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SYNTHESIS AND TESTING OF THE ELECTRO-CATALYTIC MATERIALS FOR THE HYDROGEN-PEROXIDE REDUCTION

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Abstract

In this paper, the synthesis, characterization and electrochemical testing of carbon material (graphene) modified with the Pd nanoparticles in the hydrogen peroxide reduction reaction was performed. Graphene was synthesized from glucose as a precursor, using FeCl₃ as a catalyst. The reduction of hydrogen peroxide on the synthesized material was studied by the cyclic voltammetry and square wave voltammetry.

Keywords: *synthesis, characterization, carbon material, graphene, palladium.*

1 INTRODUCTION

Carbon materials, as carriers of metal nanoparticles, offer a wide range of applications in both analytical and industrial electrochemistry. This broad applicability is precisely that stems from the carbon itself that is largely derived from their structural diversity and stability, exchange and chemically complex surfaces, as well as the strong carbon-carbon bonds within the carbon material. Compared to the other materials, they have several advantages in the electrode fabrication, evidenced by their wide range of applicable potentials, low cost, relative inertness, and pronounced electrocatalytic activity.

This study presents the results of synthesis, characterization, and electrochemical investigation of the carbon material (graphene), modified with the composite nanoparticles through the hydrogen peroxide reduction. Graphene was synthesized from glucose as a precursor, using FeCl₃ as a catalyst. The re-

duction of hydrogen peroxide on the synthesized material was studied using the cyclic voltammetry and square wave voltammetry methods.

2 EXPERIMENTAL PART

2.1 Materials and methods

2.1.1 Synthesis of graphene (G)

The procedure for graphene preparation in this study is based on the method proposed by Zhang et al [1]. Six grams of glucose and six grams of FeCl₃ · 6H₂O were measured and dissolved in 10 mL of deionized water. The water mixture was heated at 80°C for 24 hours. Carbonization of the obtained product was performed at 700 K for 3 hours under an inert nitrogen (N₂) atmosphere. The material was then ground and transferred to 100 mL of concentrated

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HCl (36%) with stirring for 6 hours. After that, the suspension was filtered and washed with 300 mL of deionized water and 80 mL of acetone. The resulting material was dried at 70°C for 1 hour [2, 3].

2.1.2 Synthesis of graphene-palladium composites

One hundred milligrams of graphene were measured and dispersed in a 20 mL mixture of ethanol/water (50%, v/v). The graphene mixture was then subjected to the ultrasonication for 5 minutes. Subsequently, 25 mg of cetyltrimethylammonium bromide (CTAB) was added, and the same ultrasonication procedure was repeated for another 5 minutes.

In a separate vial, a mixture of 50 mg PdCl₂ and 0.05 mL concentrated HCl was prepared and heated at 60°C for 30 minutes. After cooling, solution was diluted with H₂O to 2 mL and added to the graphene suspension. It was left at room temperature for 1 hour before adding 1 mL of NaBN₄ solution. The resulting suspension was transferred to a stainless-steel autoclave and heated at 160°C for 90 minutes. After hydrothermal treatment, the suspension was centrifuged and the liquid phase was decanted. The residue was washed several times with deionized water. Finally, the obtained material was dried in an oven at approximately 60°C and labeled as G-Pd [2, 4].

2.2 Characterization

The characterization of the synthesized graphene-palladium (G-Pd) composite, as well as graphene, was performed using X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. The SEM micrographs were obtained using a Zeiss Leo Gemini 1530 instrument with an Everhart-Thornley detector for collecting the secondary electrons. The acceleration voltage was set to 10 kV. The XRD diffraction patterns were obtained using an STADI P instrument with a Mythen1K detector [4].

2.3 Cleaning and preparation of a glassy carbon electrode (GCE)

First, a glassy carbon electrode (GCE) with a geometric surface area of 0.0706 cm² was polished with 0.05 mm Al₂O₃ powder on a polishing cloth, followed by rinsing with deionized water and ethanol in an ultrasonic bath. After the cleaning process, 5 mg of G-Pd was dispersed in 1 mL of ethanol/water mixture (40%, v/v), and the resulting suspension was homogenized in an ultrasonic bath for 30 minutes. 5 mL of the suspension (equivalent to 0.025 mg of material) was transferred onto the surface of the GCE and dried under a stream of N₂. Once a thin layer of electrocatalyst was formed, 5 mL of 0.05 wt.% Nafion solution in ethanol was applied and dried again under a stream of N₂. The modified GCE was used to investigate the electroreduction of hydrogen peroxide (H₂O₂).

