“BABEȘ-BOLYAI” UNIVERSITY CLUJ-NAPOCA

FACULTY OF CHEMISTRY AND CHEMICAL ENGINEERING

DOCTORAL SCHOOL OF CHEMICAL ENGINEERING

DOCTORAL THESIS

-ABSTRACT-

PhD Candidate:

Alexandra Belcovici

Scientific Supervisor:

Prof. Habil. Dr. Eng. Graziella-Liana Turdean

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NANO/MATERIALS WITH APPLICATIONS IN THE DETECTION OF IMPORTANT ANALYTES FOR LIFE QUALITY

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Table of Contents

1. Introduction

Globally, heavy metal pollution has become an increasingly serious environmental issue, making the detection of these contaminants essential for protecting both public health and the environment. Heavy metal contamination (e.g., Pb, Hg, Cd, As, Cr, Cu, Zn, and U) originates primarily from industrial emissions and discharges (including metallurgical industries, chemical manufacturing, and electronics production), agricultural runoff, and improper waste disposal [1].

Another important class of compounds with potential adverse effects on human health comprises organic compounds, as both excessive and deficient concentrations of these substances in the human body may lead to severe diseases. For example, dopamine (DA) is one of the major neurotransmitters in the mammalian central nervous system (CNS) and plays a crucial role in the functioning of the central nervous, renal, and cardiovascular systems. Another important neurotransmitter is noradrenaline (NA), which is released into the bloodstream by the adrenal glands. Clinically, noradrenaline is administered as a therapeutic agent for the treatment of bronchial asthma, hypotension, myocardial infarction, heart failure, and other cardiovascular disorders, as well as neurological diseases such as Parkinson's disease and diabetes [4].

Currently, several analytical techniques, including atomic fluorescence spectroscopy (AFS), atomic absorption spectroscopy (AAS), and inductively coupled plasma mass spectrometry (ICP-MS), have been widely employed for the determination of heavy metals and organic compounds [6]. However, these techniques generally require expensive instrumentation, sophisticated laboratory facilities, and highly trained personnel. An attractive alternative is represented by

electrochemical methods based on chemically modified electrodes (CMEs), which offer high sensitivity, rapid response, operational simplicity, low cost, and the possibility of **in situ** analysis.

The main objective of this doctoral thesis was the development of chemically modified electrodes based on nanomaterials for the detection of either heavy metals or biologically important organic compounds, namely dopamine and noradrenaline.

The thesis is organized into two major parts. The first part presents a comprehensive literature review concerning the preparation and applications of chemically modified electrodes, while the second part focuses on the original research results and discusses the application of these CMEs for the determination of various analytes [2].

Chapter 2 reviews the fundamental theoretical aspects related to the preparation and applications of chemically modified electrodes, with particular emphasis on their use for the detection of heavy metal ions (HMIs) and antioxidant compounds. The chapter discusses the operating principles of chemically modified electrodes, the materials employed for electrode modification, and the advantages and limitations of different functionalization strategies. A separate section is devoted to the experimental techniques used for the investigation of chemically modified electrodes, including cyclic voltammetry (CV), square-wave voltammetry (SWV), differential pulse voltammetry (DPV), and electrochemical impedance spectroscopy (EIS). Overall, this chapter provides the theoretical background necessary to support the experimental work presented in the thesis and contributes to a better understanding of how electrode modification improves the performance of electrochemical sensors.

Chapter 3 presents the general objectives of the research underlying this doctoral thesis. These objectives were established in response to the need for developing chemically modified electrodes with enhanced performance for the detection of heavy metal ions and biologically relevant organic compounds, considering both the significant impact of these analytes on human health and the environment and the growing demand for rapid, sensitive, and selective analytical techniques.

Chapter 4 describes the synthesis of ZnO nanoparticles, their physicochemical characterization, and their integration into a modified electrode. The electrochemical and analytical performances of the resulting electrode are evaluated, together with its applicability to real sample analysis.

The chapter concludes with a summary of the main findings regarding the performance of the ZnO-NP-Nafion/GCE electrode.

Chapter 5 describes the synthesis and characterization of ZIF-8 and its reduced graphene oxide (rGO) nanocomposite. The electrochemical behavior and analytical performance of the resulting modified electrode are investigated, with particular emphasis on sensitivity, selectivity, and practical applicability. The main findings are summarized in the chapter conclusions.

Chapter 6 presents the electropolymerization process used to prepare poly(3,4-ethylenedioxythiophene) (PEDOT) and methylene blue-doped PEDOT (PEDOT-MB) films on the electrode surface, together with the influence of polymerization conditions on the electrochemical response. The electrochemical and analytical performances of the modified electrodes, their stability, and the influence of potential interfering species are discussed, followed by applications to real samples and the corresponding chapter conclusions.

The thesis concludes with the **General Conclusions** and the **References**.

3. General Objectives of the Thesis

The general objectives of this doctoral research were:

1. To synthesize and characterize nanomaterials exhibiting redox properties.
2. To develop nanomaterial-based chemically modified electrodes for the determination of analytes of environmental importance (heavy metals) and biomedical relevance (dopamine and noradrenaline).
3. To apply and validate electrochemical methods employing chemically modified electrodes against standardized analytical methods.

To accomplish these general objectives, a series of specific objectives were established and are presented at the beginning of each chapter included in part **II – Original Contributions**.

The achievement of these objectives was demonstrated through comprehensive physicochemical characterization techniques, including Fourier-transform infrared spectroscopy (FTIR), nitrogen adsorption-desorption isotherms (BET analysis), scanning electron microscopy (SEM), X-ray diffraction (XRD), and other complementary methods. Electrochemical characterization was

carried out using cyclic voltammetry (CV), square-wave voltammetry (SWV), square-wave anodic stripping voltammetry (SWASV), and electrochemical impedance spectroscopy (EIS).

5. Preparation of the ZnO-NP-Nafion/GCE Modified Electrode

The following specific objectives were pursued in this chapter:

1. Synthesis of zinc oxide nanoparticles (ZnO-NPs) by the precipitation method using different precipitating agents.
2. Fabrication of a ZnO-NP-based chemically modified electrode (ZnO-NP-Nafion/GCE).
3. Evaluation of the electrochemical and analytical performance of the ZnO-NP-Nafion/GCE modified electrode.
4. Application of the ZnO-NP-Nafion/GCE modified electrode for the determination of heavy metals in real water samples.

