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## REPORT

on the Ph.D. dissertation of M. Sc. **Ahmed SUBRATI** entitled

### **Electrochemically derived graphite oxide: oxidation, functionalization, oxygen-clustering, Ni-electrodeposition and characterization**

(Tlenek grafitu otrzymywany metodą elektrochemiczną: utlenianie, funkcjonalizacja, tworzenie klastrów tlenowych, elektrochemiczne osadzanie niklu i charakterystyka)

submitted to the Faculty of Chemistry of Adam Mickiewicz University in Poznań

The subject of the Ph.D. dissertation of M. Sc. Ahmed Subrati is very interesting and follows the mainstream of word research over the development of facile, high-efficient and low-cost method for obtaining graphene/graphite-related materials. An important aspect in this activity is the development of such a method that makes it possible to extensively control the structure and properties of the product by changing the process parameters of material manufacturing. This will expand the potential application areas for graphene/graphite-based materials. In addition, the functionalization of graphene materials and the design on their basis of hybrid materials with metals and their compounds (oxides, sulfides, nitrides, etc.) and/or conducting polymers provide a wide field of activity in this area.

The Ph.D. thesis submitted by M.SC. Ahmed Subrati is focused on the development of graphite oxide-based materials with enlarged interlayer spaces for molecular hydrogen storage based on physisorption and Ni loaded reduced graphite oxide frameworks for hydrogen storage via spillover mechanism.

The Ph.D. dissertation is dedicated to the memory of Professor Stefan Jurga who was the promoter of this work until his death earlier this year. It has been drafted in an unconventional way. It consists of five chapters. Each chapter starts with the literature review related to the discussed topic followed by Experimental section, Results and discussion and Conclusions. Finally, there are Closing remarks which emphasizes the most important results of the thesis. The dissertation ends with Appendix which includes the description of tools used for the elaboration of XPS raw data, calculations of XRD parameters and specific capacitance.

Abstracts of the work in English and Polish are presented at the beginning of the Ph.D. thesis. A list of author's scientific achievements related to the doctoral work reports 2 papers published as co-author in highly ranked journals, i.e. Applied Surface Science (2020) with IF=6.7 and Carbon (2022) with IF=9.6. In 2018-2022. M. Sc. Ahmed Subrati participated in 8 conferences where he presented the results of his research in the form of 3 oral presentations and 8 posters. He is also co-author of 3 papers published in 2020 which are not related with the subject of Ph.D. thesis.

The Ph.D. dissertation has 253 pages including the lists of references ( ~190 items). The majority of the listed papers has been published in the last 10 years in reputed scientific journal with a high impact factor. This is an evidence that the subject of the thesis is important and prospective. The whole thesis contains 116 figures and 17 tables. The results of the experimental work are presented in 48 figures.

The thesis starts with the chapter (**Chapter I**) which presents the reason and motivation for undertaking study on the hydrogen adsorption. The precursor of the synthesized materials was graphite, which was subjected to electrochemical oxidation and, for comparison, to chemical oxidation by the Hummers method. In the next step of the work, the electrochemically-derived graphite oxide (EGO) was oxidized with  $\text{KMnO}_4$  at different EGO: $\text{KMnO}_4$  weight ratios to modify its surface chemistry. The surface C/O ratio and oxygen functional groups distribution in the obtained materials were determined by XPS. The results of this part of experimental work are presented in **Chapter 2**. In Introduction (45 pages), the author focused on the structure of graphite, the mechanism of graphite oxidation by different chemical methods, and the composition and structure of the resultant graphite oxides. Next, the novel electrochemical oxidation of graphite using perchloric acid reported by B. Gurzęda et al. (Carbon 2016, vol. 100, pp. 540-545) was described in details. This approach for electrochemical oxidation of graphite was used by the author of dissertation. Other works on electrochemical oxidation of graphite were also reported with emphasis on the mechanism of electrochemical oxidation. Finally, the formation/conversion of the oxygen functional groups during oxidation of graphite and overoxidation of EGO was discussed, including their thermal reduction.

