



Enhancing Dopamine Detection Using Glassy Carbon Electrode Modified with Graphene Oxide, Nickel and Gold Nanoparticles

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A novel and an easy method was developed to fabricate non-enzymatic electrochemical sensor for sensitive detection of dopamine (DA). A composite material contains graphene oxide and nickel nanoparticles was deposited on a glassy carbon electrode (GCE) surface by cyclic voltammetry. Then, gold particles were loaded on the surface of the resulting material via galvanic replacement method in order to obtain Ni-Au bimetallic nanoparticles combined with the electrodeposited graphene oxide (EG). The electrochemical behavior and the structure of the obtained electrode were characterized using scanning electron microscopy, cyclic voltammetry and impedance spectroscopy. The response of the modified electrode for DA detection is linear in the range from 2×10^{-7} to 10^{-4} M, the sensitivity is 0.641 A M^{-1} and the detection limits is 10^{-7} M. As well, it showed a high selectivity in the presence of Uric acid (UA), Ascorbic acid (AA) and glucose. Due to its low-cost, an easy process and great performance, this GCE/EG-Ni-Au(NPs) electrode can be a good candidate for the fabrication of non-enzymatic dopamine sensor.

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Dopamine (DA) act as a neurotransmitter and have several roles in the function of renal, central nervous and hormonal systems.¹ The abnormal concentration of dopamine in the human body can lead to several mental diseases.² Therefore, the selective and sensitive detection of DA are an urgent need. To obtain more performant sensor, several techniques have been applied for the detection of DA such as fluorescence spectrometry, mass spectrometry and electrochemical techniques.^{3,4} Surrounded by those techniques, electrochemical methods have attracted great interest due to the facile oxidation of DA electrochemically.⁵⁻⁷ Electrochemical methods draw more attention because of their low-cost, quick response and ease of use.⁸ Nowadays increasing interest is being paid on the development of sensitive devices for DA detection.⁹⁻¹⁵ In order to have more sensitive sensor and larger linearity domain for dopamine detection, various carbon materials have been employed to modify electrodes surfaces such as carbon nanotubes,¹⁶ boron-doped diamond,¹⁷ carbon nanofibers¹⁸ and graphite.¹⁹ Recently, graphene oxide (GO) have been reported to be effective for electrochemical sensors. Outstanding to its 2D-dimensional structure, GO has many unexpected properties, where electrons behave like massless relativistic particles, resulting in the observation of novel electronic properties such as the quantum Hall effect²⁰ and transport by means of relativistic Dirac fermions.²¹ Electrochemical method for selective detection of dopamine was reported by a group of researches based on gold-nanoparticles-cyclodextrin-graphene-modified electrode by square wave voltammetry.²² The sensing film was fabricated with in situ thermal reduction of graphene oxide and HAuCl₄ with cyclodextrin (CD) in alkaline aqueous solution.²² To have good analytical performances of the sensor, the method of graphene deposition on the electrode surface is an important step. Graphene films are usually deposited using simple methods like drop-casting but it was demonstrated that using this method the thickness of the film cannot be controlled.²³ Recently, electrochemical methods are used in order to have thin layers on the electrode surface.²³ In addition, the use of metallic nanoparticles (NPs) can enhance the analytical performances of sensors. Ni NPs have attracted much interest in the field of electrochemistry due to their original properties such as an ease of synthesis and low cost. Nickel nanoparticles have been used in electrode modification due to its extraordinary catalytic activities and high conductivities.^{24,25} For example, nickel nanoparticles were used as an efficient electrocatalyst for the detection of synthetic antioxidant propyl gallate [26]. In the present work, we report a facile and a low cost preparation of

nanocomposite EG/Ni-Au (NPs) modified glassy carbon electrode (GCE) by two steps: (i) an electrochemical deposition of Ni nanoparticles and graphene oxide on the glassy carbon electrode, (ii) a simple immersion of the obtained material in an aqueous solution of HAuCl₄. The electrochemical activity of Ni-Au/EG modified GCE was investigated and its selective detection toward DA was studied in the ternary mixture of glucose, ascorbic acid (AA) and uric acid (UA).

