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REVIEW OF THE DOCTORAL DISSERTATION OF AHMED SUBRATI

The doctoral dissertation entitled „Electrochemically-Derived Graphite Oxide: Oxidation, Functionalization Oxygen-Clustering, Ni-Electrodeposition and Characterization" *(in Polish "Tlenek grafitu otrzymywany metodą electrochemiczną: utlenianie funkcjonalizacja, tworzenie klasterów tlenowych, elektrochemiczneosadzanie niklu i charakterystyka")* has been prepared by Ahmed Subrati at NanoBioMedical Centre, Adam Mickiewicz University in Poznan, Poland under supervision of dr hab. Piotr Krawczyk (prof. PP) as promoter (thesis advisor) and dr Patryk Florczak as supporting promoter (subsidiary thesis advisor). The dissertation is dedicated to late Professor Stefan Jurga, a prominent scientist and a former Director of NanoBioMedical Centre.

The doctoral dissertation refers to the concepts of functionalization of graphene layer stacks through introduction of oxygen groups within, thus resulting in increasing the interlayer spacing and permitting further derivatization and modification. Among important issues is the feasibility of storing hydrogen through pumping it from bulk gas phase. The concept requires controlling the interlayer spacing and the development of graphite-based materials with enlarged interlayer spaces. The successful approaches have involved introduction of di-/tri-amine species reacting with the graphite oxide oxygen groups to form pillars within interlayer spaces and, accordingly, graphite oxide frameworks. Furthermore, the structural integrity of the basal planes has been maintained through electrochemical, rather than conventional chemical, oxidation of graphite. Among other unique observations is the correlation between thermal decomposition and distribution of oxygen sites within layers. The described results also provide new insights to diagnosis of the structural change upon nitrogen doping. Finally, such observations as the viability of electrodeposition of nickel nanoparticles within the proposed frameworks, and the feasibility of the formation of hybrid graphite-based materials capable of activating the hydrogen spill-over mechanism, which facilitates hydrogen storage, seem to be of primary importance as well.

The doctoral dissertation is organized in a way that it consists of five parts, preceded by *Acknowledgements*, *Abstracts* (in Polish and in English), *List of Figures*, *List of Tables*, and lists of papers. The first scientific part refers to motivation, objective, research hypotheses and emphasizes the importance and novelty of the pursued research (Chapter 1). Later, in Chapter 2, the author provides crucial items of information concerning carbons and graphite, the possibility of both chemical and electrochemical oxidation, as well as the feasibility of graphite oxide reduction. Here the author proposes own approach to electrochemical oxidation of graphite, describes the synthetic and mechanistic details, and addresses the problem of overoxidation. In Chapter 3, the fundamental aspects of graphite oxide synthesis, characterization, functionalization, formation of frameworks and applications including dye clean-up, energy storage and light localization are addressed. In Chapter 4, the author describes concepts of gasification of carbon backbones as well as oxygen clustering and nitrogen doping. Successful implementation of oxygen clustering toward in-plane doping configurations, formation of pillars, and thermochemical investigations of the resulting frameworks constitute a significant achievement in the area. A valuable approach aiming at introduction of nickel nanoparticles into the graphite oxide frameworks has been described in Chapter 5. The electrodeposition procedure resulted both in generation the reduced Ni sites and the reduction of the graphite oxide framework. The feasibility of hydrogen spillover through dissociative hydrogen chemisorption on Ni active sites followed by H-migration to sp^2 domains of reduced graphite oxide frameworks are of primary importance to the hydrogen storage. At the end of the doctoral dissertation, the author summarizes his scientific achievements and provides *Appendix.*

The research results described in the Ahmed Subrati's dissertation seem to significantly contribute to the state of the art of functionalized graphite oxides and the development of related hybrid materials. On the whole, Ahmed Subrati appears as coauthor of six publications. These works have been published in very good journals of international circulation (e.g., *Applied Surface Science*, *Carbon*, *Microporous and Mesoporous Materials*, and *Nature Communications*).

Going to the substantive evaluation of the dissertation, I would like to mention the importance of observations and achievements described therein. The main accomplishments concern synthesis, characterization and possible applications of frameworks from electrochemically-derived graphite oxide, important observations of oxygen clustering in graphite oxides and graphite oxide frameworks also in the context of nitrogen doping, and consideration of hybrid systems of Ni-electrodeposited framework for hydrogen storage. Among other important issues is detailed characterization of developed frameworks using various techniques. Furthermore, such potential applications ranging from dye removal to energy storage should also be noted here.

Upon reading the doctoral dissertation, my general impression is that the work is well-written: carbon materials and their properties are broadly addressed, as well as the results obtained are carefully described and interpreted. Both the results and conclusions are convincing.

I have got a few questions or comments that could be easily answered or explained during the doctoral defense.

(1) The proposed galvanostatic method for electrochemical oxidation of graphite utilizes the three-electrode potentiostatic system (page 55). While the current is flowing between the working and counter electrodes (at the latter electrode the controlled oxidation of graphite takes place), some information would be useful what is going at the counter electrode (Hydrogen evolution? Is the product removed or separated from the working compartment?).

(2) The material described in Figure 3.22 (a) is presented as truly "capacitive" system despite the fact that its voltammetric characteristics exhibits some resemblance to that of a "battery" type material. In such case, the capacitance (in F/g) has approximate meaning; perhaps capacity should also be considered (in C/g). True pseudocapacitive electrode materials display electrochemical behavior in a form of rectangular cyclic voltammogram (and linear charge/discharge characteristics). The difference between these two classes of materials has been explained in the following articles: P. Simon et al., *Perspective: Where do batteries end and supercapacitors begin?* Science, 343, 1210-1211, 2014 and T. Brousse et al., *To Be or Not To Be Pseudocapacitive?* Journal of The Electrochemical Society, 162 (5) A5185-A5189, 2015.

(3) Is there any experimental evidence for stability and durability of operation of Ni-containing hybrid systems?

In conclusion, I would like to express my high appreciation to the efforts of the author, emphasize high scientific value of the obtained results and evaluate very positively the doctoral dissertation. Furthermore, I would like to state that the dissertation meets the formal and customary criteria and expectations for doctoral works in the area of exact and natural sciences and chemistry discipline. Thus I am convinced that Ahmed Subrati should be readily admitted to the public doctoral defense at Adam Mickiewicz University in Poznan.

Having in mind the importance of pursued research, the quality, the high scientific value and the application potential of results obtained (presented in six valuable publications onto which the dissertation is based), I would like to recommend awarding the dissertation and conferring the Ph.D. degree to Ahmed Subrati with distinction (honors).

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