THE ANNALS OF “DUNAREA DE JOS” UNIVERSITY OF GALATI
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
N°. 4 - 2024, ISSN 2668-4748; e-ISSN 2668-4756
Article DOI: https://doi.org/10.35219/mms.2024.4.04

RESEARCH ON NANOSTRUCTURED HYBRID MATERIALS FOR SENSING DOPAMINE BY CYCLIC VOLTAMMETRY

Elena Emanuela HERBEI, Viorica GHISMAN, Nicoleta BOGATU, Alina-Crina MUREȘAN, Iuliana-Raluca URSACHE, Daniela-Laura BURUIANĂ

Interdisciplinary Research Centre in the Field of Eco-Nano Technology and Advance Materials CC-ITI,Faculty of Engineering, “Dunarea de Jos” University of Galati, 47 Domnească, 800008 Galati, Romania
e-mail: elena.herbei@ugal.ro

ABSTRACT

In this research, we present chemical method of obtaining hybrid nanostructured particles used to modify the screen-printed carbon electrode to detect the redox activity of dopamine. Dopamine (DA) is a neurotransmitter that plays a very important role in the functioning of mammalian systems (central nervous, hormonal, renal, and cardiovascular), and its deficiency results in the development of diseases (Parkinson's and Alzheimer's, restless legs syndrome, or schizophrenia). Magnetite and titanium oxide nanoparticles were functionalized by chemical reaction to be used to modify SPCE. The chemical method used to modify the nanoparticles was a sol-gel chemical reaction. The hybrid materials were analyzed by scanning electron microscopy (SEM/EDX) and by cyclic voltammetry (CV). The alcoholic solution based on magnetite-Fe_3O_4 (F1) and magnetite/titania-TiO_2 (F2) was used is order to be dropped cast onto SPCE surface. The modified SPCE was measured at 0.1 V/s by cyclic voltammetry. The cyclic voltammetry was conducted using a Potentiostat/galvanostat multichannel electrochemical device from OrigaLys, France, OrigaFlex model OGF+01A. Optical microscopy (OM) analyzed the modified surface of screen-printed electrodes. The TiO_2 was characterized through field emission scanning electron microscopy (FE-SEM) with EDX elemental analysis.The modified carbon electrode shows the different waveforms of the voltage applied to the working electrode depending on chemical composition of modified electrodes. The constructed sensor exhibited acceptable selectivity, but not good stability and needs more improvements of chemical composition to provide selectivity, reproducibility, and stability for repeated measurements. The CV curves show very low oxidation and reduction activity due to the unstable contact between the electrode and nanoparticles.

KEYWORDS: hybrid materials, nanostructure, cyclic voltammetry

1. Introduction

The demand for new and hybrid materials or materials with new properties is currently high. The physico-chemical modification of their surface can improve the performance of the sensors (electrochemical). For this purpose, artificial components (hybrid nanostructures, polymer films, nanoparticles), biological (enzymes), or their combination can be used. By chemically modifying the surface of the electrochemical sensor, with thin and nanostructured films or by self-assembling monolayers, its performance can be improved by: facilitating the transfer of electrons selective accumulation or diffusion of analytes the possibility of identifying substances that do not have electroactive properties. Screen-printed electrodes (SPEs) offer some advantages over traditional electrodes in the areas of cost, solution volume, and operating temperature [1]. The primary use of cyclic voltammetry is for the creation of biosensors, not for target analytes to be determined, as it is a widely used electrochemical technique. By using this technique, it is possible to evaluate the redox behavior of species that are present both in solution and sorbed to the electrode [2].

In their work, Keerthi *et al.* [3] were able to synthesize a core-shell hybrid nanomaterial of Mo NPs@f-MWCNTs using acid condensation and use it, to detect DA for the first time electrochemically. The interaction of positively charged Mo NPs on the surface of MWCNT through strong electrostatic interactions involves anchor sites for the interaction of negatively charged oxygen functional groups on the MWCNT. Cheng *et al.* [4] proposes to modify bare electrodes with hybrids made of highly purified AuNBPs and MWCNTs, which are used to enhance the selectivity and sensitivity of the electrochemical sensor, detecting DA in the presence of Ascorbic Acid and Uric Acid.