Experimental

Chemicals and materials.—Ferricyanide ($\text{K}_4\text{Fe}(\text{CN})_6$) and ferrocyanide ($\text{K}_3\text{Fe}(\text{CN})_6$), Potassium monohydrogen phosphate (K_2HPO_4) and Potassium dihydrogen phosphate were purchased from Fluka. Commercial nanopowder of nickel with an average particle size $<100 \text{ nm}$, graphene oxide (GO) dispersion in H_2O (4 mg ml^{-1}) and Chloroauric acid tetrahydrate (HAuCl_4) were purchased from Sigma-Aldrich. Aqueous solutions were prepared using ultrapure water (Millipore milli-Q, resistivity $>18.2 \text{ M}\Omega \text{ cm}$).

Instruments and measurements.—Surface morphology characterization was performed using a scanning electron microscope JSM 5100 from JEOL with carbon screen printed electrode. Experimental electrochemical measurements were carried out with electrochemical cell containing three electrodes a glassy carbon electrode (GCE) with a geometric area of 0.07 cm^2 , a platinum wire as a counter electrode and an Ag/AgCl/ (sat. KCl) electrode as a reference. The cyclic voltammetry (CV) and square wave voltammetry (SWV) were investigated using a potentiostat (DY200 POT Eco-chimie). An Autolab PGSTAT 320 N potentiostat was used for impedance spectroscopy spectra measurements controlled by a computer with a software (NOVA 1.5) for data analysis. Square wave measurements were recorded from 0 to 0.5 V with a step potential of 4 mV , an amplitude of 40 mV and a frequency of 10 Hz in the presence of phosphate buffer solution (PBS) 0.1 M ($\text{pH} = 6$).

Electrode preparation and modification procedure.—The electrode surface modification was done using many steps shown in Fig. 1. The first step is cleaning the electrode surface in order to remove impurities and to have reproducible results. The working electrode (GCE) was polished using Al_2O_3 ($1 \mu\text{m}$) water slurry using a polishing cloth and then the electrode surface was rinsed with pure water. After, the electrode was sonicated in acetone for 10 min and rinsed with pure water. The freshly cleaned GCE was electrochemically activated in an electrochemical cell containing

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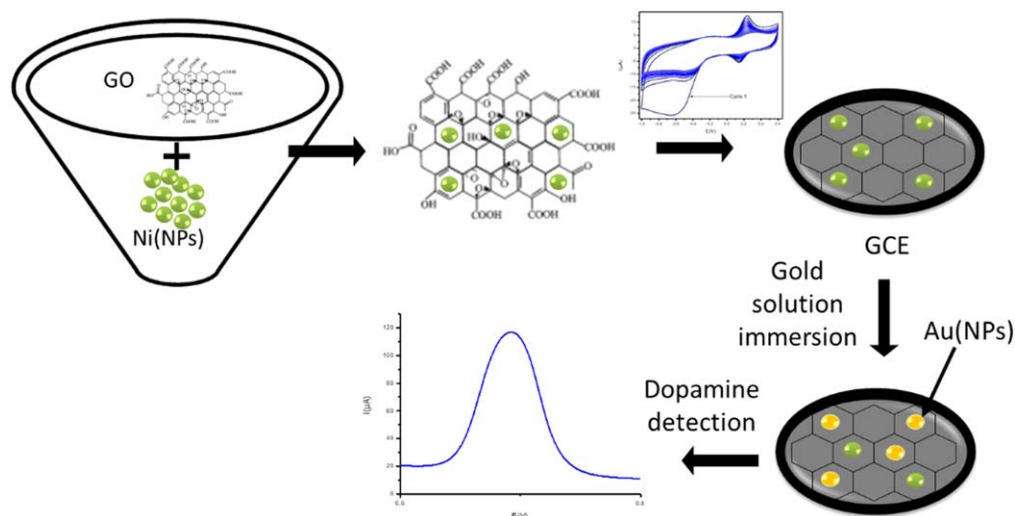


Figure 1. Schematic illustration of the different steps involved in the fabrication of the modified glassy carbon electrode.