The nominal metal loading in the Pd-based electrocatalyst was 82 µg cm⁻². The thickness of Nafion was estimated to be approximately 0.2 µm using the following equation:

$$t = m/(A\rho) \quad (1)$$

where *m* is the mass of ejected Nafion (2.500 · 10⁻⁶ g), *A* is the film area, and *ρ* is the approximate film density (1.980 g cm⁻³).

It is worth nothing that oxygen and hydrogen peroxide can penetrate the Nafion membranes of a few microns in thickness and thus can be reduced at the electrode surface. The electroreduction of H₂O₂ was studied using the cyclic voltammetry (CV) and square wave voltammetry (SWV).

The three-electrode system consisted of a G-Pd modified GCE as the working electrode, saturated calomel electrode (SCE) as the reference electrode, and graphite rod as the auxiliary electrode. 5 mM H₂O₂ solution in 0.1 M KOH was used to study the electrocatalytic behavior of G-Pd. Purified nitrogen was bubbled through the electrolyte for thirty minutes before the addition of the appropriate amount of hydrogen peroxide.

The electrolytic cell was shielded from light with aluminum foil. Prior to the electrochemical measurements, the activation of each electrocatalytic film was performed by continuous potential cycling with respect to the SCE in a N₂-saturated 0.1 M KOH solution until a stable and reproducible cyclic voltammogram was recorded.

All measurements were carried out under the same conditions for each electrode to allow for comparison of the obtained results. Electrochemical investigations were

conducted using cyclic voltammetry and square wave voltammetry methods [2, 4].

3 RESULTS AND DISCUSSION

3.1 Characterization of the graphene and graphene-palladium composites

The characterization of graphene and graphene-palladium was performed using the XRD, and the corresponding diffractograms are shown in Figure 1.

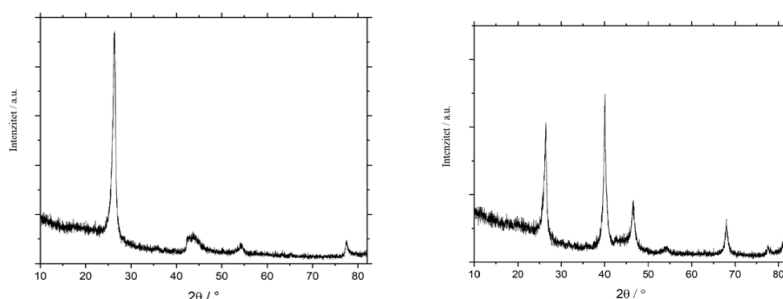


Figure 1 XRD diagram of graphene (left) and graphene-palladium (right)

The sharp peak at about 26.3° belongs to the (002) crystallographic plane of the graphene nanoparticles, composed of several layers of graphene sheets (Figure 1, left). The corresponding spacing between the graphene layers is 0.38 nm, and is obtained using the Bragg equation:

$$2d \sin \theta = n\lambda \quad (2)$$

After the deposition of palladium particles on graphene under the hydrothermal conditions, the (002) peak is observed at the same 2θ value (Figure 4.1.1, right) indicating

that the palladium particles were not incorporated between the graphene layers. In Figure 1, on the right, the diffraction peaks at 2θ ~ 40.2°, 46.8°, 68.1° and 82.3° are observed, which correspond to the Pd (111), (200), (220) and (311) crystallographic planes of the centered cubic lattice of palladium.

The morphology of graphene and graphene-palladium was analyzed using the SEM and corresponding photomicrographs are shown in Figure 2.

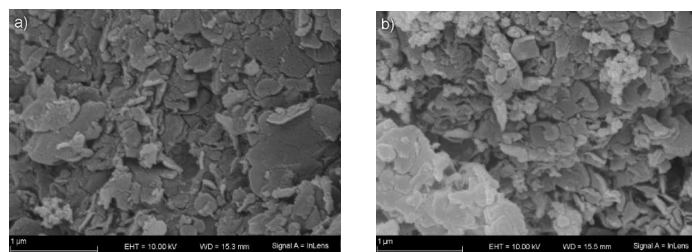


Figure 2 SEM micrographs of (a) graphene; (b) graphene-palladium [2]

The SEM microphotographs show that the synthesized graphene (Figure 2.a) has a sheet-like morphology consisting of multiple layers, which provides more active sites for palladium nucleation. After the deposition of palladium nanoparticles, graphene retained the same morphology (Figure 2. b).