As follows from the experimental work presented in Chapter 2, the electrochemical oxidation of graphite flakes (size > 500  $\mu\text{m}$ ) provided EGO with a lower oxygen content and different oxygen groups distribution than GO obtained by Hummers method (C/O 4.36 vs. 1.78). A crucial finding is the observation that electrochemical oxidation leads to less degradation of the EGO flake size than chemical oxidation, which is very important for the formation of skeletal structures based on these materials. Furthermore, the author revealed that electrochemical oxidation promotes the formation of epoxy and hydroxyl groups, significantly reducing the content of carboxyl groups. The presence of epoxy groups is strongly emphasized because of their role in the formation of backbone structures with amine linkages, which is one of the aims of the dissertation.

In order to increase the amount of hydroxyl and epoxide groups in graphite oxide, and in particular the epoxide groups, while maintaining the size of the graphite flakes of the precursor, EGO was subjected to oxidative treatment with  $\text{KMnO}_4$ . In conclusion, the differences in the structure of GO obtained by the chemical method and overoxidized electrochemically obtained graphite oxide (OEGO) are presented in Fig. 2.34.

**Chapter 3** describes the results of the study on the synthesis and characterization of electrochemically-derived graphite oxide frameworks with amine pillars. At the beginning of this chapter, the author included a brief literature review (12 pages) on the intercalation of graphite oxide with linear aliphatic amines and aromatic amine compounds, paying particular attention to the mechanism of their attachment/interaction with graphite oxide layers. The amine compounds introduced between the layers (pillars) prevent their aggregation, thus giving the material of permanent skeletal structure with an interlayer distance and porosity that determine its potential application.

M. Sc. Ahmed Subrati in his work used five amines (1,8-diaminoacetane, p-phenyldiamine, 3,3'-dimethoxy-benzidine, 6-methyl-1,3,5-triazine-2,4-diamine and melamine) to functionalize electrochemically-derived graphite oxide. Four fractions of EGO with different flake sizes ranging from 100 to  $>500 \mu\text{m}$  were the subject of investigation. Amine grafting was carried out at room temperature for 24 h. The composition, structure and texture of the resulting products were determined by a wide range of advanced analytical techniques such as XRD, FTIR,  $^{13}\text{C}$  NMR, XPS, EA, TGA/DTG and  $\text{N}_2$  sorption at 77K.

As can be expected the distance between graphene layers in the framework structure was strongly dependent on the amine used. The highest interlayer spacing ( $\sim 1 \text{ nm}$ ) determined by XRD was obtained for the 200-300  $\mu\text{m}$  fraction of graphite flakes when p-phenyldiamine was used as a spacer (EGOF-A2), which is a 40% increase compared to EGO ( $\sim 0.6 \text{ nm}$ ). The chemical structure of all synthesized framework materials and the extent of functionalization of EGO with different amines were successfully determined. Author calculated the density of pillars based on the elemental composition indicating that p-phenyldiamine was the most effective as a spacer molecule to develop graphite oxide-based frameworks.

Very interesting conclusions were drawn from the analysis of thermogravimetric curves in the temperature range 150-300  $^\circ\text{C}$ , where a significant decomposition of the oxygen functional groups takes place. Much lower mass losses were observed for frameworks compared to EGO (16-20 vs. 28%) at these temperatures and lower decomposition onset temperatures, which could indicate a different conversion mechanism for the oxygen groups of the frameworks. Moreover, the onset temperature of decomposition of the frameworks was higher with increasing nitrogen content. Certainly, the use of a thermogravimetric analyzer with simultaneous analysis of gaseous products, as made possible by a coupled MS detector, would allow a deeper insight into the mechanism of the clustering of oxygen functionalities studied in this work.

As mentioned in Chapter 1 the graphite oxide functionalized with amines was planned to be used for hydrogen storage. However, the synthesized graphite oxide-based frameworks exhibit very low BET specific surface area of approximately  $2 \text{ m}^2/\text{g}$  measured by  $\text{N}_2$  sorption at 77 K (Fig. 3.17), indicating their uselessness in adsorption of hydrogen. For efficient adsorption of hydrogen, the adsorbent should be characterized by developed porous texture with high contribution of pores with a size of  $\sim 0.7 \text{ nm}$ .