Other researchers used ZnO/CuO to modify SPCE [5], the nanocomposite of ZnO/CuO is grown on the gold-coated glass substrate by hydrothermal growth technique in two steps and the hybrid material is used for the selective determination of dopamine by cyclic voltammetric and amperometric techniques. The response was found linear for the concentration of 10^{-3} M to 8.0 mM dopamine. The sensitivity of 90.9 μAmM^{-1} cm^{-2} and a detection limit of 1.0×10^{-4} mM were also observed for the presented dopamine sensor. There are also carbon nano coils and copper tetra(p-methoxyphenyl) porphyrin nanocomposite used for electrochemical detection of dopamine [6]. The electroanalytical performances of SPCE/rGO/Ru complex/RuO_2 and SPCE/rGO/RuO_2 to individually and simultaneously detect dopamine and uric acid were estimated by differential pulse voltammetry method (DPV) At room temperature, the developed modified sensor's stability towards 10 µM of DA was tested for nine days [7]. An eco-friendly carbon paste electrode (BHA/rGO/CPE), crafted from an innovative hydroxyapatite/reduced graphene oxide hybrid, is used to detect dopamine (DA). Eggshells, sourced from environmental bio-waste, were utilized to produce hydroxyapatite (BHA) in this experiment [8].

Hybrid materials have been developed to meet certain new performance requirements.

Modification of surface solid supports is one of the most common methods for enhancing the sensitivity and selectivity of electroanalytic compounds involved in physiological processes. Various fields of materials science can benefit from the use of inorganic-organic hybrids due to their simple processing and molecular design capabilities. This work reports the preparation of hybrid materials based on magnetite-Fe_3O_4 and magnetite/titania-TiO_2 for SPCE surface modification to be used in dopamine detection. We measured a buffer solution with 0.1 µM dopamine solution to observe the redox activity.

2. Experimental

Reagents: All chemicals are of analytical grade and used without any further purification and proceeded from Sigma Aldrich, TiO_2 nano-powder, <100 nm particle size, 99.5% trace metals basis, and magnetite was prepared by coprecipitation method.

Preparation of sols and experimental method: Sols based on magnetite and titania were prepared using an alcoholic solvent and functionalized agent (3-(trimethoxysilyl) propyl methacrylate) and were obtained by mixing the magnetite and titania with (3-(trimethoxysilyl) propyl methacrylate 1:1 molar ratio under vigorous agitation at 60 °C tantalum in an alcoholic solvent. Screen-printed carbon electrodes (SPCEs) from the Methrom Drop Sens model C110, measuring L33 × W10 × H0.5 mm, were used. The modified working electrode (WE) was carbon-based with a 4 mm diameter, the auxiliary electrode (AE) was made of carbon, and the reference electrode (RE) was composed of silver. A 1 µL sol of nanohybrid suspension was drop-cast onto the SPCE's working electrode surface and air-dried at room temperature.

3. Results and discussion

3.1. SEM analysis

The SEM images (Figure 1) show a non-homogenous, discontinuous aspect regarding the distribution of particles, a high roughness. The magnetite particles are of different sizes, not uniform (Fig. 1. a, b), covered with maghemite spherules probably due to incomplete oxidation of magnetite (Fig. 2. a, b) but also coated with titanium oxide in the form of symmetrical flowers (Fig. 3. a, b).

The top view of magnetite samples F1 to F2 indicates generally the agglomeration of magnetite and also the coated magnetite with titania. In F1 and F2 SEM images, we observe irregularly agglomerated forms of magnetite with dimensions varying from hundreds of nanometres to microns. Also, here we observe different morphologies such as spheres and flowers.

Nº. 4 - 2024, ISSN 2668-4748; e-ISSN 2668-4756
Article DOI: https://doi.org/10.35219/mms.2024.4.04

