Doctoral Thesis of Shi Xiaoze

"Multifunctional Carbon-Based Composites for Different Applications"

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Thesis assessment

The research work of Shi Xiaoze was done in the Nanomaterials Physicochemistry Department of Faculty of Chemical Technology and Engineering, at West Pomeranian University of Technology in Szczecin, Poland. Her work was supervised by Prof. Dr hab. Ewa Mijowska, a recognized expert in the field of nanotechnology. The work had led to the Ph.D. Dissertation of Shi Xiaoze which I have the honor to review.

The dissertation comprises 147 pages and it is divided into nine distinct chapters, consisting of a literature review, experimental techniques, results and discussion of the six research work and conclusions. The thesis is well balanced and shows a good distribution of pages for each chapter. The literature review is in my opinion well-structured and touches all the main issues in the field, namely the classification and properties of three-dimensional (3D) carbon materials; a full description of how to prepare nanoporous carbon (NPC), hollow carbon sphere (HCS) and

multifunctional carbon-based composites; and their potential applications, especially their electrochemical and environmental applications. The number of bibliographic references used is adequate and it comprises all the key publications in the field. A good compliment of this part is the section 1.4, aim and objectives, in which the student describes challenges and questions remaining still open in the literature, and proposes a direction for the research in this area. The latest researches of using multifunctional materials as both electrode materials and pollutants adsorbents provide a significant impact on future trends of the research. Due to the well-known properties of carbon materials, such as very large surface area, extreme mechanical strength, specific electrical conductivity, they became very competitive in many different applications, especially in environmental and energy storage applications. The potential success of technologies based on carbon-based composites depends on the mastery of their synthesis, doping and functionalization methods. The ability to deal with controlled synthesis to obtain the product with the proposed properties is a key challenge in the development of this research field. This doctoral thesis points a route in the right direction and thus constitutes a relevant contribution to the development of this research field and to the improvement of knowledge in this particular area.

In chapter II, all the experimental methods and techniques are described. This description was very useful when reading the thesis. The student shows good understanding skills and capacity to discriminate the different routes to synthesize carbon materials and carbon-based composites. Therefore, the first part of the work is written clearly and in a simple way providing the reader a good overview of the research field where the work was done. In the following chapters, the author demonstrated the preparation and application of a series of carbon materials and carbon-based composites for electrode materials, dye adsorbent, and CO_2 storage.

In Chapter III & IV, the author firstly introduced HCSs prepared from core-shell silica templates. Due to their low density, good surface permeability, large specific surface

area (SSA), high porosity, and big inner cavities, HCSs can be used to encapsulate metal oxides like Fe_3O_4 and Mn_3O_4, and the composites (HCS-Fe_3O_4 and HCS-Mn_3O_4) can be used as electrode materials for symmetric supercapacitors. HCS-Fe_3O_4 presents the highest specific capacitance of 193 F g^{-1} at a scan rate of 1 mV s^{-1} and retains 94.75% up to 10000 cycles. The highest specific capacitance of HCS-Mn_3O_4 is 430 F g^{-1} at a scanning rate of 1 mV s^{-1} with 93.15% retention after 10,000 cycles, and the largest energy density is 22.6 Wh kg^{-1}.

In Chapter V, NiO@HCS was synthesized and exhibited advantages such as large surface area, suitable pore size distribution, and good electrical conductivity. Besides, the small number of metal oxide nanocrystals inside HCS can provide more efficient electrochemical reaction within NiO compared with bulk NiO with large size. When investigated as anode materials for a lithium-ion battery, NiO@HCS possesses a high capacity of 598 mA h g^{-1} at 0.1 A g^{-1} and superior rate capability. Owing to the strong interaction of HCS and NiO crystals, NiO@HCS exhibited excellent cycle stability at a high current density.

In Chapter VI & VII, the interconnected NPC and nitrogen-doped NPC (N-NPC) was prepared from direct annealing of ultra-small Al-based metal-organic complex (Al-MOC) or the hybrid of Al-MOC and urea. NPC and N-NPC present high SSA. NPC shows good dye adsorption properties and capacitance of 249 F g^{-1} at 1 A g^{-1} in an aqueous electrolyte. N-NPC exhibits good adsorption for CO_2 under high-pressure and a high initial discharge capacity of 820 mA h g^{-1} and reversible charge capacity of 762 mA h g^{-1} at a rate of 0.1 A g^{-1}.

In Chapter VIII, NPC-MnOOH with outstanding capacitive performance in symmetric devices has been demonstrated. NPC-MnOOH electrodes can be scanned with a wide voltage window from $0 \sim 1.6$ V without obvious hydrolysis process. The two-electrode supercapacitor NPC-MnOOH//NPC-MnOOH with 26.7 wt% of

MnOOH shows the highest specific capacitance of 410 F g^{-1} and a maximum energy density of 33.5 Wh kg^{-1}. It also shows 86 % retention even after 10,000 cycles.

Finally, the main conclusions are summarized in the last chapter of the thesis. In my opinion, the scope of the dissertation was achieved since multifunctional carbon-based composites and their good performance was obtained. The methodology used was well explored in many different ways in order to optimize the preparation of the materials. I also believe that this work has remarkable novelty and its original input to the field will have a strong contribution to the knowledge of carbon nanomaterials.

However, I have a number of comments and questions that I would like to discuss with the candidate as follows:

1) Please be careful about the emotional expresses such as "excellent". It is better to find a more objective way to indicate the results.

2) Page 87 the last paragraph: "NPC-950" is not defined.

3) It would be useful to provide XRD characterization of the Al-MOC.

4) On page 104 and line 4, it's hard to understand what "a loos morphology" is. Should it be "A loose morphology"?

5) It would be more helpful to index all the XRD patterns of Figure 8-2.

6) What will you do to improve the energy density of carbon-based composites you prepared?

I would like also to highlight the candidate list of publications. The student has made a contribution to 5 publications and demonstrated 12 submitted research work done by the candidate and the supervisor. All of them are international with high impact factors.

The manuscript is nicely organized, written in a good English level with a significant number of tables, graphs and illustrations which generate an enjoyable thesis to read. The thesis starts and finishes in a smooth way by having a well-structured, concise but complete abstract and conclusion, which provides a nice summary of the work carried out during the preparation of the Dissertation. In between those two sections the results are correctly discussed, well-illustrated and nicely inserted in the thesis. Reading the candidate list of publications, I observed that Shi Xiaoze also developed contacts abroad leading to collaborations with foreign scientific groups. These are very important skills for a young scientist.

The doctoral thesis of Shi Xiaoze presents a significant amount of original and innovative work. Therefore, I suggest the Scientific Council of the Faculty of Chemical Technology and Engineering of West Pomeranian University of Technology the admission of Shi Xiaoze to the next stage which is the public defence of her doctoral thesis. I formally declare that I accept the thesis as it is.

I would like to state here that after my evaluation the Ph.D. thesis of Shi Xiaoze is very high quality and I recommend to the Scientific Council of the Faculty of Chemical Technology and Engineering of West Pomeranian University of Technology to proceed and let Shi Xiaoze become a doctor. Additionally, due to the described outstanding scientific results, I recommend this thesis for Award for Excellence.

(Prof. Dr Xi Zhao) Xi Zhao (赵熹)

Changchun, 08 April, 2019