The author M. Sc. Ahmed Subrati attempted to prove that  $\text{N}_2$  sorption at 77 K is not adequate method for determination of specific surface area (SSA) of synthesized materials which is a controversial statement. He proposed the adsorption of methylene blue (MB) from aqueous solution as a method of SSA evaluation which cannot be accepted. The proposed procedure determines just the MB amount adsorbed by frameworks, in some cases exfoliated to some extent resulting in improved surface access confirmed by higher adsorption capacity. Furthermore, the author recommended the studied frameworks to be used for the removal of dyes, whereas their molecule size usually exceeds 1 nm which is higher than the interlayer spacing of frameworks. Also, the synthesized frameworks are not suitable as an electrode materials of supercapacitor due to low specific surface area leading to low capacitance values and poor cycling stability.

**Chapter 4** is focused on the oxygen clustering observed during heat treatment of synthesized materials. Two publications on the thermal deoxygenation of graphene/graphite oxide, i.e. Ganguly et al. in Journal of Physical Chemistry C 115 (2011) 17009 and Szabo et al. in Chemistry of Materials 18 (2006) 2740 were inspiration for this study. Chapter 4 starts with an insightful review (45 pages) on the changes in the structure of GO induced by thermal treatment (annealing). Compilation of the results obtained by different advanced analytical techniques (XPS, VB, XRD, Raman spectroscopy, TPD, DFT), provides the full image of mechanisms underlying the deoxygenation of GO during annealing at different temperatures up to  $1000^\circ\text{C}$ . This is very important for obtaining reduced graphite oxide with limited defects and vacancies in the lattice. Differences in the mechanism of deoxygenation of GO with low and high surface density of oxygen atoms have been discussed on several pages of the thesis based on the relevant paper of Larciprete et al. published in Journal of American Chemical Society 133 (2011) 17315. In this paper the term *gasification* is attributed to the evolution of  $\text{O}_2$ ,  $\text{CO}$  and  $\text{CO}_2$  during thermal reduction of GO to form rGO. The next paper (Klemeyer et al. ACS Materials Letters 3 (2021) 511) that was discussed in detail concerns the influence of the packing density of GO on the evolution of gases. Further, the role of  $\text{CO}$  in inducing reduction reactions affecting oxygen groups on GO sheets is also considered on several pages based on the paper of Narayanan et al. published in Journal of Vacuum Science & Technology A 31 (2013) 040691. Finally, clustering of the oxygen functionalities and its influence on the evolution of  $\text{CO}$  and  $\text{CO}_2$  during thermal decomposition of GO, and the enhancement of oxygen clustering due to the presence of nitrogen atoms in GO structure are widely discussed. Finally, the nitrogen doping mechanisms of GO developed via molecular dynamics (MD) simulations is outlined.

In experimental part of Chapter 4 regarding oxygen clustering, EGO and EGOF-A2 (200-300  $\mu\text{m}$ ) were the subject of the study. EGOF-A2 was selected due to the highest pillar density among all functionalized EGOF samples. Both samples were preheated at 80°C in air for 24 h to study the influence of oxygen clustering on the structure of reduced graphite oxide (rGO) and N-doped reduced graphite oxide (N-rGO) obtained by two approaches, i) thermal reduction at 850°C (flash pyrolysis) and ii) heat treatment in a TGA apparatus with a heating rate of 5°C/min to 900°C. For comparison, the respective reduced samples were prepared in the same conditions without oxidative treatment step. SEM, XRD, DSC, XPS and Raman spectroscopy were used for the characterization of the obtained materials. It is interesting that air treatment of functionalized EGO results in nearly double higher weight loss compared with the initial EGO (7.7 vs. 4.6 wt.%). Moreover, the elemental composition of EGO was preserved on air treatment while in case of EGOF-A2 the elimination of nitrogen and oxygen occurred (15 and 5%, respectively). The DSC study led to the conclusion that EGO-80 is an oxygen-clustered derivative of EGO which is more susceptible to reduction. Moreover, functionalized EGO (EGOF) was revealed to exhibit majority of oxygen functionalities in clustered form that explains its higher extent of reduction compared to non-functional EGO (C/O 25.5 vs. 14.2). Much higher susceptibility of air treated EGOF to reduction compared with EGO is explained by Author by closely packed (ether-)lactone-ether groups on the EGOF-80 sheets minimizing activation energy of thermal decomposition of GO. Functionalization of EGO also affects the morphology of the obtained rGOs. An inflated morphology is characteristic of pyrolyzed frameworks whose creation was convincingly presented by the author. Such morphology formed as a result of collapse of pillar during pyrolysis facilitates CO-induced reduction mechanism that explains higher reduction extent of framework compared with EGO.