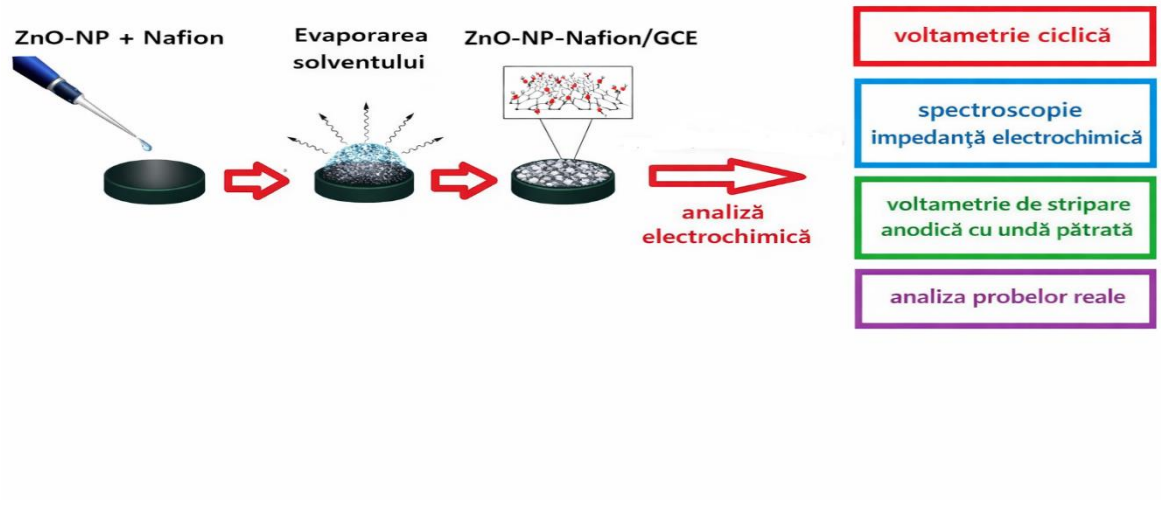


Figure 5.1. Schematic representation of the fabrication of the ZnO-NP-Nafion/GCE modified electrode and the electrochemical techniques employed for its characterization.

For the preparation of the ZnO-NP-Nafion/GCE modified electrode, 1 mL of a modifier suspension was prepared containing 2 mg of ZnO nanoparticles (ZnO-NPs), 0.5 mL of Nafion solution in ethanol, and 0.5 mL of deionized water (H_2O).

For the preparation of the ZIF-8-rGO-Nafion/GCE modified electrode, 1.5 mL of a modifier suspension was prepared containing 1 mg of ZIF-8, 1 mg of reduced graphene oxide (rGO), 0.5 mL of Nafion solution, and 1.0 mL of distilled water.

5.4. Electrochemical Characterization of the Chemically Modified Electrode (Estimation of Electrochemical Parameters: Effect of Scan Rate, pH, Electroactive Surface Area, and EIS Measurements)

Figure 5.3 shows the cyclic voltammograms recorded in 0.1 M KCl containing 5 mM $[Ru(NH_3)_6]^{3+}$, using glassy carbon (GC), Nafion/GCE, and ZnO-NP-Nafion/GCE as working electrodes. As expected, a pair of well-defined redox peaks corresponding to the quasi-reversible $[Ru(NH_3)_6]^{3+/2+}$ redox couple was observed.

The electrochemical parameters estimated from the cyclic voltammograms obtained with the three types of electrodes included the peak-to-peak separation ($\Delta Ep = Epa - Epc$), the formal potential ($E°'$), calculated as the arithmetic mean of the anodic and cathodic peak potentials, $(Epa + Epc)/2$, and the anodic-to-cathodic peak current ratio (Ipa/Ipc). The calculated values are summarized in Table 5.1.

Table 5.1. Electrochemical parameters of the bare GCE, Nafion/GCE, and ZnO-Nafion/GCE electrodes in 0.1 M KCl solution containing 5 mM $[Ru(NH_3)_6]^{3+}$.

Working electrode	ΔE_p / V *vs.* Ag/AgCl/KCl_{sat}	$E^{o'}$ / V *vs.* Ag/AgCl/KCl_{sat}	I_{pa}/I_{pc}
GC	0.082	-0.109	0.914
Nafion/GCE	0.108	-0.193	1.235
ZnO-Nafion/GCE	0.237	-0.237	1.294

The data presented in Table 5.1 indicate that the peak-to-peak separation (ΔEp) increases, whereas the anodic and cathodic peak currents decrease following the incorporation of ZnO nanoparticles into the modifier matrix deposited on the electrode surface. This behavior suggests

that the presence of ZnO-NPs affects the quasi-reversible redox process and creates a diffusion barrier for the redox probe, namely $[Ru(NH_3)_6]^{3+}$, thereby hindering both electron transfer and mass transport, as illustrated in Figure 5.3A.

The effect of the scan rate on the electrochemical behavior of the $[Ru(NH_3)_6]^{3+/2+}$ redox couple was investigated over the scan rate range of 5–150 mV s^{-1}. As shown in Figure 5.3B, the oxidation and reduction peak potentials of the $[Ru(NH_3)_6]^{3+/2+}$ redox couple exhibit slight shifts toward more positive and more negative potentials, respectively, with increasing scan rate.

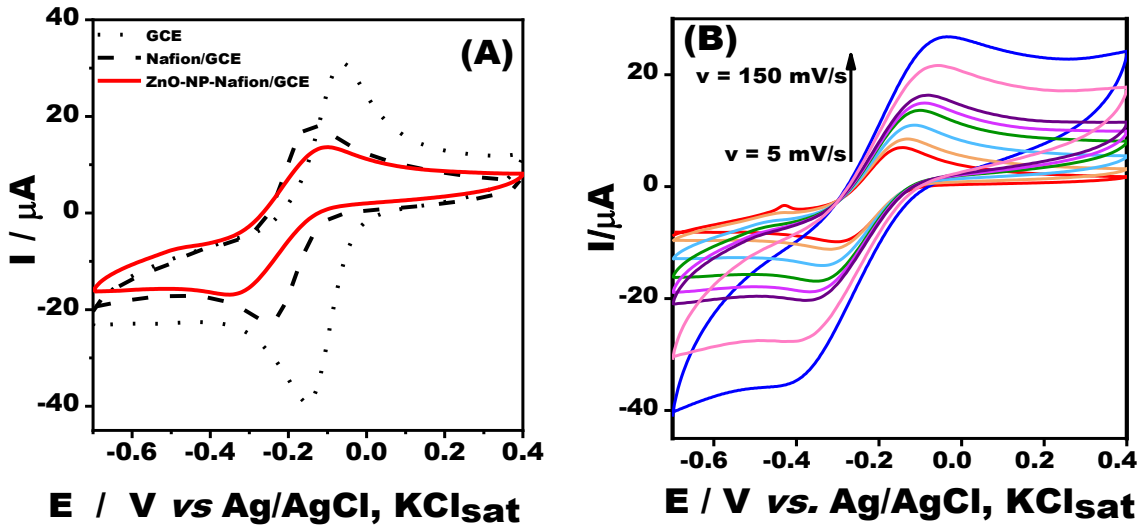


Figure 5.3. Cyclic voltammograms recorded at GC, Nafion/GCE, and ZnO-NP-Nafion/GCE electrodes (A). Effect of scan rate on the electrochemical behavior of the ZnO-NP-Nafion/GCE modified electrode (B). Experimental conditions: supporting electrolyte, 0.1 M KCl solution containing 5 mM $[Ru(NH_3)_6]^{3+}$; scan rate, 50 mV s^{-1} (A), see legend (B); initial potential, −0.7 V vs. Ag/AgCl/KCl.

5.4.2. Simultaneous Detection

One of the objectives of this study was the determination of heavy metals in drinking water collected from groundwater wells located in a mountainous mining area, where elevated concentrations of **Pb^{2+}** and **Cu^{2+}** are commonly encountered. In this environment, the likelihood of the presence of organic pollutants that undergo oxidation at highly positive stripping potentials is considered to be very low. Therefore, the simultaneous electrochemical determination of all the investigated metal ions, namely **Cd^{2+}, Pb^{2+}, Cu^{2+}, and Fe^{3+}**, was carried out.

