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Report on the dissertation entitled "Multifunctional Carbon-Based Composites for Different Applications"

A dissertation submitted by Mrs. Xiaoze Shi consists a basis for awarding the Doctoral degree. The thesis has been conducted under the supervision of Prof. Ewa Mijowska at the West Pomeranian University of Technology in Szczecin, and it is the continuation and further extension of research, developed very intensively and effectively in this team. Due to the highly multidisciplinary character of the research work presented in this thesis as well as considerable number of experiments performed, the report will be divided into separate sections describing the various aspects of the thesis.

1) Thesis content and contribution to the field

This dissertation is focused on gaining an in depth understanding of relation between the structure of the generated materials and physicochemical properties that they possess. The thesis contains very extensive research program that concerns generation of a series of structurally distinct carbon-based materials and composites for variety of different applications such as: electrode devices, dye adsorbent and CO_2 storage. The research aims formulated in the doctoral thesis concerning the synthesis of new multifunctional materials suitable for number of applications e.g. pollutants adsorbents perfectly fits the currently prevailing trends in the fields of nanotechnology and nanoengineering. The excellent reputation of both the PhD student's supervisor, Prof. Ewa Mijowska and the research team in which the work was conducted let me to expect very good quality of the results presented in the dissertation, which is indeed confirmed by a closer look at the results. Based on the fact that in the last thirty years we observe constantly growing interests of chemists and material scientists in the development of new and efficient systems for sustainable and renewable energy resources as well as

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technologies for removal of pollutants from the environment I believe that the scope of the work presented in the doctoral thesis is extremely important and useful not only from a purely scientific point of view but also because of the high application potential of the results presented.

The thesis consists of nine chapters out from which experimental work is divided into seven main parts: 1) describes the methods of preparation and analysis of carbon-based materials and composites; 2) concerns the investigations of effect of iron oxide (Fe_3O_4) enclosed in hollow carbon nanosphere for the potential use of this material as symmetric supercapacitors; 3) depicts the controlled growth and incorporation of nanoparticles of manganese oxide (Mn_3O_4) into the carbon shell of hollow carbon spheres for the application as energy storage devices; 4) illustrates the preparation and investigation of electrochemical performance of hybrid material based on a unique carbon hollow structure and nickel oxide (NiO); 5) reports on the generation of nanoporous carbon materials synthesized by strategic application of Al-MOF-based complex as a scaffold in the view of its application as high-performance symmetrical supercapacitor and high-efficiency device for removal of dyes; 6) describes preparation of nitrogen-'rich' nanoporous materials generated from MOF complexes for dual application i.e. efficient CO_2 adsorption and storage as well as high-performance lithium-ion batteries; 7) contains description of the synthesis and application of interconnected nanoporous carbon system 'enriched' with manganite (MnO(OH)) as symmetric supercapacitor device.

The introduction is divided into three sub-chapters. The first subchapter focuses on detailed characteristics of structurally distinct carbon based materials, their physicochemical properties and applications in the fields of material science and nanotechnology. The second describe precisely energy storage applications of such materials with the focus on the LIBs and supercapacitor devices. The last sub-chapter constitutes on the description of employment of novel nanosize carbon systems in environmental applications, particularly in dye adsorption and CO_2 capture. The literature section is written very clearly with concise language and constitute an ideal

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introduction for the reader of this dissertation, including those who are not entirely familiar with this field of research.

It is worth noting that the PhD student in order to perform and analyze all experiments employed an impressive number of different analytical techniques such as Raman spectroscopy, thermogravimetric analysis (TGA), X-ray crystallography or high-resolution transmission electron microscopy (HR-TEM). I find noteworthy, that these techniques are typically used by different scientific communities (e.g. HR-TEM is used in molecular biology, Raman spectroscopy in materials science/electronics), which shows strong involvement of the PhD student in the highly multidisciplinary research projects as well as unquestionable high experimental and analytical skills.