NaOH ($0.5 \text{ mol} \cdot \text{l}^{-1}$) with a repetitive cyclic potential sweeps in the range of 0.6 to 1.2 V at a scan rate of $50 \text{ mV} \cdot \text{s}^{-1}$. The modification of the electrode was done by cyclic voltammetry in an electrochemical cell (10 ml) containing graphene oxide (1 mg ml^{-1}) and nickel nanoparticles (Ni(NPs)) (1 mg ml^{-1}) by 15 cycles at a scan rate of $20 \text{ mV} \cdot \text{s}^{-1}$ as shown in voltammograms reported in Fig. 2. Then the electrode was immersed in an aqueous solution of $2 \cdot 10^{-4} \text{ M HAuCl}_4$ for 30 min. For details about the Au adhesion on the electrode surface containing the Ni(NPs), the reader is invited to refer to our previous publication.²⁶

Results and Discussion

Characterization of the modified glassy carbon electrode.—The morphology of the modified electrodes was examined by scanning electron microscopy (SEM) in order to verify the homogeneity of those surfaces and the adhesion of the deposited materials. Figure 3 illustrates the surface morphologies of modified electrodes by SEM. Figure 3a represents the SEM for bare screen-printed carbon electrode and it was taken as a reference, it is clear that the morphology of the electrode surface changes after electrodeposition of GO, which confirms the formation of electrodeposited graphene (EG) layer on the GC surface. Figure 3c shows a SEM image of EG + Ni(NPs) layer adsorbed on the electrode surface. Figure 3d indicates that Ni-Au bimetallic nanoparticles have larger surface area and they consist of small spherical particles which are highly dispersed on the surface. The SEM images reveal that the best electrode is GCE/EG-Ni-Au(NPs). The modified electrodes were also characterized using two electrochemical methods: cyclic voltammetry and impedance spectroscopy. To characterize the formation of the deposited layer on the working electrode surface, cyclic voltammograms were recorded in a three electrode cell containing the redox active compounds: $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ in 0.1 M PBS at pH = 6. Figure 4 shows the cyclic voltammograms before and after modification of the GC electrode. The voltammograms recorded in redox system present a reversible behavior at the bare and modified electrodes with a small peak separation for the bare electrode $\Delta E = 89 \text{ mV}$ and a larger peak separation for the modified electrode $\Delta E = 129 \text{ mV}$ for the GCE/EG-Ni(NPs) and $\Delta E = 146 \text{ mV}$ GCE/EG-Ni-Au(NPs). As it is shown in Figs. 4b and 4c, after the modification of the GC electrode by GCE/EG-Ni(NPs) and GCE/EG-Ni-Au(NPs) an increase in the peak current is observed due to the effect of Ni–Au bimetallic nanoparticles. Due to their synergistic effects Ni and Au NPs can enhance the oxidation of electroactive molecules which serve as efficient species for highly sensitive

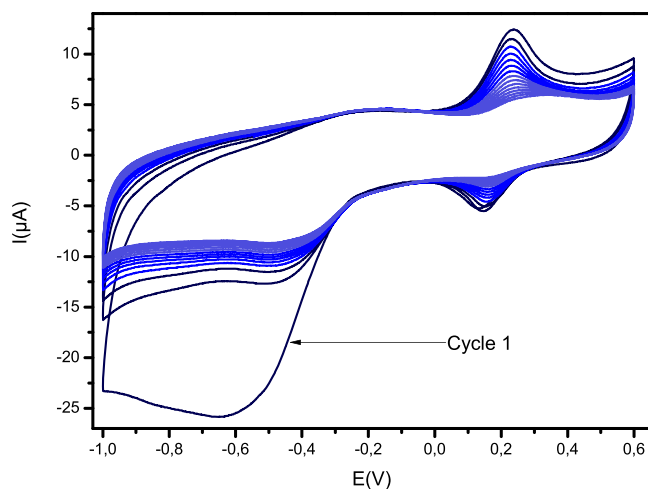


Figure 2. Electrochemical deposition of GO/Ni on GCE using cyclic voltammetry for 15 cycles at 20 mV s^{-1} .

electrochemical sensing applications²⁷ (Table I). The characterization of the deposited layer on the GC electrode was also performed by impedance spectroscopy method at an applied potential of 215 mV in the presence of redox compounds in 0.1 M KCl as shown in Fig. 5. Impedance spectra were fitted to equivalent circuits using NOVA 1.5 and the obtained results are given in Table II. Based on the adopted equivalent circuits (Fig. 5) many parameters were estimated such as the solution resistance (R_s), the charge transfer resistance (R_{ct}), the constant phase element (CPE) and the diffusion impedance (W) (Table II). The nyquist plots of the bare GC electrode represents at low frequency a straight line with a small semi-circle at high frequency region. A decrease in the semi-circle is observed after modification of the electrode surface due to the effect of the deposited layer which is

Table I. Electrochemical parameters of bare and modified GC electrode of the cyclic voltammograms for 1.0 mM $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ solution (in 0.1 M KCl).