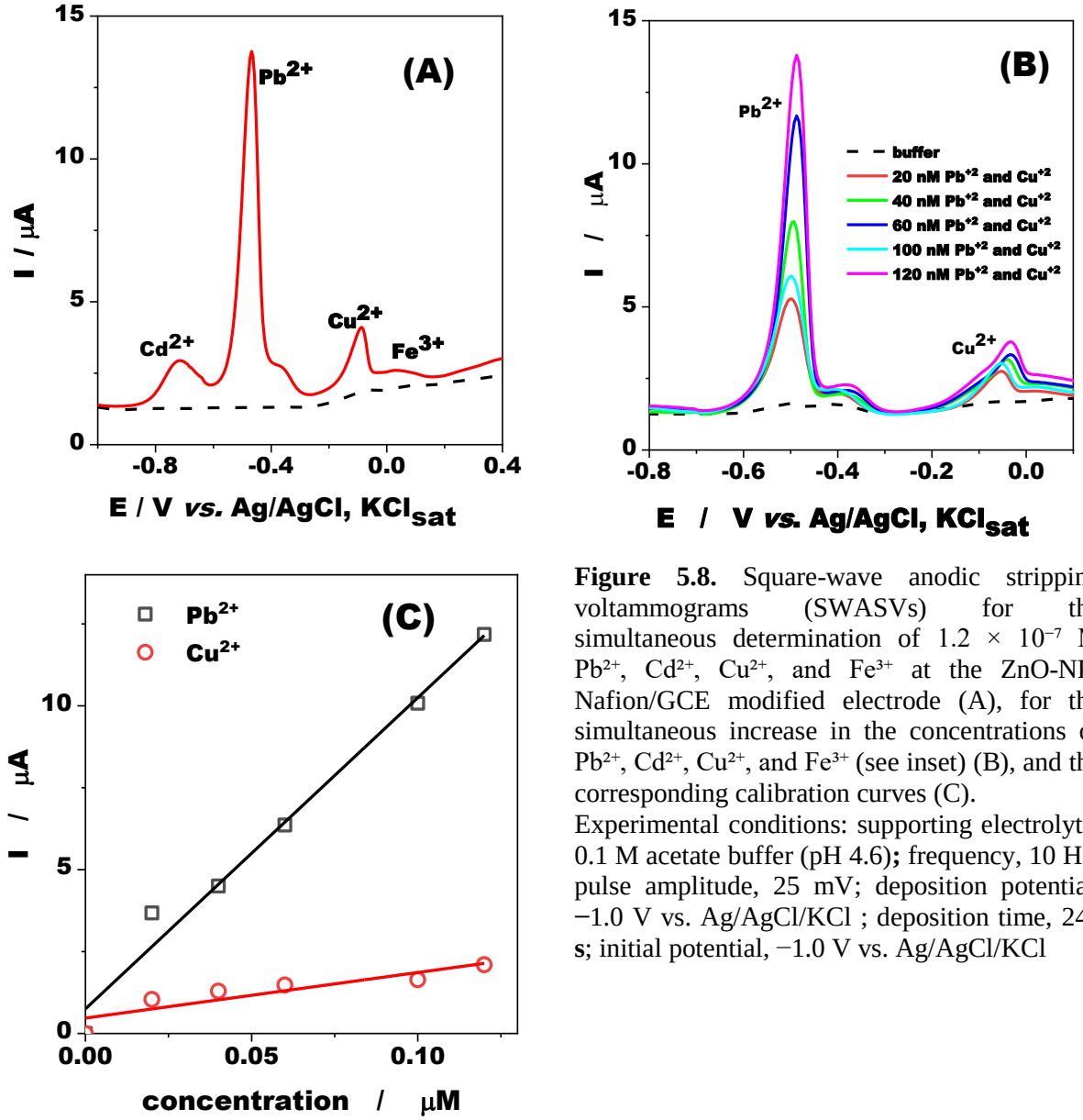


Figure 5.8. Square-wave anodic stripping voltammograms (SWASVs) for the simultaneous determination of 1.2×10^{-7} M Pb^{2+}, Cd^{2+}, Cu^{2+}, and Fe^{3+} at the ZnO-NP-Nafion/GCE modified electrode (A), for the simultaneous increase in the concentrations of Pb^{2+}, Cd^{2+}, Cu^{2+}, and Fe^{3+} (see inset) (B), and the corresponding calibration curves (C).
Experimental conditions: supporting electrolyte, 0.1 M acetate buffer (pH 4.6)**;** frequency, 10 Hz; pulse amplitude, 25 mV; deposition potential, −1.0 V vs. Ag/AgCl/KCl ; deposition time, 240 **s**; initial potential, −1.0 V vs. Ag/AgCl/KCl

5.5. Analytical Application of the ZnO-NP-Nafion/GCE Modified Electrode to Real Samples

Under the optimized experimental conditions, the ZnO-NP-Nafion/GCE modified electrode was applied to the simultaneous determination of heavy metals in real groundwater samples collected from a mining area in Alba County, Romania. The results obtained using the ZnO-NP-Nafion/GCE modified electrode were compared with those obtained by the standard atomic absorption spectroscopy (AAS) method. The comparative results are summarized in Table 5.3**.**

The obtained results demonstrate good agreement between the heavy metal concentrations determined by the electrochemical method employing the ZnO-NP-Nafion/GCE modified electrode and those measured using the standard AAS method.

Recovery values of 98.38% and 101.5% were obtained for Cu(II) and Pb(II)**,** respectively. These results indicate that the ZnO-NP-Nafion/GCE modified electrode has considerable potential as an alternative analytical platform for practical applications. The proposed electrochemical method provides sufficient sensitivity for the determination of heavy metals in real groundwater samples.

Table 5.3. Comparative determination of Pb^{2+} and Cu^{2+} in groundwater samples using the ZnO-NP-Nafion/GCE modified electrode and the standard atomic absorption spectroscopy (AAS) method.

Sample	$[HM]_{AAS}$ / M	$[HM]_{SWASV}$ / M		Recovery/ %
		addedt	recovered	
Apa, Cu^{2+}	8.05×10^{-8}	8.0×10^{-8}	7.87×10^{-8}	98.38
Apa, Pb^{2+}	3.97×10^{-8}	4.0×10^{-8}	4.06×10^{-8}	101.5

6. Preparation of the ZIF-8-rGO-Nafion/GCE Modified Electrode

In this chapter, the following specific objectives were pursued:

1. To utilize ZIF-8 for the fabrication of a ZIF-8-rGO-Nafion/GCE modified electrode.
2. To evaluate the electrochemical and analytical parameters of the ZIF-8-rGO-Nafion/GCE modified electrode.
3. To apply the ZIF-8-rGO-Nafion/GCE modified electrode for the determination of an electroactive analyte (dopamine).