3.2 Electrochemical tests

Electrochemical testing of the hydrogen peroxide reduction reaction was carried out using the cyclic voltammetry and square wave voltammetry methods. A 0.1 M potassium hydroxide solution was used as the

background electrolyte. The experiments were first conducted in a pure electrolyte without hydrogen peroxide, and then in electrolytes containing hydrogen peroxide at concentrations of 5, 10, 15, 20, and 25 mM. During the electrochemical measurements, nitrogen gas was purged into the electrolyte to remove oxygen. Cyclic voltammograms were recorded at the scan rates of 0.01, 0.02, 0.05, 0.08, and 0.1 V/s.

Figure 3 shows the obtained cyclic voltammograms for the commercial glassy carbon electrode and modified electrode in an alkaline electrolyte without the presence of hydrogen peroxide.

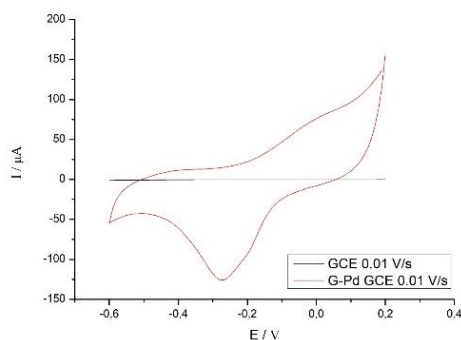


Figure 3 Cyclic voltammograms for a commercial glassy carbon electrode (GCE) and modified electrode (G- Pd GCE) in 0.1 M KOH solution, at a potential change rate of 0.01 V/s

Figure 4 shows the obtained cyclic voltammograms for a commercial glassy carbon electrode and modified electrode in an

alkaline electrolyte containing 5 mM hydrogen peroxide.

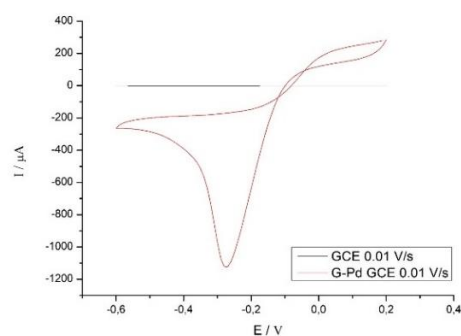


Figure 4 Cyclic voltammograms for a commercial glassy carbon electrode (GCE) and modified electrode (G- Pd GCE) in 5 mM H₂O₂, 0.1 M KOH, at a potential change rate of 0.01 V/

The data obtained and presented in the previous figures demonstrate that the modified electrode (G-Pd GCE) exhibits a superior electrocatalytic activity compared to the commercial glassy carbon electrode. The shape of cyclic voltammogram, obtained in the electrolyte without hydrogen peroxide (Figure 3), is characterized by a prominent cathodic voltametric peak, which is attributed to the reduction of trace amounts of oxygen adsorbed on the palladium particles.

The modified electrode (G-Pd GCE) shows a strong reduction peak in the presence of 5 mM H₂O₂ at a scan rate of 0.01 V/s (Figure 5). The cathodic peak corresponds to a peak current value of $I_p = -1075 \mu\text{A}$, while the potential value of $E_p = -0.270 \text{ V}$ corresponds to the position of the main reduction peak in the voltammogram, obtained in a 0.1 M KOH solution without the presence of hydrogen peroxide.

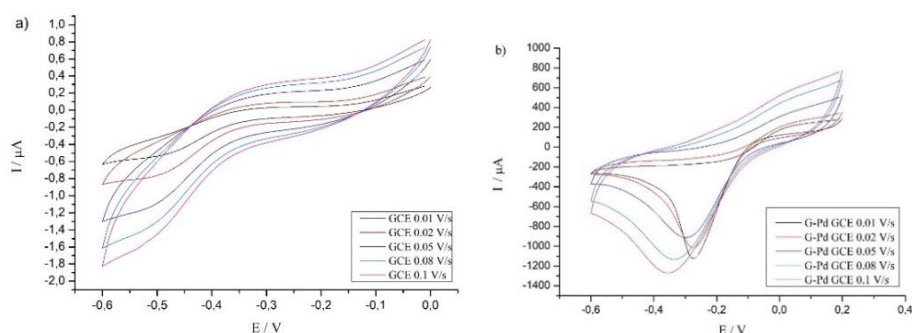


Figure 5 Cyclic voltammograms for: a) commercial glassy carbon electrode (GCE), b) modified electrode (G-Pd GCE) in 5 mM H₂O₂, 0.1 M KOH

