

STATEMENT

By Prof. DSci. Krasimir Ivanov Ivanov, Department of General Chemistry, Agricultural University-Plovdiv, (now retired) on dissertation for the award of the educational and scientific degree "PhD"

Field of higher education: 4. Science, Natural Sciences, Mathematics and Informatics

Professional field: 4.2. Chemical sciences

Doctoral programme: 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. Dr Nina Dimcheva, Faculty of Chemistry, Plovdiv University "Paisii Hilendarski"

1. General presentation of the procedure and the PhD student

By Order No. RD-21-245 dated 30.01.2024 of the Rector of Plovdiv University "Paisii Hilendarski" (PU) I have been appointed as a member of the scientific jury for the procedure for the defense of the dissertation thesis entitled "*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 field 4.2. Chemical Sciences, doctoral programme " Physical Chemistry ". The author of the dissertation is Maria Genova Pimpilova - PhD student in full-time study at the Department of Physicochemistry with scientific supervisor Assoc. Prof. Dr. Nina Dimcheva from Paisii Hilendarski University.

The set of materials submitted by the PhD student is in accordance with Article 36 (1) of the Regulations for the Development of the Academic Staff of PU. The dissertation is written in 134 standard typewritten pages, including 44 figures, 6 tables and 12 diagrams, 238 sources are cited, all in latin. The abstract is prepared according to the requirements of the relevant regulations and correctly reflects the work carried out and the results obtained.

The PhD student has attached 2 out-of-print articles. She has also co-authored a patent application which is not attached to the papers and will not be discussed.

Candidates for the degree of PhD must meet the minimum national requirements as regulated in the Regulations for the Application of the Law on the Development of Academic Staff in the Republic of Bulgaria. From the list of publications submitted by PhD student Pimpilova, it is evident that she exceeds the minimum requirements for obtaining the claimed PhD.

2. Relevance of the topic and appropriateness of the aims and objectives

The basis of the thesis work is the idea to create catalytically active electrode-catalysts and sensitive and selective electrochemical sensors for the quantitative analysis of biologically relevant compounds by suitable modification of electrodes from catalytically inactive conductive material. The formulated three research tasks are a logical consequence of the literature review and are subordinated to the ultimate *goal of obtaining and investigating two types of modified glassy carbon electrodes*: (1) an enzymatic electrode for the quantitative analysis of the catecholamines dopamine and adrenaline by electrochemical deposition of gold nanostructures and (2) an electrode-catalyst for the electrochemical reduction of water-soluble and non-water-soluble peroxide compounds.

The relevance of such research is undisputed and it has been identified as a priority area in a number of national and EC documents. In recent years, both public opinion and legislative initiatives have been particularly sensitive to issues related to healthy lifestyles, food quality control and prevention with regard to common diseases and, in particular, the development of rapid diagnostic methods. The research carried out is directly related to these priorities.

3. Characteristics and evaluation of the thesis and contributions

➤ *Knowing the problem*

The topic of the proposed PhD thesis is a continuation of the traditional for the Department of Physicochemistry of PU and in particular of the scientific supervisor Assoc. Prof. Dimcheva's research on electrode modifiers in the design of electrochemical chemosensors and biosensors. The literature review includes 218 literature sources, mostly from the last 10 years, detailing the current state of what is known in the scientific literature. The formulated research tasks are a logical consequence of the analysis, show a thorough knowledge of the problem and directions for upgrading and searching for innovative solutions.

➤ *Study methodology*

The selected research methodology is a consequence of the detailed literature review and the set aim and specific objectives. Different approaches (electrochemical deposition of gold, modification of electrodes with graphitic carbon nitride $g-C_3N_4$, immobilization of laccase on gold-modified glassy carbon electrodes and immobilization of catalase enzyme on glass substrates) and a large number of complementary electrochemical methods were used in the characterization of glassy carbon electrodes. Scanning electron microscopy with EDX was used to determine the morphology in the surface modification phase study.

➤ *Contributions and significance of the development for science and practice*

The original character of the results obtained is undisputed, and some of them are of a pioneering nature. In my opinion, the most important contribution of this dissertation is the upgrade in the systematic study of efficient and highly selective electrocatalytic systems with potential applications in pharmaceutical and clinical analysis, food quality monitoring, etc. by (1) Extending the scope of traditional research by obtaining electrodes modified with different catalysts - $g-C_3N_4$, Co-Mg- $g-C_3N_4$, Co-Bi₂- $g-C_3N_4$, Co/ $g-C_3N_4$ и Co_3O_4 ; (2) Contributed to the development of electrochemical techniques that have advantages over conventional analytical techniques in terms of rapid response, high sensitivity and high resolution and (3) Achieved very good electroanalytical results that allow the determination of the studied biologically relevant compounds in real samples and established a method for electrochemical determination of peroxide value in vegetable oils that has potential for practical application.

4. Assessment of publications and personal contribution of the PhD student

The publication activity of the PhD student includes 2 full-text publications in journals with high impact factor (4.5 and 5.4) and Q1 rank. In both publications she is first author. The first publication (Catalysts. 2022 vol. 12 , no. 8 p. 807) has been cited by 2 and the second (Biosensors 2022 vol. 12, no. 9 p. 719) by 8 independent authors, which is indisputable evidence of the relevance of the topic and the quality of the publications. Both publications are out of print 2022 and their potential for a wide response in the scientific literature is high. PhD student Pimpilova has participated in 7 scientific forums (in 5 of them as first author), where 3 oral and 4 poster papers were presented. I have no personal impressions of the PhD student's work, but the materials presented give me reason to assume that her contribution to the development of the dissertation, the

description and interpretation of the results, and their formulation as scientific publications is substantial.

I will also allow myself one recommendation: in the preparation of electrode-catalysts a spinel catalyst $\text{CuO/Cr}_2\text{O}_3$ can be used, which is easily obtained with very good reproducibility and extremely high activity in oxidation processes.

CONCLUSION

The dissertation submitted for my opinion complies with all the requirements of the Academic Staff Development Act in the Republic of Bulgaria, the Regulations for the Implementation of the Regulations for the Application of the Law on the Development of Academic Staff in the Republic of Bulgaria and the Regulations of the PU. It contains scientific and applied results that represent an original contribution to science and its development has helped to build PhD student Pimpilova as an independent researcher capable of obtaining, analyzing and presenting original scientific results. This gives me a reason to give a positive assessment of the conducted research and to recommend with conviction to the honorable scientific jury to award the educational and scientific degree "Doctor" to Maria Genova Pimpilova in the field of higher education: 4. Natural Sciences, Mathematics and Informatics, Professional field, 4.2 Chemical Sciences, Doctoral programme Physical Chemistry.

20.03. 2024 г.

Reviewer:

Prof. DSci. Krasimir Ivanov