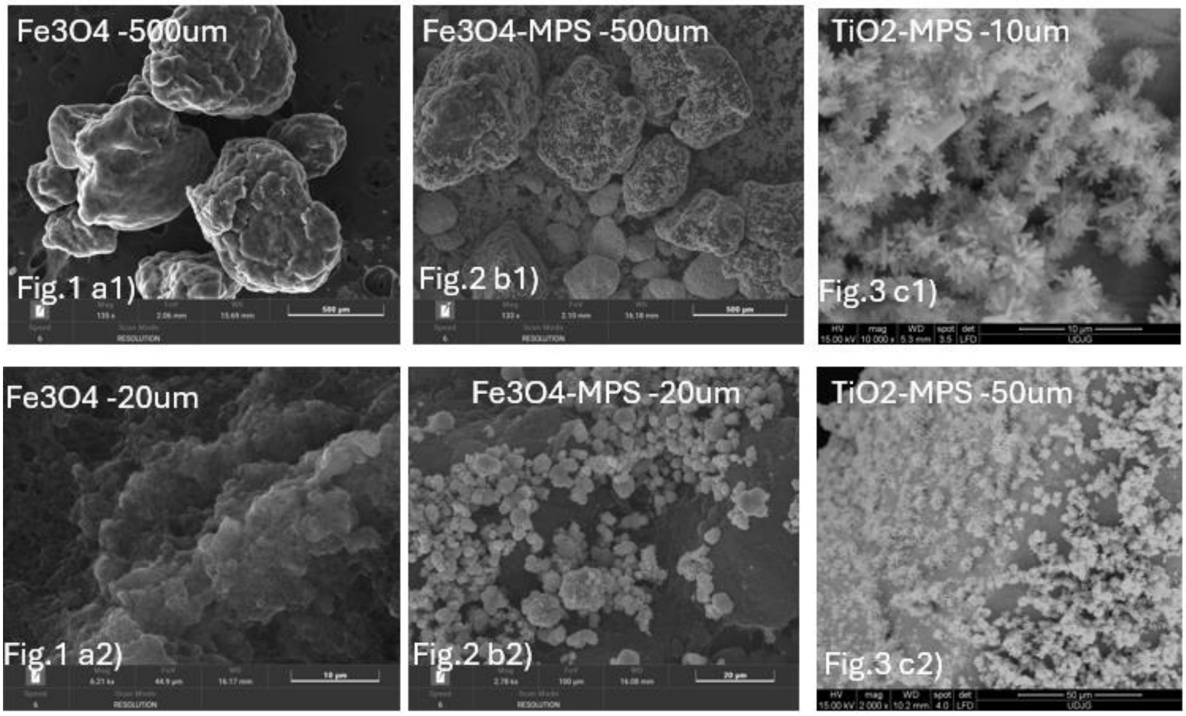

Fig. 1. *Top view (a) SEM images of Fe_3O_4 (a1-500 um, a2-20 um), (b) of Fe_3O_4-MPS (b1-500 um, b2-20 um), (c), Fe_3O_4/TiO_2-MPS (c1-10 um, c2-50 um)*

