapter 4 is the most important part of the work. The presented results and discussion are 23 pages long, which results from the fact that only the main ideas and methods of solving the problem are presented, as well as unpublished results, while in most cases, instead of details, relevant articles collected in the Annex are referenced. This solution makes reading a doctoral dissertation much more attractive. With the traditional approach, descriptions would be repeated many times, or the scope of the materials and techniques discussed would have to be severely limited. In the reviewed work, appropriately selected examples are presented, but the reading is accompanied by the belief, that the research was conducted comprehensively and the obtained conclusions are general.

The final two chapters (Chapters 5-6) provide a summary and conclusions. I like the visible increase in the Author's self confidence, which is both acceptable and justified at this stage of reading

the manuscript. The Author directly indicates the main advantages of the presented study (reference to an ambitious issue, scientific potential of the analyzed phenomenon, application significance). The conclusions are divided into three groups, related to methodology, physicochemical and application properties.

The bibliography (Chapter 7) covers both laterature references and recent publications. The selection of the cited works is correct and confirms a good knowledge of the current literature on the issues analyzed in the dissertation.

3. Assessment of the doctoral dissertation

The PhD candidate presented a convincing motivation of her research, described the stages of its implementation and explained the research methods used. She correctly presented the research results and the final conclusions of the dissertation. The thesis contains all the required elements of a correct doctoral dissertation, but the accents have been placed in a way, which increases its attractivity, compared to the classic layout. This form is much better to read and review, but probably requires a lot more work to write.

Carbon materials are among the most extensively researched and at the same time the most surprising materials. Characterization of their crystal and electronic structure requires a lot of experience. They are not very diverse in terms of their chemical composition - apart from carbon, they contain only a few, in addition, light elements, which makes their detection and distinguishing difficult. Additionally, carbon atoms can be connected in many different ways. Therefore, a correct characterization requires complex application of several techniques and taking into account their limitations. Among the achievements of the presented doctoral dissertation, I would like to emphasize the correct application of XPS, LDI-MS and SIMS to assess the effectiveness of functionalization of various carbon surfaces, supplemented by qualitative and quantitative evaluation of functional groups using spectroscopic techniques.

A very interesting issue presented in the doctoral dissertation is the measurement of the work function of the analyzed carbon materials and its changes as a result of oxygen functionalization. The Author has conducted experiments showing how this value changes for various carbon materials depending on the duration of the plasma operation and the type of functionalization (oxygen plasma, HNO_3). The obtained results showed that the use of oxygen plasma allows to modify the properties of the surface in a wider range, easier and in a shorter time than with the use of concentrated acids. A significant achievement of the PhD candidate is also explaining the stability of changes caused by the functionalization using of oxygen plasma. The wettability of the surface is the highest immediately after the process, and then it systematically decreases, but even after 60 days the difference remains visible.

The PhD candidate also attempted to evaluate the influence of oxygen plasma on the structure of carbon nanotubes. An interesting and convincing result is the possibility of using the value of the work function to determine critical parameters (especially pressure and plasma operating time) for the functionalization and amorphization of carbon nanotubes. It is worth emphasizing that the obtained result were confirmed by DTF calculations and other experimental techniques (TEM, XPS, RS). PhD candidate presented the process of degradation of the CNT crystal structure as a result of the influence of oxygen plasma and concentrated HNO_3. She used the TEM technique to confirm that the oxygen plasma destroys only the outer walls of the nanotubes. With the help of the TGA technique, she confirmed that the time of oxygen functionalization does not significantly affect the structure and resistance to oxidation of carbon nanotubes, but these factors are dependent on the concentration of hydrochloric acid used.

The results of application research are the culmination of the presented work. The first part deals with biological applications. Analyzing the share of surfaces covered by bacteria for the known values of oxygen concentration, wettability angle and the work function, the PhD candidate showed that lowering the latter parameters reduces the surface colonization by bacteria. The second part concerns the activity of electrocatalysts in the oxygen reduction reaction, which is the basis for the operation of fuel cells. After describing the advantages and potential of fuel cells and justifying the importance of the need to achieve progress in controlling the course of the ORR reaction, she focused on the structure of platinum nanoparticles deposited on a carbon support. This part of the dissertation contains the results presented in the article "Thermal oxygen activation followed by in situ work function measurements over carbon-supported noble metal-based catalysts" and some results that have not been published so far. The values of electrochemical parameters in the ORR reaction were obtained using the technique based on linear sweep voltammetry tests in O_2-saturated electrolyte and compared with the measured values of the work function. In-situ measurements made for various temperatures and oxygen partial pressures revealed a direct correlation between the work function, oxygen adsorption and electrochemical activity of the analyzed catalysts. Oxygen plasma functionalization also proved to be of practical importance in the preparation of the surface of carbon supports. Plasma treatment of the carbon support allowed to obtain a catalyst with improved Pt nanoparticles distribution and ECSA value. The PhD candidate showed that plasma treatment improves the quality of the ink used in the measurements of electrocatalytic performance in ORR - by improving its homogeneity and wettability. It was also valuable to demonstrate the effect of carbon support functionalization on the ORR mechanism. Using rotating disk electrode (RDE) tests, the PhD candidate showed that the calculated number of electrons indicates direct oxygen reduction to water with a very limited H_2O_2 production for Pt deposited on CNT treated by oxygen plasma. In case of Pt deposited on raw CNT it was 4e- reduction in the kinetic-diffusion control zone and mixed $2e^-/4e^-$ reduction in the diffusion-controlled region.

4. Critical remarks

The greatest advantage of the evaluated work is the high scientific level of the well presented and interpreted results. Most of them were published in reputable journals and were then subjected to professional evaluation. As it is interesting and easy to read, it is difficult to notice its disadvantages.

In the previous part of the review, I appreciated the precision and correctness of the description of the research techniques used (Chapter 3.4). Therefore, I am a bit disappointed that the work does not contain the Author's conclusions resulting from their application to various carbon materials. An example is Raman spectroscopy results, where different values of the ID/IG parameter were obtained. The assessment of the shape of Raman spectra is accompanied by the statement that „the presence of amorphous carbon materials can be indicated by the D band broader than the G band'' and that „the intensity ratio (ID/IG) increases with the generation of structural defects''. Considering that the PhD candidate used a number of methods for various groups of carbon materials, it is worth answering the question: Which statements and interpretation methods are general and apply to any carbon materials?

As a reviewer, I am impressed by the quality of the presented drawings. I appreciate the work put into their implementation and the Author's effort to make it easier for readers to understand the content described. But I would be grateful for a more detailed discussion of Figure 4.7. It shows packages of parallel black lines that could suggest the presence of graphite domains, but their size and arrangement are surprising. In my opinion, Figure 4.13 also makes it more difficult than easier to understand the presented content.

I would like to ask a PhD candidate to critically evaluate the information (given on page 36) that d_{002} values can change in the range from 0.32 nm to 0.35 nm. She also attempted to assess the value of interplanar distances in carbon nanotubes. I would like to ask how she assesses the measurement uncertainty of her results. The above remarks do not detract from the high evaluation of the work, especially as they are mainly polemical and result from my curiosity.

5. Final evaluation statement

The reviewed doctoral dissertation of Joanna Duch "Surface chemistry of carbon materials - from models to functional composites" meets the conditions for doctoral dissertations specified in the act of 14 March 2003 „Law on Academic Degrees and Title and Degrees and Title in the Arts''. Therefore, I am asking for its public defense. Due to the high scientific value and significant contribution to the knowledge in the field of functionalization of carbon materials with the use of oxygen plasma, I apply to the Faculty of Chemistry Scientific Council for its award.

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