The structural changes of graphite oxide and its functionalized form due to air treatment at 80°C and heat treatment with a low heating rate to 900°C in an argon flow (TGA) were thoroughly analyzed by XRD to determine the interlayer spacing ( $d_{001}$ ) and the crystalline height ( $L_c$ ), and Raman spectroscopy to evaluate the contribution of the in-plane crystalline  $sp^2$  domain size and defect density (the  $I_D/I_G$  ratio). Moreover, XPS technique was used to determine the surface elemental composition and the distribution of oxygen and nitrogen functional groups of the studied materials. In-depth analysis of the XPS results confirmed the clustering of oxygen functionalities via formation lactone/lactol rings due to heat treatment in air. Furthermore, enhanced oxygen clustering of frameworks was explained by presence of pillars in their structure. It was found that deoxygenation follows by restoration of the C=C component during pyrolysis is promoted by oxygen-clustered derivatives. Based on the deconvolutions of N1s spectra, Author also indicated increased contribution of graphitic N in framework-based reduced graphene oxide due to higher oxygen clustering extent. The author M. Sc. Ahmed Subrati proposed mechanisms of oxygen clustering in graphite oxide and graphite oxide-based framework (Fig. 4.28). This is a very valuable part of the work with great novelty. Author concluded that nitrogen doping of rGO can be controlled by oxygen clustering extent. Finally, an attempt was made to use pyrolyzed frameworks as electrode material for

supercapacitor. Their electrochemical properties were determined in a three-electrode system by cyclic voltammetry using 6M KOH as electrolyte. However, no promising results were obtained.

Experimental part of **Chapter 5** was preceded by literature review (25 pages) with a high contribution of theoretical studies on hydrogen storage based on Kubas interaction and spillover mechanism. This is related to Author's idea to develop framework-based materials with transition metal nanoparticles for hydrogen storage. The main focus was put on the relationship between the size of metal nanoparticles and their catalytic activity towards dissociation of hydrogen molecules, hydrogen chemisorption on the graphene layers, and finally carbon-supported Ni catalysts in terms of their performance in different processes such as synthesis of carbon nanofibers, hydrogenation of unsaturated hydrocarbons or alcohols. The role of carbon as a support for Ni-C system was also discussed. Literature review in Chapter 5 ends with graphene-supported Ni nanoclusters in view of mechanisms of adsorption of molecular hydrogen and its dissociation on Ni clusters.

Experimental part of this Chapter describes the results of the study regarding electrochemical deposition of Ni nanoparticles within EGOF-A2 framework with simultaneous its reduction. Two different electrochemical setups were proposed for obtaining Ni-loaded reduced frameworks which were subsequently characterized using XRD, SEM/EDS and HR-TEM. For the more promising method providing smaller Ni particles in size, the interlayer spacing was reduced from 8.8 for EGOF-A2 to 3.5 Å for REGOF-A2@Ni. Ni occurred in the form of large clusters with an average size of 0.7 µm. The reduction of framework led to undesirable elimination of pillars as confirmed by XRD. Author revealed based on the electron diffraction pattern that the deposited Ni particles result in rotation or translation of graphene layers leading to appearance of turbostratic domains.

