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Review of the doctoral dissertation of Mrs. Daria Minta entitled *Modified graphene materials for electrochemical sensing applications*

The doctoral thesis was carried out at the Department of Process Engineering and Technology of Polymer and Carbon Materials of the Faculty of Chemistry of the Wrocław University of Science and Technology under supervision of Prof. dr. hab. Grażyna Gryglewicz in cooperation with dr. Zoraida González from the Materiales Compuestos group of the Insituto de Cienca y Tecnología del Carbono, INCAR-CSIC, Oviedo – Spain as the assistant supervisor.

The thesis has been written in English. It has 180 pages including the list of 241 references. The form of the thesis is typical for the works in the field of chemical sciences. It starts with the introduction to the sensing design, electrochemical techniques useful for sensing construction and description of graphene and graphene-related materials. The literature introduction is closed by the formulation of the goal of the studies. In the next chapter Author describes the details of the experimental procedures used for the characterization of the materials and the testing of the proposed sensing methods. Subsequently, the results are presented and the closing conclusions. The text of the thesis is very well written. Author uses formal language, though the text is readable not only for the experts in the field. The more complicated concepts are illustrated with clear schemes, what is very big advantage in my opinion. From the formal point of view the thesis is prepared excellently.

Graphene and graphene oxide (GO) related materials are extensively studied as possible electrode modifiers, due to their high conductivity, abundant surface groups - enabling easy chemical modification, tunable physic-chemical properties. Example of such tunable properties is that upon removal of oxygen surface groups material becomes more hydrophobic, what might improve adsorption of organic analytes. The interest in reduced graphene oxide stems also from its intrinsic electrocatalytic properties and synergy in electrocatalysis, when combined with metallic nanoparticles (for example: Sens. Actuat. B: Chem, 2018, 258, 745-756, Electrocatalysis, 2020, 11, 215-225). Such interesting properties of graphene materials inspired probably the Author and her Supervisors to choose them as possible electrode materials for dopamine, ascorbic acid, uric acid and diclofenac sensors.

The studies were concentrated on the three groups on the reduced graphene oxide (RGO) related nanocomposites: the first group were the nanocomposites of RGO or nitrogen doped reduced graphene oxide (NRGO) with electrodeposited gold nanoparticles. The second involved the nanocomposites with polyaniline (PANI). Finally, the third group were materials based on the binary Fe_2O_3-SnO_2/RGO or ternary Fe_2O_3-SnO_2/RGO/PANI materials. The GOs synthesized by the Hummers-Offeman method were reduced by the hydrothermal treatment in autoclave. Alternatively, the GO mixed with urea was used to obtain the nitrogen doped graphene oxide (NRGO).

Another part of the thesis concerns the development of novel concept of the inkjet printed electrodes (IPEs) on the Kapton® support, printed using GO - carbon black-based inks optimized in the scope of this work. All research objectives are very clearly described in the chapter three. Author has prepared very descriptive Scheme (Scheme 1) explaining her idea and the research plan. Taking into account the broad research scope the Scheme is very valuable.

The literature concerning the use of GO, RGO and related materials is extremely broad. Entering the keywords “graphene oxide” and “electrochemical sensor” into the Web of Science base yields ca. 12430 results, therefore preparing the literature survey for this thesis

must have been difficult, though the survey does present the most important aspects of the thermal reduction of GO and of the research of GO materials as electrochemical sensors. The role of the doping by nitrogen or other heteroatoms is well presented. There is relatively little space in this part for the role of surface groups and the role of defects in the electrochemical properties of graphene oxide. The discussion could be found for example in works of Martin Pumera (10.1039/c6cs00136j). Such effects could be valuable for the discussion of the mechanism of the electrode reactions of dopamine, ascorbic acid and diclofenac. Despite this, the literature survey is well written in general.

The experimental part of the thesis contains several novel and important results. Among others, the novel sensors for the simultaneous detection of dopamine, ascorbic acid and uric acid were developed. The sensors were based on the gold nanoparticles electro-deposited on RGO or nitrogen doped reduced graphene oxide (NRGO) obtained by the hydrothermal reduction of GO or of the mixture of GO and urea. The conditions of the hydrothermal process are optimized for the highest sensitivity. It is shown, that doping with nitrogen improves the analytical signal of dopamine. The effect is explained by the homogenous electro-deposition of gold nanoparticles on NRGO, what in turn causes increased electrocatalytic activity. The sensor based on AuNPs and NRGO showed promising long term stability. The discussion is very convincing in my opinion. These results have been already published (Sensors 20:1-13, 2020 (IF = 3.576, MEiN =100).