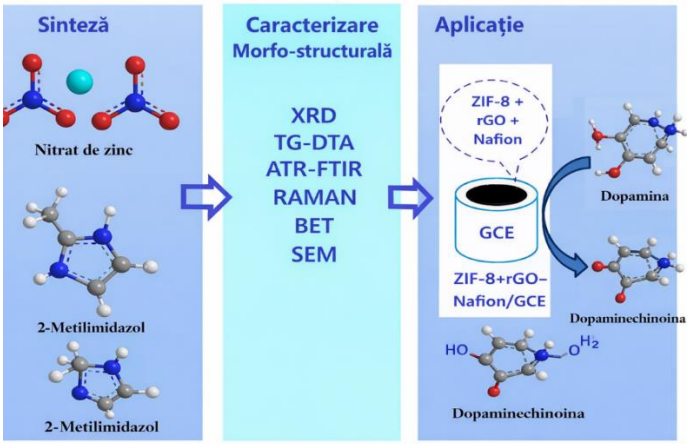


Figura 6.1. Reprezentare schematică a procesului de obținere a electrodului modificat ZIF-8-rGO-Nafion/GCE

6.4. Electrochemical Characterization of the ZIF-8-rGO-Nafion/GCE Chemically Modified Electrode

The electrochemical behavior of dopamine (10^{-4} M) at the interface of different modified electrodes, namely Nafion-rGO/GCE, ZIF-8-Nafion/GCE, and ZIF-8-rGO-Nafion/GCE, is presented in Figure 6.4A. As expected, the cyclic voltammograms exhibit a pair of redox peaks corresponding to the quasi-reversible redox reaction when ZIF-8 is incorporated into the electrode modification matrix.

The calculated electrochemical parameters include the peak-to-peak potential separation (ΔEp), determined as the difference between the anodic peak potential (Epa) and the cathodic peak potential (Epc); the formal potential (E°′), calculated as the arithmetic mean of Epa and Epc; and the anodic-to-cathodic peak current ratio (Ipa/Ipc). The obtained values are summarized in Table 6.1.

Table 6.1. Electrochemical parameters of the ZIF-8-Nafion/GCE and ZIF-8-rGO-Nafion/GCE electrodes in a 10^{-4} M dopamine solution.

Type of electrode	ΔE_p / V *vs.* Ag/AgCl/KCl_{sat}	$E^{o'}$ / V *vs.* Ag/AgCl/KClsat	I_{pa}/I_{pc}
ZIF8-Nafion/GCE	+0.452	+0.278	0.85
ZIF8-rGO-Nafion/GCE	+0.260	+0.230	0.63

To estimate the electrochemically active surface area (EASA) of the ZIF-8-rGO-Nafion/GCE modified electrode, cyclic voltammograms were recorded with the electrode immersed in a 0.1 M KCl solution containing 5 mM $K_4[Fe(CN)_6]/K_3[Fe(CN)_6]$ at different scan rates (Figure 6.4B).

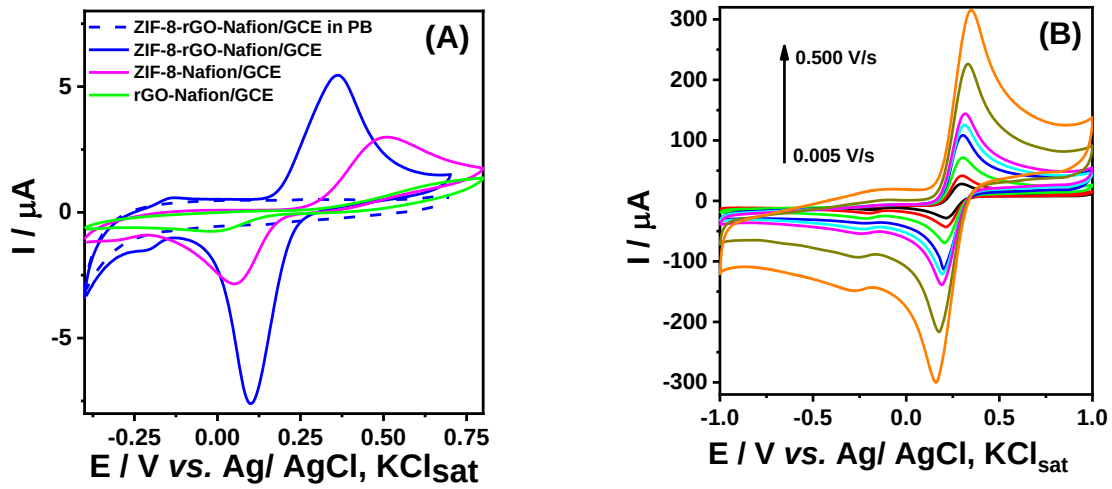


Figure 6.4. (A) Cyclic voltammograms recorded at different modified electrodes (see inset) in the absence (dashed line) and presence (solid colored line) of 10^{-4} M dopamine. (B) Effect of the scan rate (see inset) on the response of the ZIF-8-rGO-Nafion/GCE modified electrode. Experimental conditions: electrolyte: 0.1 M PBS solution (pH 7.0) (A) and 0.1 M KCl solution containing 5 mM $K_4[Fe(CN)_6]/K_3[Fe(CN)_6]$ (B); scan rate: 0.05 V s^{-1} (A) and as indicated in the inset (B); initial potential: −0.4 V vs. Ag/AgCl (sat. KCl) (A) and −1.0 V vs. Ag/AgCl (sat. KCl) (B).

6.5. Analytical Characterization of the ZIF-8-rGO-Nafion/GCE Chemically Modified Electrode

The electroanalytical performance of the ZIF-8-rGO-Nafion/GCE modified electrode was investigated by square-wave voltammetry (SWV) for the quantitative determination of dopamine. As shown in Figure 6.9A, the peak current increases with increasing dopamine concentration in the solution. The corresponding calibration plot exhibits a linear response over the concentration range of 0.5–1.4 µM (Figure 6.9B).