In my opinion the synthesized Ni-loaded reduced graphite oxide-based frameworks are not suitable materials to be used for hydrogen storage via spillover mechanism. Firstly, the size of Ni particles is too large to exhibit reasonable catalytic activity towards dissociation of hydrogen molecules. Secondly, REGOF-A2, which plays the role of the receptor, shows a low degree of surface development, implying a low number of hydrogen atom adsorption sites.

Summarizing, the Ph.D. thesis prepared by M.Sc. Ahmed Subrati presents a high scientific level in terms of synthesis graphite oxide-based frameworks, the reaction mechanisms of the processes under investigation and the characterization of synthesized materials using a wide spectrum of advanced analytical techniques. The obtained results are well presented and thoroughly discussed, confirming author's in-depth knowledge of chemistry and physics of carbon materials. However, the dissertation leaves a fundamental deficiency. It is devoted to the development of innovative hydrogen storage materials but does not include any attempt to experimentally evaluate their adsorption capacity.

Regarding the reviewing process, some questions and comments have arisen, which should be discussed during the defense.

1. Author used the term *unsaturated units of graphene* which is chemically incorrect. The same is concerned the term *unsaturated  $sp^2$  receptors* (page 196) corresponding to graphene-based materials. The abbreviation GO is commonly used for graphene oxide, while here GO corresponds to graphite oxide for which GRO is more often used in the literature.
2. Moreover, I have a comment on the use of the term *gasification* for thermal treatment of carbon material in an inert atmosphere. Gasification is a process based on the reaction of carbon with a reactive gasifying agent, in most cases with oxidative gases such as CO<sub>2</sub>, steam, air, oxygen, a mixture of oxygen and steam. Carbon gasification reactions form the basis of several important industrial processes, e.g. combustion of coals, coal gasification to produce gas, carbon activation to produce activated carbon. Therefore, the title of section 4.1.1. Carbon backbone gasification as function of temperature should be formulated as Carbon backbone thermal degradation as a function of temperature.
3. How to explain the higher amounts of oxygen in the form of carboxyl groups in water-washed graphite oxide compared to acetone-washed graphite oxide.
4. What solvent was used for washing of overoxidized EGO and EGOF which subsequently were subjected to pyrolysis (Fig. 4.19). What conditions were used for drying of materials?
5. Fig. 2.32 presents fractions of C-O, C=O and COOH groups determined by XPS for EGO, overoxidized EGOs and chemically oxidized graphite. Deconvoluted XPS spectra should be also presented in the thesis.
6. Elemental analysis results of EFO and EGOF are presented in Table 3.3, therefore at.% should be replaced with wt. %. Moreover, the results of the elemental analysis are given to three decimal places. Such accuracy of determination is not provided by elemental analyzer.
7. A significantly lower interline spacing in EGO-80 compared with EGO (5.8 vs. 6.5 Å) is explained by “loss of some oxygen functional groups and emergence of defects” (page 170). However, this is not in line with surface elemental composition in Table 4.4 which shows comparable amounts of oxygen in both samples. Please comment on this.
8. Table 4.3. The values of  $d_{001}$  for pyrolyzed samples should be given to higher number of decimal places.
9. To realize Kubas interaction and hydrogen spillover, the designed hybrid system for this purpose should be composed of transition metal into large surface area materials. However, the synthesized framework-based materials exhibits low specific surface area as shown in this work. Hence my doubt about the validity of conducting research into the use of graphite oxide-based framework as a receptor.
10. The last question concerns Ni-loading of frameworks. Two electrochemical approaches were applied for this purpose, however, for different frameworks EGOF-

A1 (Fig. 5.16) and EGOF-A2 (Fig. 5.17). To what extent could this affect the selection of the loading method?

Concluding, the thesis prepared by M.Sc. Ahmed Subrati under supervision of Professor Stefan Jurga and then Dr. hab. Piotr Krawczyk as promoter and Dr. Patryk Florczak as co-promoter meets the requirements for receiving the PhD degree in Chemical Sciences. I recommend the submitted thesis for public defense.

A handwritten signature in blue ink, appearing to read "P. Florczak".