Very good analytical parameters (LODs in order of 400 nM) were also obtained for electrodes combining PANI and the thermally reduced graphene oxide (TRGO). Both effects: the relative amounts of PANI to GO and the temperature of the hydrothermal process were optimized to achieve the highest sensitivity to dopamine.

Table 17 (page 99) shows that PANI-TRGO materials contain imines, protonated imines, amines and protonated amines – similarly to the pure PANI, therefore peaks coming from PANI could be visible on cyclic voltammograms. The Figure 55 shows cyclic voltammograms of the PANI-TRGO materials in the solution containing 100μM of dopamine.

Have you studied the cyclic voltammograms without dopamine and were the peaks form PANI visible? This question might not be crucial for the analytic performance of the sensor, but it might contribute to the understanding of the mechanism of the electrode reaction, which could object of further studies. The current results PANI are published in well recognized journal (Surfaces and Interfaces 28:1-10, 2022, IF =6.137; MEiN = 70).

The electrochemical detection of diclofenac seems to be less popular comparing to dopamine. Author studied the graphene based nanocomposites with PANI as possible materials for the diclofenac sensing, obtaining very good analytical parameters (Table 35).

Finaly, the novel materials involving SnO_2, F_2O_3, PANI and RGO were synthesized. The semiconductive nanoparticles were applied as alternative for gold nanostructures as catalysts for the electrooxidation of dopamine. The materials were optimized towards dopamine sensing, giving excellent analytical parameters with LODs significantly better comparing to the previously mentioned materials (Molecules, 25:1-18, 2020 (IF = 4.412, MEiN =140).

Very interesting alternative for the conventional glassy carbon electrodes covered by the layer of the electrocatalytic modifier is use of the inkjet printed electrodes (IPE). The electrodes prepared and studied in the thesis is novel, easy to prepare and very efficient alternative for the traditional electrochemical setups. The thermal reduction of graphene oxide printed on the Kapton® support gives similar material as the thermal reduction of the bulk material at the same conditions. Comparing Figure 68 and 101, it is visible that IPEs are characterized by smaller capacitive currents comparing to the traditional RGO electrodes, what author notice on page 151. The peaks are thus better resolved. The interesting feature of the diclofenac reaction on IPEs is significant irreversibility of the oxidation. It is interesting whether oxidation products bloc the electrode or they are soluble and diffuse away from the electrode surface. Despite this doubt, the IPE proposed in the thesis are very promising for future analytic applications. The concept has been published in Progress of Organic Coatings 185:1-9, 2023 (IF = 6.206; MEiN = 100).

Mrs. Daria Minta has co-authored 10 scientific publications at the moment, when the dissertation has been printed. She is the first author in 5 of these articles, what is very good result taking into account that all these works were prepared in a relatively short time. She presented her results on 9 Polish and 5 international conferences in the form of posters or oral presentations. Meaning, that Mrs. Minta is hard working person with considerable experimental and presentation skills.

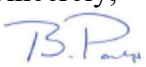
The minute critical remarks, which I mentioned above do not influence my very good impression about the dissertation in general. There are two points, which I hope I will have the opportunity to discuss with Mrs. Minta during the defense of the thesis. These are:

1. What could be the role of the oxygen groups on GO surface on the mechanism of dopamine and other redox reaction catalyzed by GO -based composites?
2. Did you consider using electrochemically reduced graphene oxide instead of the hydrothermally reduced GO? If yes, why did you choose TRGO?

Taking into account the very good scientific level of the work, important elements of scientific novelty and the publication achievements of the doctoral student, I conclude that the reviewed dissertation more than meets the requirements for doctoral theses specified in Art. 187 of the Act of July 20, 2018 Law on Higher Education and Science (Dz. U. z 2023 r., poz. 742 with later changes), therefore I am recommending the admission of Mrs. Daria Minta to the next stages of the doctoral process.

Furthermore, the dissertation fulfils the conditions for awarding the distinction to the thesis stated in the Act nr 36/08/RDND05/2021-2024 of Discipline Council of Chemical Engineering of May 7, 2021 and I recommend the distinction of the thesis of Mrs. Daria Minta.

Sincerely,



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