R E V I E W

by Assoc. Prof. Totka Mihaylova Dodevska, PhD

University of Food Technologies, Plovdiv

Dept. "Organic Chemistry and Inorganic Chemistry"

on the doctoral thesis for acquisition of educational and scientific degree “Doctor” in:

scientific area: 4. Natural Sciences, Mathematics, and Informatics

professional area: 4.2 Chemical Sciences

doctoral program: Physical Chemistry

Author: Maria Genova Pimpilova

Topic: Modification of glassy carbon electrodes with electrodeposited gold or 2D-nanomaterials: characterization and applications

Scientific supervisor: Assoc. Prof. Nina Dimitrova Dimcheva, PhD, Plovdiv University "Paisii Hilendarski"

1. General description of the presented materials

According to order № РД 21-245/30.01.2024 of the Rector of Plovdiv University "Paisii Hilendarski" (PU), I have been appointed as a member of the scientific jury to ensure a procedure for the defense of a PhD thesis on the topic "Modification of glassy carbon electrodes with electrodeposited gold or 2D-nanomaterials: characterization and applications" for the acquisition of the educational and scientific degree "doctor" in the field of higher education 4. Natural sciences, Mathematics and Informatics, professional area 4.2. Chemical Sciences, doctoral program: Physical Chemistry. The author of the PhD thesis is Maria Genova Pimpilova - a full-time PhD student at the Department of Physical Chemistry with scientific supervisor Assoc. Prof. Nina Dimitrova Dimcheva, Plovdiv University "Paisii Hilendarski".

The presented set of materials is in accordance with Art. 36 (1) of the Regulations for the Development of Academic Staff at PU and includes the following documents:

– A request to the Rector of PU for opening the procedure for public defense of doctoral thesis;

– Doctoral student’s CV;

– Record of the departmental council for preliminary discussion of the dissertation and the decision taken for opening the procedure for public defense of the doctoral thesis;

– Doctoral thesis;
– Extended abstract of the doctoral thesis in Bulgarian and English;
– List of scientific publications on the dissertation;
– Copies of two scientific publications;
– List of citations;
– Declaration of originality and authenticity of the attached documents;
– Certificate of compliance with the specific requirements of the Faculty.

The PhD student has attached 2 scientific publications on the topic of the dissertation, which are accepted for review.

2. Brief biographical data for the PhD candidate

Maria Pimpilova was born on January 02, 1982. In 2017 she graduated as a Bachelor of Chemistry at the Faculty of Chemistry of PU "Paisii Hilendarski". One year later, she completed her higher education at the same university (educational and qualification degree Master in Food Chemistry). In March 2020, she was appointed as an assistant to Department of Physical Chemistry. Fluent in English.

3. Relevance of the subject and appropriateness of the aims and objectives to the field of research

The dissertation is dedicated to a current topic in a field of practical interest. The PhD thesis is relevant both to the development of modern fundamental and applied electrochemistry, as well as to the analytical laboratory practice. The work is devoted to obtaining new types of modified electrodes-catalysts. On the base of the novel electrocatalysts electrochemical sensors have been created, applicable for: 1/ selective quantitative analysis of the catecholamines dopamine and L-epinephrine (fast-degrading components of medicinal forms), and 2/ hydrogen peroxide and its water-insoluble organic homologues. The research in the dissertation is directly related to the development of new reliable, time-saving electroanalytical methods that provide high selectivity and low detection limit of these analytes. Therefore, the topic of the dissertation work is relevant and significant, and the obtained results have a potential for application in the analytical practice.

4. Knowledge of the problem

Maria Pimpilova presented a thorough and critical review covering a significant number of references. The approach in writing this part of the dissertation leaves a very good impression and shows the doctoral student's ability to systematize and critically analyze literature data. Maria Pimpilova has in-depth theoretical knowledge in the field of research. She managed to show the relevance of the topic and highlighted the problems in a scientific and scientific-applied aspect. The main goal of the dissertation and the research tasks are precisely and clearly defined.

5. Research methodology

All the methods used in the experimental work are appropriate and suitable for solving the tasks and achieving the goal of the dissertation work. The used materials, apparatus and methods of the experiments are correctly described in detail.

6. Characteristics and evaluation of the doctoral thesis

The PhD thesis covers 134 pages; it is illustrated with 44 figures, 12 schemes and 6 tables. The reference list includes 238 items. The dissertation work is purely experimental, written in good scientific language, concise and clear. It is structured according to the requirements of this type of scientific work and includes the following well-balanced sections: Literature review; Purpose and tasks; Experimental part; Results and Discussion; Conclusions; References.

The first part of the dissertation is a well-structured literature review devoted to the problems of the scientific research. The overview does not exceed the recommended 1/3 of the total volume and it is relevant to the target study. This section shows the good theoretical knowledge of the PhD student, her competence to formulate the goal of the dissertation and the research tasks arising from it, as well as to use a scientific research approach in planning the research. The set tasks are feasible and properly arranged.

The presentation in the section "Results and Discussion" follows the order in which the research tasks of the dissertation are formulated. The research has been carried out logically and consistently. The comments on the experimental results are made precisely; Maria Pimpilova uses the specific terminology appropriately. The PhD student was able to present the results graphically and tabularly, so that the reader can easily navigate the considerable volume of factual material. The presented results and their analysis are original, the experimental studies were performed precisely with the necessary repeatability.