Electrodes	$I_a (\mu\text{A})$	$I_c (\mu\text{A})$	$\Delta E (\text{V})$
Bare GCE	50.35	50.20	89
GCE/EG-Ni(NPs)	58.86	58.87	129
GCE/EG-Ni-Au(NPs)	69.66	69.34	146

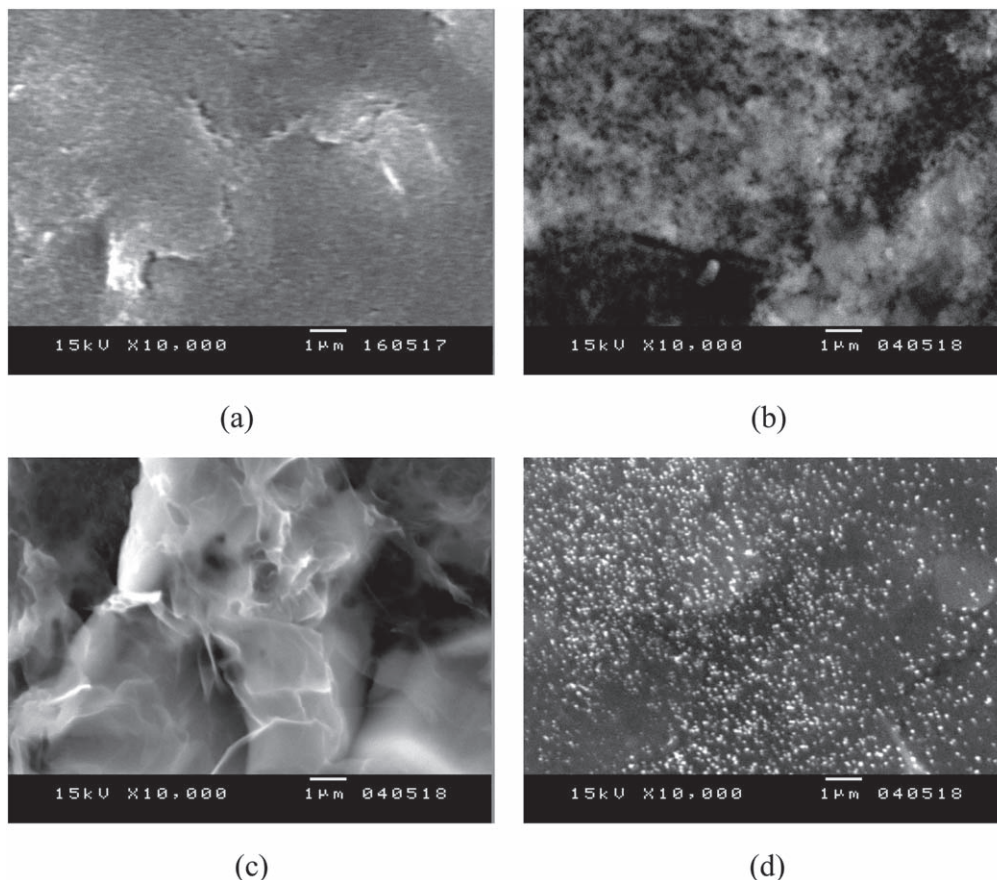


Figure 3. Scanning electron micrographs, (a) bare screen-printed carbon electrode (SPCE), (b) GCE/EG, (c) GCE/EG-Ni(NPs), (d) GCE/EG-Ni-Au(NPs). Resolution of 1 μm , magnification of 10,000 and accelerating potential of 15.0 kV were used.