From the shown cyclic voltammograms, it is evident that the modified electrode exhibits the clear peaks at all scan rates, resulting in the higher cathodic current values compared to the cathodic current values, obtained from the cyclic voltammograms of

the commercial glassy carbon electrode. Table 1 presents the parameters obtained from the cyclic voltammetry method in 5 mM H₂O₂, 0.1 M KOH, at a scan rate of 0.01 V/s.

Table 1 Electrochemical parameters obtained by a cyclic voltammetry in 5 mM H₂O₂, 0.1 M KOH, at a potential change rate of 0.01 V/s.

E electrode	E_p (V)	I_p (μA)
GCE	-0.480	-0.1
G-Pd GCE	-0.270	-1075

As it can be seen, the cathodic peak current of the modified electrode (-1075 μA) has a significantly higher value than the cathodic peak current of the commercial electrode. The peak has shifted from -0.480 V for the commercial glassy carbon elec-

trode to -0.270 V for the G-Pd modified electrode. These parameters indicate the pronounced electrocatalytic activity of the G-Pd material in the HPRR process.

Electrochemical investigation of the hydrogen peroxide reduction reaction was

performed using the square wave voltammetry under the same conditions as the cyclic voltammetry. The background electrolyte was 0.1 M KOH, which did not contain hydrogen peroxide in one cycle of the experiment, contained 5 mM H_2O_2 in the next cycle, and H_2O_2 concentration was increased in the third cycle of the experiment. During all experiments, nitrogen gas was introduced into the electrolyte to remove oxygen.

The parameters for obtaining the square wave voltammograms were as follows: amplitude value of 0.25 V, frequency of 2 Hz, and potential step of 0.01 V.

Figure 6 shows the obtained square wave voltammograms for the commercial glassy carbon electrode and modified electrode (G-Pd) in an alkaline electrolyte without the presence of hydrogen peroxide.

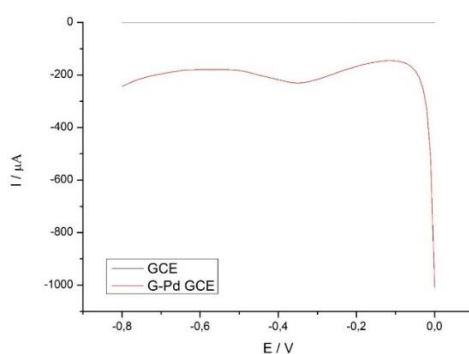


Figure 6 Square wave voltammograms for the commercial glassy carbon electrode (GCE) and modified electrode (G-Pd GCE) in 0.1 M KOH solution

As it can be seen in the obtained voltammogram, the modified electrode gives a clearly visible peak compared to the commercial glassy carbon electrode under the conditions without the presence of H_2O_2 .

The following Figure 7 compares two voltammograms, obtained by the square wave voltammetry method for a commercial electrode made of glassy carbon, and a modified electrode, in the conditions when the electrolyte contains 5 mM H_2O_2 .

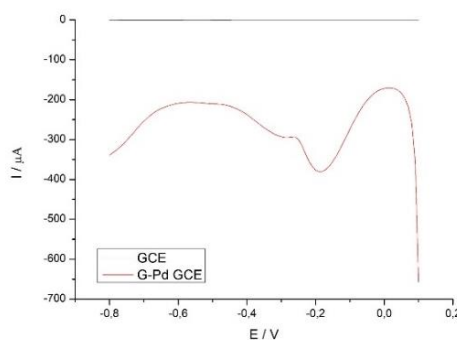


Figure 7 Square wave voltammograms for the commercial glassy carbon electrode (GCE) and modified electrode (G-Pd GCE) in 5 mM H_2O_2 , 0.1 M KOH

From the presented figure, it is clearly seen that the modified electrode gives a visible peak compared to the commercial glassy carbon electrode when the electrochemical test was performed in an electrolyte containing 5 mM H_2O_2 .