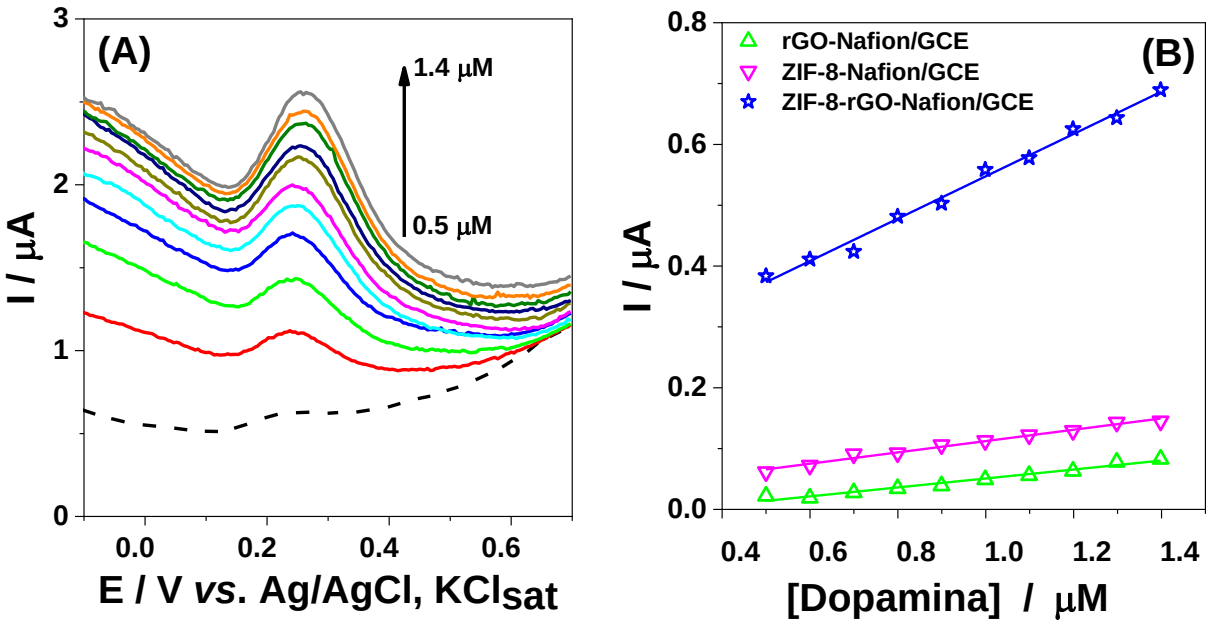


Figure 6.9. Square-wave voltammograms (SWVs) recorded at the ZIF-8-rGO-Nafion/GCE modified electrode in the absence (black dashed line) and presence (solid colored lines) of different dopamine concentrations (A), together with the corresponding calibration plot (B). Experimental conditions: electrolyte, 0.1 M phosphate buffer (PB, pH 7.0); frequency, 10 Hz; pulse amplitude, 0.05 V; step potential, 0.0045 V; initial potential, −0.4 V vs. Ag/AgCl (sat. KCl); analyte stock solution, 10^{-4} M dopamine.

6.6. Analytical Application of the Modified Electrode to Real Sample Analysis

To demonstrate the practical applicability of the developed electrode, the determination of dopamine in injectable ampoules was investigated. For this purpose, square-wave voltammograms (SWVs) were recorded using the standard addition method. The obtained results are summarized in Table 6.4.

Table 6.4. Results of the analysis of real samples using the standard addition method.

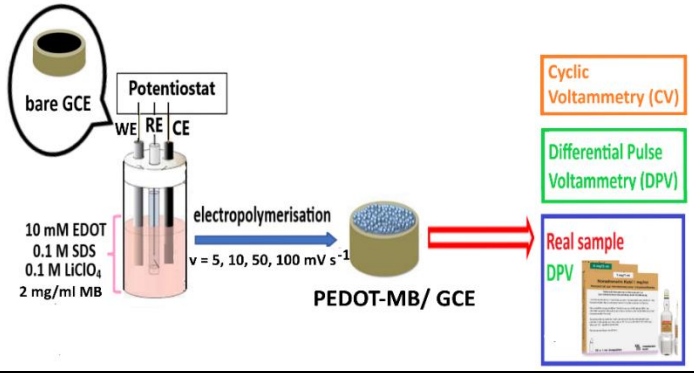
Sample	$[DA]_{adăugată}$ / μM	[DA] / μM	Recovery / %
1	0.5	0.554	110.8
2	0.5	0.559	111.8
3	0.5	0.563	112.6
mean	0.5	0.56 ± 0.003	112.0

The recovery values, ranging from 110.8% to 112.6%, are likely attributable to the presence of a small amount of maleic acid, which may be adsorbed onto and oxidized at the electrode surface [47]. Nevertheless, recovery values below 120% are generally considered acceptable for pharmaceutical analysis [48]. Therefore, it can be concluded that the ZIF-8-rGO-Nafion/GCE modified electrode demonstrates satisfactory accuracy and reliability for the analysis of real pharmaceutical samples.

7. Preparation of the PEDOT/GCE and PEDOT-MB/GCE Modified Electrodes

In this chapter, the following specific objectives were pursued:

1. To fabricate a PEDOT-MB/GCE modified electrode by electropolymerization of the monomer 3,4-ethylenedioxythiophene (EDOT), yielding the conducting polymer PEDOT, in the presence of methylene blue (MB).
2. To evaluate the electrochemical and analytical performance of the PEDOT-MB/GCE modified electrode toward the determination of norepinephrine (NE).
3. To apply the PEDOT-MB/GCE modified electrode to the determination of norepinephrine in pharmaceutical formulations.



7.4. Electrochemical Characterization of the PEDOT-MB/GCE Chemically Modified Electrode

The electrochemical performance of the PEDOT/GCE and PEDOT-MB/GCE electrodes toward the determination of norepinephrine (NE) was investigated by cyclic voltammetry (CV) (Figure

7.9A) and differential pulse voltammetry (DPV) (Figure 7.9B). Measurements were performed at the bare and modified electrodes in the absence and presence of NE.

The pair of peaks observed in the cyclic voltammograms (Figure 7.9A) corresponds to the oxidation/reduction of norepinephrine to its corresponding *o*-quinone.

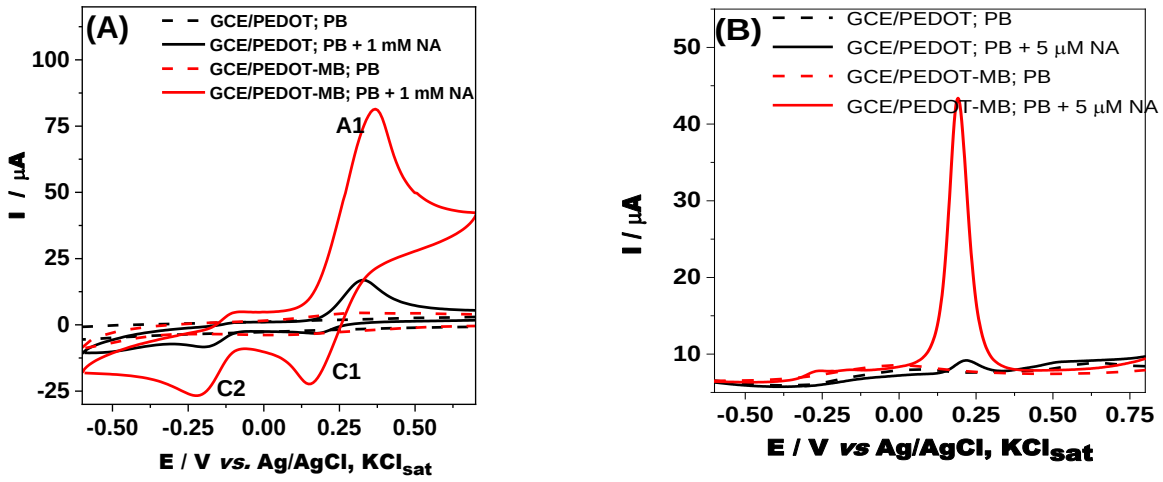


Figure 7.9. Cyclic voltammograms (A) and differential pulse voltammograms (DPVs) (B) recorded at the PEDOT/GCE and PEDOT-MB/GCE modified electrodes in the absence and presence of 1 mM (A) and 5 µM norepinephrine (B). Experimental conditions: electrolyte, 0.1 M phosphate buffer (pH 7.0); scan rate, 50 mV s^{-1} (A); initial potential, −0.6 V vs. Ag/AgCl (sat. KCl) (A, B); potential step, 0.005 V (B); pulse amplitude, 0.05 V (B); pulse time, 0.05 s (B); pulse period, 0.10 s (B).