The presentation and the relevance of the results in this part of the dissertation reveal that Maria Pimpilova has theoretical knowledge and analytical skills to collect, summarize, process, and interpret data to make decisions and solve problems.

The doctoral student possesses knowledge within the fields of electrochemistry, biocatalysis, analytical chemistry and physical chemistry, which indicates the interdisciplinary nature of the PhD thesis.

7. Contributions and significance for science and practice

The dissertation contains original research contributions:

1/ An electrochemical biosensor has been developed for the quantitative detection of dopamine using two different electrochemical techniques – differential pulse voltammetry

and constant potential amperometry, the latter being also suitable for the analysis of L-epinephrine.

2/ The practical application of the laccase electrode for the quantitative analysis of dopamine and L-epinephrine in ampoules of injection solutions has been demonstrated.

3/ For the first time, the electrocatalytic effect of Co-g-C_3N_4/Nafion catalyst in the electrochemical reduction of hydrogen peroxide and tert-butyl hydroperoxide in a wide range of concentrations from 0.4 to 14 mM was demonstrated.

4/ The developed peroxide electrode is applicable for the determination of catalase enzyme activity in a neutral medium, and the obtained results are unprecedented in the scientific literature.

5/ The developed electroanalytical method based on the catalytic peroxide electrode has a significant potential to be used as an alternative to titrimetric methods for determining the peroxide content of vegetable oils.

8. Evaluation of publications on the dissertation work

The main part of the results are published in 2 scientific papers in peer-reviewed international journals: Biosensors (Q1) and "Catalysts" (Q2). The cumulative IF is 10.34, which is an objectively high score for the quality of the experimental work and the importance of the results. In both publications, the PhD student is the first author, which undoubtedly proves her main contribution to the work. The total number of points is 45 and it exceeds the required minimum of 30 points. To date, 8 independent citations (Scopus data) on the articles included in the PhD thesis have been noticed.

Seven presentations on the topic of the PhD thesis were presented on national and international scientific events. Concerning the research activity of the PhD student, the registered patent application for an invention should also be noted.

The publishing activity of the PhD student meets all the requirements for the educational and scientific degree "doctor" at the Plovdiv University "Paisii Hilendarski" in the professional area "4.2. Chemical Sciences".

9. Personal participation of the doctoral student

The results and contributions presented in the dissertation work are undoubtedly the personal merit of the PhD student, achieved under the expert guidance of the scientific supervisor Assoc. Prof. Dimcheva.

10. Assessment of the extended abstract of the doctoral thesis

The extended abstract provides sufficient information and accurately reflects the main scientific results and contributions of the dissertation.

11. Critical remarks and recommendations

Maria Pimpilova has been complied with the recommendations that were made to departmental council for her deduction and edited the indicated inaccuracies and technical errors in the dissertation. In my opinion, PhD student could have presented some of the figures (Figures 8A, 32, 42) in better quality to make the data clearer and more readable. Some of the calibration plots (Figures 32, 40, 42) do not show confidence intervals. These remarks do not affect the quality of the thesis and do not change the overall excellent impression of the research.

I have the following questions:

1/ With respect to the operational stability of the modified Co-g-C_3N_4/Nafion/GCE. Does the catalytic electrode is applicable for repeated measurements of the concentration of peroxides in real samples (massage oil) or a loss of catalytic activity occurs after the first measurement and the sensor is disposable?

2/ Have you investigated the residual activity of this electrode in long-term storage to assess the stability of the deposited catalytically active phase?

3/ Why the studies on the interfering effect of L-ascorbic acid on the signal of the laccase electrode were carried out in a ratio of 1:1 (L-ascorbic acid:catecholamine)? The concentration of ascorbic acid is 4-5 times higher than that of the target analytes in biological samples.

12. Personal impressions

I have no personal impressions of the PhD student. Based on her report on department council and the materials provided, I remain convinced that she is a motivated researcher who has the potential to continue to develop in the chosen research field.

13. Recommendations for future use of dissertation contributions and results

I would recommend Maria Pimpilova to continue experiments in order to prove the practical application of the developed sensor systems in other real samples.

CONCLUSION

The dissertation **contains scientific, scientific-applied and applied results, which represent an original contribution to science and meet all the requirements of the Law of the Development of Academic Staff in the Republic of Bulgaria** (LDASRB), the Regulations for the Implementation of LDASRB and the Regulations of Plovdiv University "Paisii Hilendarski".

The content of the reviewed dissertation convincingly shows that the doctoral student Maria Pimpilova **has** in-depth theoretical knowledge and professional skills in the field of Physical Chemistry, **demonstrating** qualities and skills for independent research work.

Due to the above, I confidently give my **positive assessment** of the research presented by the above reviewed dissertation, abstract, results and contributions, and **I am completely convinced to propose to the honored scientific jury to award Maria Genova Pimpilova the educational and scientific degree "Doctor"** in the area of higher education: 4. Natural sciences, Mathematics and Informatics, professional area: 4.2. Chemical Sciences, doctoral program: Physical Chemistry.

March 27, 2024 Reviewer: .....

/Assoc. Prof. T. Dodevska, PhD/