The third cycle of experiments refers to the study of changes in H_2O_2 concentration in electrolyte. Figure 8 shows the obtained voltammograms for the commercial electrode from glassy carbon and modified electrode (G-Pd), respectively.

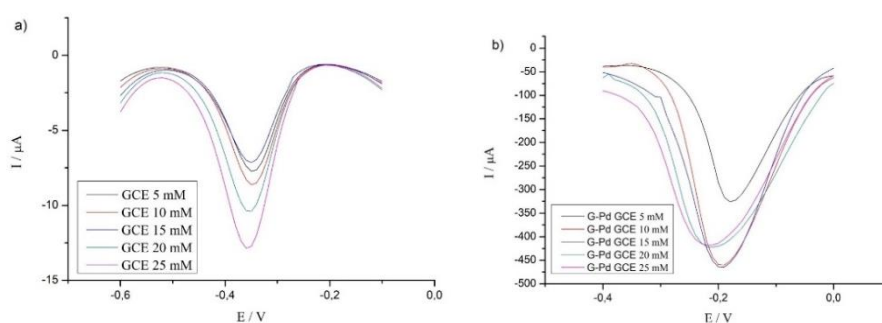


Figure 8 Square wave voltammograms for: a) commercial glassy carbon electrode (GCE), b) modified electrode (G-Pd GCE) in 0.1 M KOH at different concentrations of H_2O_2

It could be seen from presented figures that with a change in H_2O_2 concentration, the peak current also changes. Tables 2 and 3 show the parameters obtained by the square wave voltammetry for a commercial glassy carbon electrode and modified elec-

trode (G-Pd), respectively. The change in peak current intensity with increasing hydrogen peroxide concentration is not linear due to the adsorption phenomena and secondary chemical processes that lead to degradation of H_2O_2 .

Table 2 Electrochemical parameters for a commercial glassy carbon electrode, obtained by square wave voltammetry in 0.1 M KOH at different concentrations of H_2O_2

Concentration (mM)	E_p (V)	I_p (μ A)	FWHM (V)
5	-0.44	-0.574	0.128
10	-0.45	-0.572	0.129
15	-0.45	-0.863	0.132
20	-0.45	-0.993	0.127
25	-0.448	-1.164	0.132

Table 3 Electrochemical parameters for the modified electrode (G-Pd GCE), obtained by square wave voltammetry in 0.1 M KOH at different concentrations of H_2O_2

Concentration (mM)	E_p (V)	I_p (μ A)	FWHM (V)
5	-0.186	-197.44	0.227
10	-0.175	-167.54	0.266
15	-0.180	-163.77	0.237
20	-0.170	-151,598	0.225
25	-0.167	-127,642	0.201

4 CONCLUSION

On the basis of the obtained results and conducted discussion, the following conclusions can be made:

- The G-Pd hybrid material was successfully synthesized using a simple hydrothermal method and used as an electrocatalyst for HPRR. The obtained material exhibited significant electrocatalytic activity towards the electrochemical reduction of H_2O_2 compared to the unmodified and modified glassy carbon electrode under alkaline conditions. The investigation showed that the modified glassy carbon electrode had much higher sensitivity to the presence of H_2O_2 than the unmodified GCE.
- The nanohybrid G-Pd material was successfully synthesized, as confirmed by the analysis of microphotographs obtained through the scanning electron microscopy (SEM). A layered Pd-G structure was observed, and X-ray diffraction (XRD) confirmed the presence of peaks attributed to the graphene crystallographic planes and immobilized Pd nanoparticles [2].
- The electrocatalytic mechanism was predominantly controlled by a strong adsorption of hydrogen peroxide and oxygen on palladium nanoparticles. It was found that there were traces of adsorbed oxygen on the surface of palladium nanoparticles even in the absence of dissolved oxygen in the electrolyte.
- The electroreduction reaction of H_2O_2 on G-Pd was investigated using the cyclic voltammetry (CV) and square wave voltammetry (SWV) in the presence and absence of oxygen to uncover the main aspects of the electrocatalytic mechanism. A highly pronounced electrocata-

lytic activity of G-Pd was observed, manifested by a very high value of the reduction peak current and positive shift in the reduction potential value.

- From the obtained results, it can be also concluded that the experimental results agree with the theoretical results [5].

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