7.5. Analytical Characterization of the Chemically Modified Electrode

To construct the calibration curves for the PEDOT/GCE and PEDOT-MB/GCE modified electrodes (Figure 7.14C), differential pulse voltammograms (DPVs) were recorded at increasing concentrations of norepinephrine (Figure 7.14A,B).

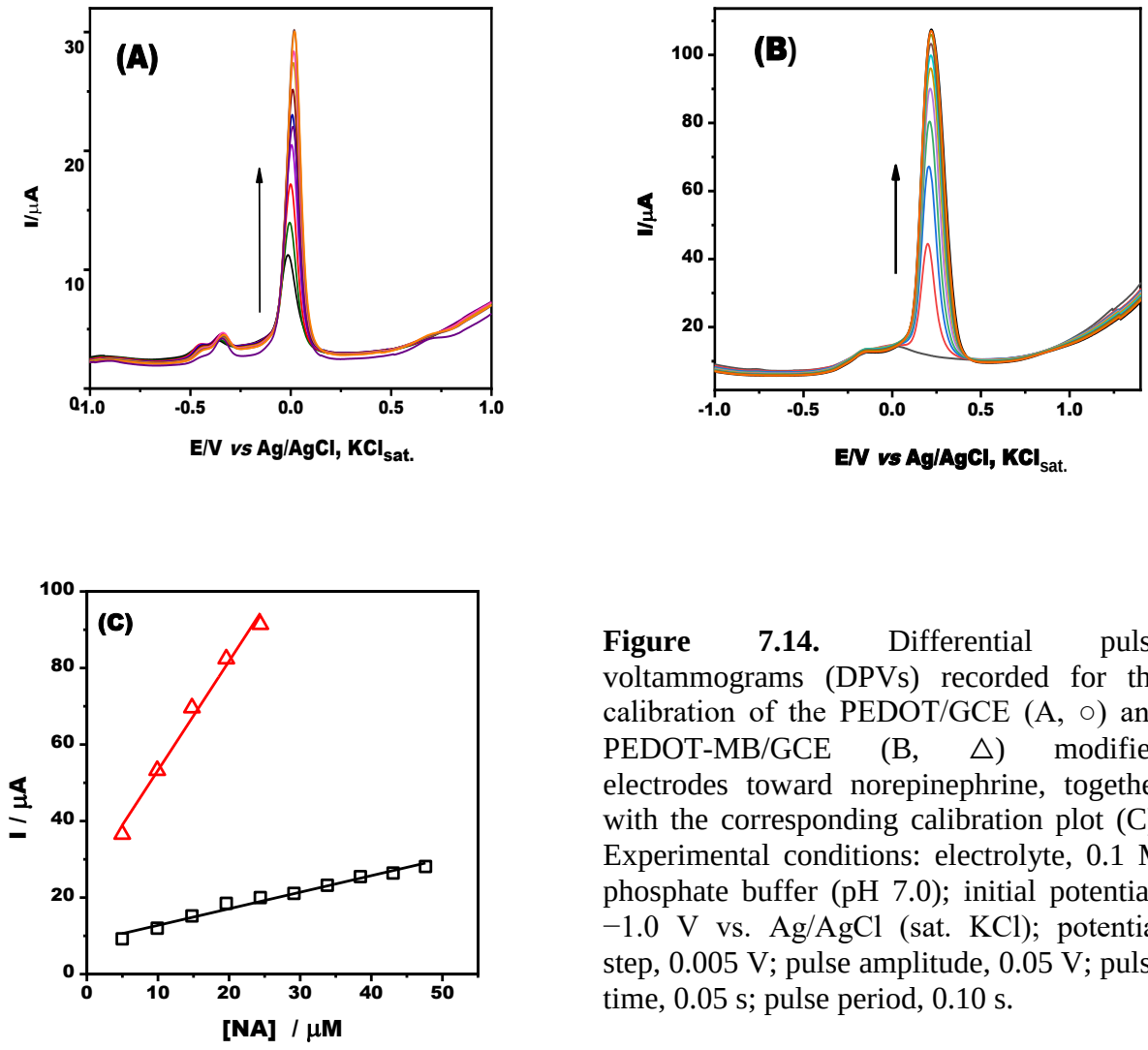


Figure 7.14. Differential pulse voltammograms (DPVs) recorded for the calibration of the PEDOT/GCE (A, ○) and PEDOT-MB/GCE (B, △) modified electrodes toward norepinephrine, together with the corresponding calibration plot (C). Experimental conditions: electrolyte, 0.1 M phosphate buffer (pH 7.0); initial potential, −1.0 V vs. Ag/AgCl (sat. KCl); potential step, 0.005 V; pulse amplitude, 0.05 V; pulse time, 0.05 s; pulse period, 0.10 s.

The analytical parameters of the calibration curves are summarized in the following table.

Table 7.3. Analytical parameters of the calibration curves obtained with the modified electrodes.

	GCE/PEDOT	GCE/PEDOT-MB
Sensitivity (A/M)	0.43 ± 0.02	2.86 ± 0.18
Linear Range / M	4.98×10^{-6} ÷ 38.5×10^{-6}	4.98×10^{-6} ÷ 25×10^{-6}
Limit of Detection* / M	4.67×10^{-6}	3.15×10^{-6}

*The limit of detection (LOD) was calculated at a signal-to-noise ratio (S/N) of 3 using the equation: LOD = 3 × s_a/sensitivity, where s_a is the standard error of the intercept of the calibration curve.

From the calibration plots and the data presented in Table 7.3, it can be observed that the presence of methylene blue (MB) on the electrode surface results in an approximately 6.6-fold increase in sensitivity, accompanied by a reduction in both the upper limit of the linear range (from approximately 38.5 μM to 25 μM) and the limit of detection (by 48%). Further improvement of the analytical performance could be achieved by focusing on the low-concentration range (below 4.975×10^{-6} M).

7.6. Real Sample Analysis

The PEDOT/GCE and PEDOT-MB/GCE modified electrodes were employed for the determination of norepinephrine in commercial norepinephrine ampoules (1 mg mL^{-1}, concentrate for solution for infusion; manufacturer: Fresenius Kabi, Germany) by differential pulse voltammetry (DPV) using the standard addition method.

The standard addition procedure consisted of recording the oxidation currents generated by the pharmaceutical sample at the modified electrodes, followed by successive additions of five aliquots of a 10^{-3} M norepinephrine standard solution, with the corresponding oxidation currents recorded after each addition.

The obtained results are summarized in Table 7.5.

Table 7.5. Determination of norepinephrine in pharmaceutical formulations.