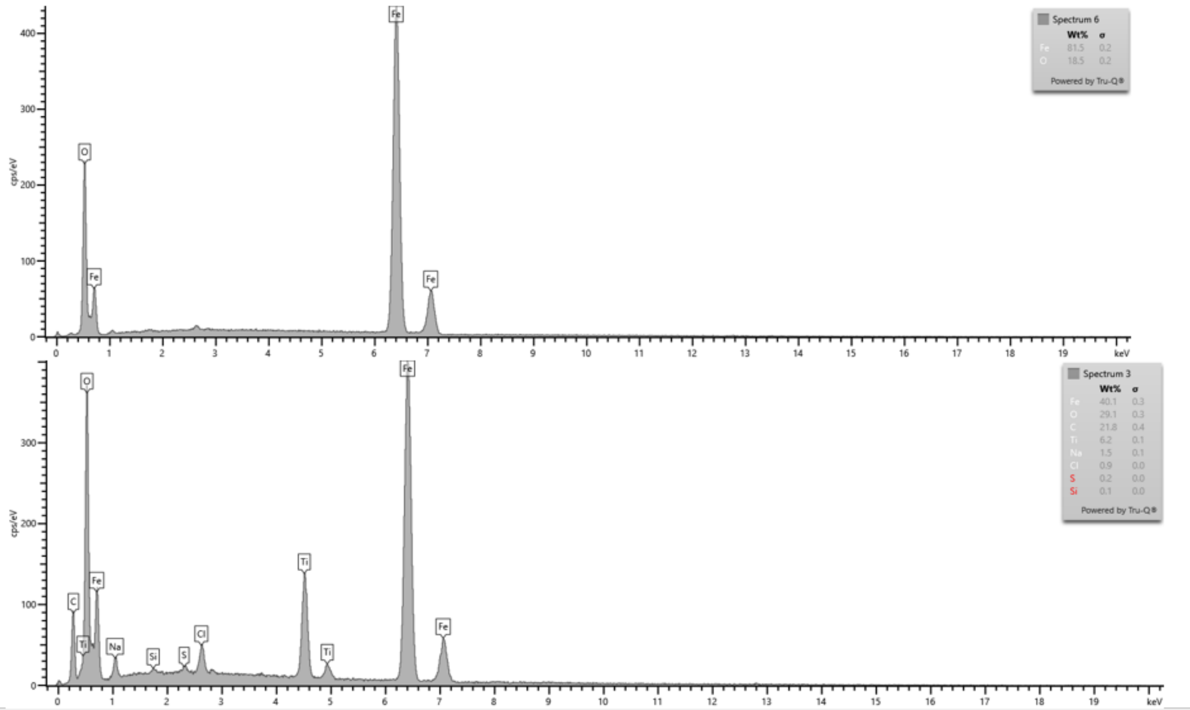

Fig. 2. *EDX of Fe_3O_4 and Fe_3O_4/TiO_2*

THE ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
N°. 4 - 2024, ISSN 2668-4748; e-ISSN 2668-4756
Article DOI: https://doi.org/10.35219/mms.2024.4.04

Table 1. *Results from EDX element composition (%)*

Sample code	T (°C)	Elemental percent from EDX analysis (%)			pH
		Fe	O	Ti	
F1	T = 96	56.2	31.23	8.7	11-12
F2	T = 96	81.5	18.5	-	11-12

3.2. Cyclic voltammetry for the modified SPCE with magnetite and titania hybrid materials

The potential graph assessing the electrochemical stability of electrolytes is crucial for identifying oxidation and reduction potentials. The study focused on evaluating the electrochemical behavior to observe the effects of surface-modified SPCEs in a standard redox analyte. Initially, the experiment involved measuring the unmodified SPCE in a buffer and dopamine solution to activate necessary parameters. The electrochemical signal was recorded at a 0.1 V/s scan rate across five cycles to stabilize the electrode, depicted by the blue curves in Figure 3. These voltammograms revealed irregular anodic and cathodic peaks throughout the five cycles.

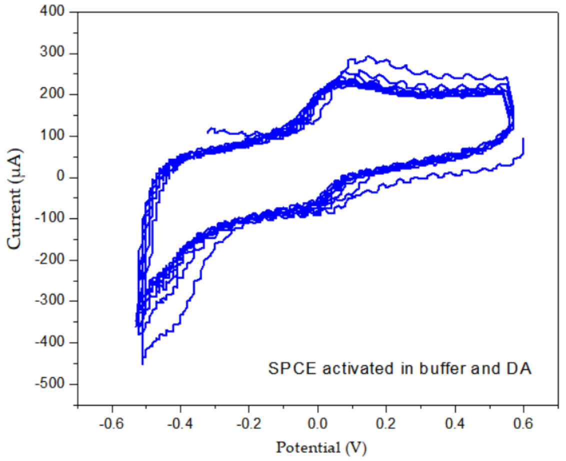

Fig. 3. *Cyclic voltammograms for unmodified SPCE in buffer and DA solution*

After this measurement, we conducted the CVs for the modified SPCE with Fe_3O_4-MPS (Figure 4) and Fe_3O_4/TiO_2-MPS (Figure 5) in buffer and the 1 μM dopamine solution. The scan rates for all the measurements were 0.1V/s. The measurements were done for 5 times for each electrode to observe modification of redox activity. In the case of electrode modified with magnetite the oxidation and reduction peaks are very decreased almost similar with the measurements for the unmodified SPCE. This can be assumed to the morphology of the magnetite grains.

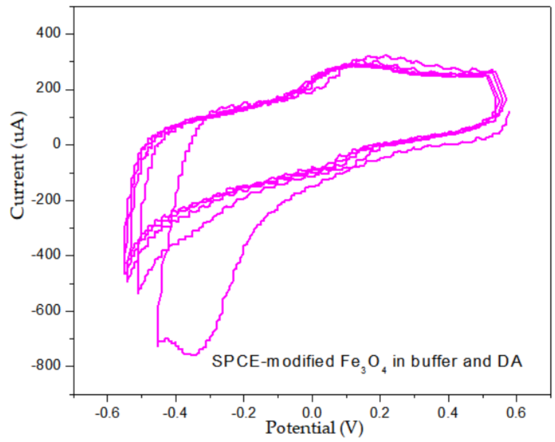

Fig. 4. *Cyclic voltammograms for Fe_3O_4 modified SPCE in buffer and DA solution*

For the samples Fe_3O_4/TiO_2-MPS the voltammograms showed lower oxidation and reduction activity for all the measurements. Probably the presence of TiO_2 on the magnetite surface increased the electron transfer from the solution.