The last chapter consists of summary and conclusion with some outlooks on the scientific approaches mentioned above.

2) Quality of the work

In the dissertation the candidate showed to possess a good knowledge and understanding on the basic principles of material science with the focus of carbon based materials and their applications in variety fields of research from nanotechnology, through environmental science to physical chemistry. This is a broad arsenal of fields and related topics. The discussion of the results is profound. Some parts of the results described in the doctoral thesis have already been published in very good specialist journals such as *Electrochimica Acta* (x2) or *Bioresource Technology*, in which the quality of results and their originality is scrupulously evaluated by external reviewers and editorial board. For this reason, I think that re-describing and re-evaluating the quality of these data and summarizing them again is unnecessary. Despite this, I think that the quality of the presented results is very high as they cover very extensive investigations of the synthesis and properties of important group of materials that due to their potential applications in number of different fields are subject of intensive research in many top research teams. What is worth emphasizing is the fact of very logical utilization of the same type of base material e.g. hollow carbon spheres in several distinct aspects of research, i.e. incorporation of iron, manganese or nickel oxides. The

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applied approach allowed for quick investigation of many application possibilities of the materials obtained and their in-depth structural (e.g. microscopically) and physicochemical (e.g. electrochemical) analysis. However, while reading this doctoral thesis, I came up with couple of questions that I would like the PhD student to answer during defense presentation i.e. a) in two separate chapters MOF-type systems have been applied in the generation of porous materials – what dictated by the choice of particularly this type of MOF complex ?; b) does the student see the possibility of using other types of porous materials for the same purpose, e.g. Covalent Organic Frameworks (COFs) or Hydrogen-bond Organic Frameworks (HOFs) ?; c) do you see a possibility of applying nanoporous carbon materials obtained in the frame of this dissertation in highly selective capture and removal of structurally similar dyes or gases ?.

3) Presentation:

The presentation is very good, in particular in view that the candidate is not a native speaker. The quality of figures and graphics used for the schematic representation of the results obtained is very high. Descriptions and the format of the thesis are clear. The experimental data are presented concisely and clearly. There is a good balance between the different parts of the dissertation. The references seem to be well adapted and up-to-date.

4) Originality

There are several aspects of the scientific novelty contained in this doctoral thesis, of which preparation of hierarchical nanoporous carbon by annealing of nano-scale Al-based MOF, I found particularly attractive as is led to the material of exceptionally high surface area and conductivity which in turn is highly demanded for energy storage applications. Also, cost-effective preparation of N-doped activated carbon materials from cheap and commercial precursors is highly attractive approach especially in the view of their application as efficient symmetric supercapacitor devices. In addition, the potential application of this system also includes the use of this material at the industrial scale

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e.g. in energy storage field thus making it a great candidate for multitasking carbon-based device.

5) Summary

Summing up, I would like to point out that the research undertaken by the PhD student and her supervisor concerns the most current issues in one of the most dynamically developing fields of modern science – carbon-based materials. A reflection of scientific innovations and the effectiveness of formulated tasks are results that have already been published in specialist and reputable journals. I can only assume that subsequent publications covering the results contained in this dissertation are in preparation. I find the dissertation of Mrs. Xiaoze Shi a conceptually very attractive investigation on an important question on how carbon-based materials can be used to fabricate multifunctional devices for number of distinct applications. The work was properly conducted and reported with care and competence, the analysis of the experimental result is deep. In light of this I believe that the dissertation meets all the requirements specified by the Ministry of Science and Higher Education (Act on Academic Degrees and Academic Title) and I recommend the Faculty Council of Chemical Technology and Engineering of the West Pomeranian University of Technology in Szczecin awarding the candidate the degree of Doctor. At the same time, due to the high quality of experimental results included in the doctoral dissertation, reliable and systematic implementation, innovative solutions that will certainly impact on the development of the studied field, I recommend for its distinction.

Yours sincerely,