Type of electrode	[NA] **In the ampoule**	[NA] **Found by DPV**	**Recovery / %**
PEDOT-MB/GCE	5.91 μM	5.51 μM	93.2
PEDOT/GCE/		5.72 μM	96.7

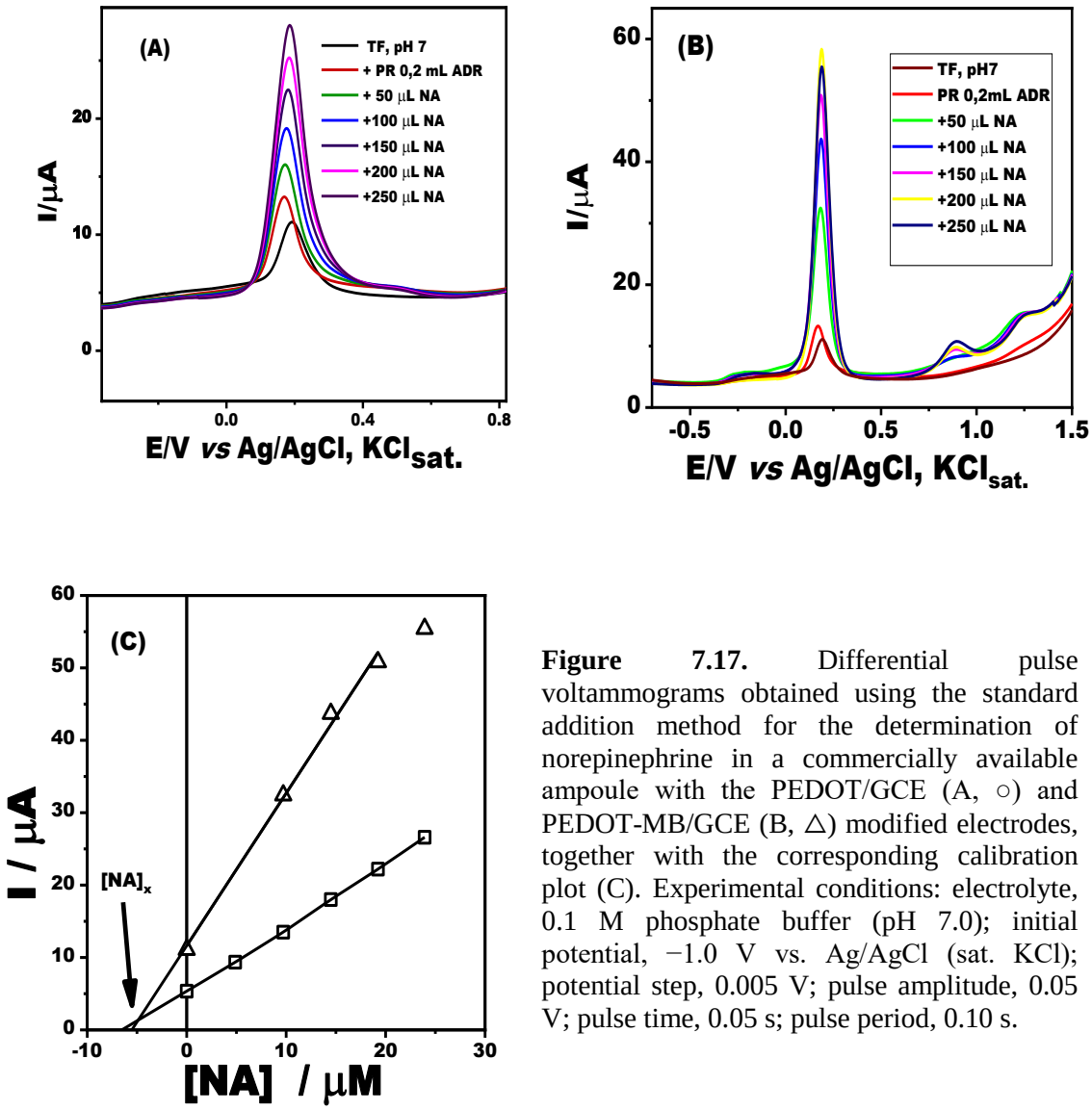


Figure 7.17. Differential pulse voltammograms obtained using the standard addition method for the determination of norepinephrine in a commercially available ampoule with the PEDOT/GCE (A, ○) and PEDOT-MB/GCE (B, △) modified electrodes, together with the corresponding calibration plot (C). Experimental conditions: electrolyte, 0.1 M phosphate buffer (pH 7.0); initial potential, −1.0 V vs. Ag/AgCl (sat. KCl); potential step, 0.005 V; pulse amplitude, 0.05 V; pulse time, 0.05 s; pulse period, 0.10 s.

8. General Conclusions

In order to achieve the overall objectives of this doctoral thesis, a series of experimental studies was carried out to accomplish the specific objectives. Based on the obtained results, the following general conclusions can be drawn.

(a) Different types of ZnO nanoparticles (denoted as ZnO-NPs) were successfully synthesized by a simple and cost-effective precipitation method at room temperature using various precipitating agents, including cationic surfactants (cetyltrimethylammonium bromide, CTAB), nonionic surfactants (Tween 20 and heptaethylene glycol monododecyl ether), and silane-based agents (3-aminopropyltriethoxysilane and tetraethyl orthosilicate). The obtained samples were characterized by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), nitrogen adsorption–desorption isotherms (BET method), electron paramagnetic resonance (EPR) spectroscopy, and photoluminescence spectroscopy. The characterization results demonstrated the interaction of the different additives with the ZnO surface through covalent, electrostatic, and hydrogen bonding, as well as their influence on the defect states responsible for the luminescence emission. All synthesized samples exhibited luminescent properties, while the sample prepared using CTAB showed an emission intensity approximately 40% higher than the others.

(b) The synthesized nanomaterials and fabricated films were morphologically and structurally characterized by FTIR, nitrogen adsorption–desorption isotherms (BET method), XRD, and SEM (ZnO-NP-Nafion/GCE, Chapter 5; ZIF-8-rGO-Nafion/GCE, Chapter 6; PEDOT-MB/GCE, Chapter 7), as well as by thermogravimetric analysis (TGA), Raman spectroscopy (ZIF-8-rGO-Nafion/GCE, Chapter 6), and atomic force microscopy (AFM) (PEDOT-MB/GCE, Chapter 7).

(c) Three types of chemically modified electrodes were fabricated: ZnO-NP-Nafion/GCE (Chapter 5), ZIF-8-rGO-Nafion/GCE (Chapter 6), and PEDOT-MB/GCE (Chapter 7). The ZnO-NP-Nafion/GCE and ZIF-8-rGO-Nafion/GCE electrodes were prepared by the drop-casting technique, which consisted of depositing a known volume of a suspension containing known amounts of nanoparticles (ZnO-NPs, ZIF-8, and rGO) dispersed in Nafion onto the surface of the glassy carbon electrode (GCE). The PEDOT-MB/GCE electrode was fabricated by electropolymerization using cyclic voltammetry from a solution containing EDOT and methylene blue (MB). In all cases, a stable modifier film was successfully formed on the surface of the glassy carbon electrode used as the substrate.

(d) The fabricated chemically modified electrodes were successfully applied to the detection of heavy metals (ZnO-NP-Nafion/GCE, Chapter 5), the electrochemical oxidation of dopamine (ZIF-8-rGO-Nafion/GCE, Chapter 6), and the electrochemical oxidation of norepinephrine (PEDOT-MB/GCE, Chapter 7).