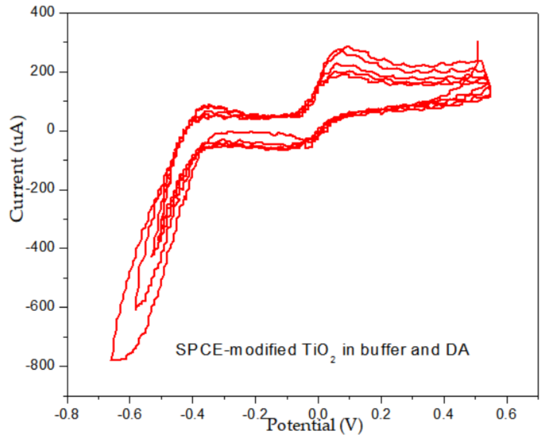

Fig. 5. *Cyclic voltammograms for Fe_3O_4/TiO_2 modified SPCE in buffer and DA solution*

4. Conclusions

In this work, we prepared 2 hybrid alcoholic sols based on magnetite and magnetite/titania to modify the screen-printed carbon electrode to observe the redox activity of dopamine of 1 μL concentration. The SEM/EDX images showed a non-homogenous, discontinuous aspect regarding the distribution of particles, a high roughness surface. The magnetite particles are of different sizes, not uniform covered with maghemite spherules probably due to incomplete oxidation of magnetite and also coated with titanium oxide in the form of symmetrical flowers. The dimension of magetite is varying from few hundred of nanometres to microns agglomeration particles. The voltammograms showed lower to minimum oxidation and reduction activity for the samples based on magnetite. In the case of magnetite /titania modified SPCE the presence of TiO_2 on the magnetite surface increased the electron transfer from the solution and the redox activity was increased.

Funding

"This research was funded by "Support and development of CDI-TT activities in the "Dunărea de Jos" University of Galați - Internal grant RF2473/ 31.05.2024 - title project „Materiale hibride nanostructurate utilizate în structura unor senzori modificați pentru identificarea dopaminei MH-SPCED (Acronim MH-SPCED)".

References

[1]. Reducks D., *et al.*, *Screen-Printed Electrode Information*, Pine Res. Instrum., vol. 10036, p. 1-10, 2019.
[2]. Banerjee S., *et al.*, *Electrochemical Detection of Neurotransmitters*, Biosensors, vol. 10, no. 8, doi: 10.3390/bios10080101, 2020.
[3]. Keerthi M., *et al.*, *A core-shell molybdenum nanoparticles entrapped f-MWCNTs hybrid nanostructured material based non-enzymatic biosensor for electrochemical detection of dopamine neurotransmitter in biological samples*, Sci. Rep., vol. 9, no. 1, p. 1-12, doi: 10.1038/s41598-019-48999-0, 2019.
[4]. Cheng J., *et al.*, *A novel electrochemical sensing platform for detection of dopamine based on gold nanobipyramid/multi-walled carbon nanotube hybrids*, Anal. Bioanal. Chem., vol. 412, no. 11, p. 2433-2441, doi: 10.1007/s00216-020-02455-5, 2020.
[5]. Khun K., *et al.*, *An electrochemical dopamine sensor based on the ZnO/CuO Nanohybrid structures*, J. Nanosci. Nanotechnol., vol. 14, no. 9, p. 6646-6652, doi: 10.1166/jnn.2014.9367, 2014.
[6]. Aqsa Batool Bukhari S., *et al.*, *Efficient electrochemical detection of dopamine with carbon nanocoils and copper tetra(p-methoxyphenyl)porphyrin nanocomposite*, Arab. J. Chem., vol. 15, no. 12, p. 104375, doi: 10.1016/j.arabjc.2022.104375, 2022.
[7]. Guerniche D., *et al.*, *Novel hybrid material based on Ru complex and its RuO2 oxide for dopamine and dopamine-uric acid simultaneous determination*, J. Organomet. Chem., vol. 997, p. 122769, doi: 10.1016/j.jorganchem.2023.122769, 2023.
[8]. Gopal T. V., *et al.*, *Eco-friendly and bio-waste based hydroxyapatite/reduced graphene oxide hybrid material for synergic electrocatalytic detection of dopamine and study of its simultaneous performance with acetaminophen and uric acid*, Surfaces and Interfaces, vol. 24, no. October 2020, p. 101145, doi: 10.1016/j.surfin.2021.101145, 2021.