(e) For the ZnO-NP-Nafion/GCE (Chapter 5) and ZIF-8-rGO-Nafion/GCE (Chapter 6) electrodes, cyclic voltammetry was employed to estimate the electrochemically active surface area using the $[Ru(NH_3)_6]^{3+}$ redox probe for ZnO-NP-Nafion/GCE and the $K_4[Fe(CN)_6]/K_3[Fe(CN)_6]$ redox couple for ZIF-8-rGO-Nafion/GCE, based on the Randles–Ševčík equation. In addition, electrochemical impedance spectroscopy (EIS) was used to evaluate the electron-transfer resistance of these electrodes in $K_4[Fe(CN)_6]/K_3[Fe(CN)_6]$ solution.

(f) Cyclic voltammetry was also employed to determine the electrochemical parameters of the redox processes of dopamine (ZIF-8-rGO-Nafion/GCE, Chapter 6) and norepinephrine (PEDOT-MB/GCE, Chapter 7), including the peak-to-peak potential separation ($\Delta Ep = Epa - Epc$), the formal potential ($E^{\circ\prime}$), and the anodic-to-cathodic peak current ratio (Ipa/Ipc). Furthermore, the influence of scan rate and electrolyte pH on the electrochemical oxidation of dopamine and norepinephrine was investigated. In each case, the quasi-reversible nature of the redox mechanism was established, together with the optimum pH corresponding to the maximum oxidation current.

(g) In order to maximize the analytical performance and sensitivity of the developed sensors, the operational parameters were optimized. For heavy-metal detection by square-wave anodic stripping voltammetry (SWASV) using the ZnO-NP-Nafion/GCE electrode (Chapter 5), the accumulation/deposition potential, accumulation time, and electrolyte pH were optimized. For norepinephrine determination by differential pulse voltammetry (DPV) at the PEDOT-MB/GCE electrode (Chapter 7), the electropolymerization scan rate was optimized.

(h) The analytical performance of the fabricated chemically modified electrodes was evaluated using advanced electroanalytical techniques, namely square-wave anodic stripping voltammetry (SWASV) for ZnO-NP-Nafion/GCE (Chapter 5), square-wave voltammetry (SWV) for ZIF-8-rGO-Nafion/GCE (Chapter 6), and differential pulse voltammetry (DPV) for PEDOT-MB/GCE (Chapter 7). Calibration curves were constructed from voltammograms recorded after successive

additions of the analytes, allowing the determination of the analytical parameters, including sensitivity, linear range, and limit of detection. The repeatability and reproducibility of all modified electrodes were evaluated, yielding relative standard deviation (RSD) values below 10%, in agreement with values generally accepted in the literature. The influence of potential interfering species commonly found in biological media was also investigated for the ZIF-8-rGO-Nafion/GCE electrode (paracetamol, citric acid, K^+, Na^+, and glucose) and for the PEDOT-MB/GCE electrode (uric acid and ascorbic acid). Simultaneous determination of analytes was successfully demonstrated using the ZnO-NP-Nafion/GCE electrode for Pb^{2+} and Cu^{2+} (Chapter 5) and the ZIF-8-rGO-Nafion/GCE electrode for dopamine, citric acid, and paracetamol (Chapter 6).

(i) All fabricated and investigated electrodes proved suitable for analytical applications owing to their low limits of detection. The ZnO-NP-Nafion/GCE electrode was successfully applied to the determination of heavy metals in groundwater samples (Chapter 5), while the ZIF-8-rGO-Nafion/GCE and PEDOT-MB/GCE electrodes were successfully employed for the determination of dopamine and norepinephrine, respectively, in pharmaceutical formulations (Chapters 6 and 7). In all real-sample analyses, the standard addition method was applied to minimize matrix effects. The obtained results were in good agreement with those obtained by the reference analytical method (for groundwater samples) or with the manufacturer's declared values (for pharmaceutical formulations), with recovery values ranging from 93% to 112%.

Dissemination of Research Results

Publications

1. **Belcovici A**., Fort I. C., Mureşan L. E., Perhaiţa I., Borodi G., Turdean G. L., Zinc oxide nanostructured platform for electrochemical detection of heavy metals, Electroanalysis, **2023**, 35, e202200395, https://doi.org/10.1002/elan.202200395; **IF/2024: 2.3, quartila Q3**
2. I. Perhaţia, L.E. Mureșan, **A. Belcovici**, A. Popa, G. Borodi, A. Mesaroș, and L. Barbu Tudoran, "Influence of different additives on the morphology, defect state and luminescence of ZnO nanoparticles", Colloids and Surfaces A: Physicochem. Eng. Asp., **2024**, 684, 133102. doi: 10.1016/j.colsurfa.2023.133102; **IF/2024: 5.4, quartila Q1**

3. **Belcovici A.,** Tocco D., Fratini E., Salis A., Turdean G. L., Composite material based on ZIF-8, reduced graphene oxide, and Nafion as electrode modifier for dopamine electrooxidation, Microchemical Journal, **2025**, 216, 114769, DOI: 10.1016/j.microc.2025.114769; WOS:001555663400002; **IF/2024: 5.1, quartila Q1**

1. **A. Belcovici,** C. I. Fort, G. L. Turdean, Highly sensitive determination of noradrenaline at a Methylene Blue–PEDOT modified glassy carbon electrode, **2026**, manuscris trimis spre publicare.

Scientific Presentations at National and International Conferences

1 Cotolan N., **Belcovici A**., Turdean G. L., Determination of noradrenaline using a conductive polymer based on a modified electrode, Electrochemistry for Nano & Nano for Electrochemistry Elecnano9 – November 23 - 24, 2020, Paris, France, (prezentare orală).

2 **Belcovici A**., Muresan L. E., Perhaita I. M., Turdean G. L., Heavy metals electrochemical detection using zinc oxide nanoparticles, ISE Regional Meeting, Praga (Czech Republic), 15-19 August **2022**, (oral presentation).

3 **Belcovici A.**, Fort I. C., Mureşan L. E., Perhaiţa I., Borodi G., Turdean G. L, *Electrochemical detection of lead at zinc oxide nanostructure-based modified electrode*, 28th International Symposium on Analytical and Environmental Problems, University of Szeged, Szeged (Hungary), 14-15 November **2022**, (poster presentation).

4 **Belcovici A.**, Carmen Ioana Fort, Nicoleta Cotolan, Graziella Liana Turdean, *Nanostructured-based chemically modified electrode for heavy metals detection in water*, Water and Wastewater Treatment in the Industry 2023- Challenges of circular water management, Ernő Soós Research and Development Center, Zalakaros (Hungary), 18-19 October **2023**, (oral presentation).

5 **Belcovici A.**, Davide Tocco, Andrea Salis, Graziella Liana Turdean, *Metal-organic frameworks as electrode's modifier for dopamine detection*, 30th International Symposium on Analytical and Environmental Problems, ISAEP 2024, Szeged, Hungary, 7 - 8 October **2024**.

6 **Belcovici A.**, Fort C. I., Cotolan N., Turdean G. L., *Sustainable water management: clean water using chemically modified electrodes for heavy metal detection*, XII International Beremzhanov Congress on Chemistry and Chemical Technology, Al-Farabi Kazakh National University, Almaty (Kazakhstan), 4-6 December **2024** (oral presentation).

Research Projects

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