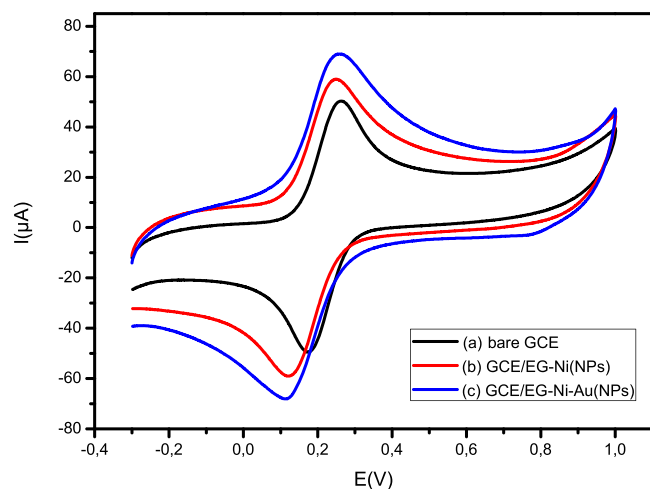


Figure 4. Cyclic voltammograms of 1.0 mM of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ in 0.1 M PBS pH 6 of (a) bare GCE, (b) GCE/EG-Ni(NPs), (c) GCE/EG-Ni-Au(NPs). At potential sweep rate of 100 mV s^{-1} vs Ag/AgCl/(sat. KCl).

related to lower charge transfer resistance (R_{ct}) than it was estimated for the bare GC. This indicates the excellent electrical conductivity of the deposited layer.

Cyclic voltammetry behavior of dopamine at modified GCE.—

The CV responses of DA at bare electrode, GCE/EG-Ni(NPs) and GCE/EG-Ni-Au(NPs) are shown in Fig. 6. It is clear that GCE/EG-Ni-Au(NPs) shows a higher oxidation peak current if it compared with bare electrode and GCE/EG-Ni(NPs). The increase of the peak current after the modification of the electrode with Au(NPs) could be attributed to the excellent electrical conductivity of the Au(NPs).²⁸

Effect of pH.—The effect of pH on the electrochemical responses of GCE/EG-Ni-Au(NPs) in the detection of DA has been investigated. As shown in Fig. 7, the anodic peak potentials of DA shift negatively with the increase of pH from 2.0 to 10.0. The anodic peak currents increase as the pH value increases up to 6.0 and then a slight decrease with continuing increase of pH is observed Fig. 8b. Therefore, 0.1 M PBS solution with pH = 6.0 is chosen for our research. The relationship between pH and anodic peak potential was further studied. Figure 8a display that the

Table II. Electrochemical parameters of bare and modified GC electrode obtained from the analysis of impedance data with the equivalent circuits.

Electrodes	R_s (Ω)	CPE (μF)	R_{ct} (Ω)	W (μF)	χ^2
Bare GCE	169.88	12.2	642.04	529	0.0522
GCE/EG-Ni(NPs)	246.96	8.96	524.53	664	0.0649
GCE/EG-Ni-Au(NPs)	179.86	12.3	448.36	662	0.0649

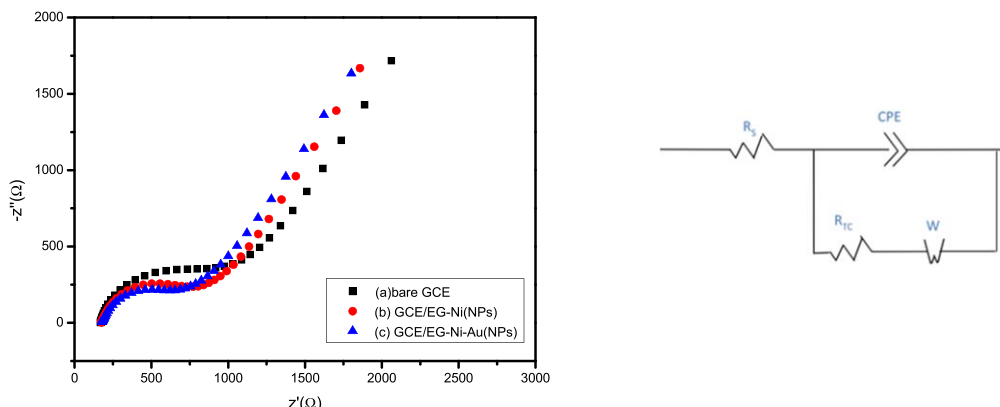


Figure 5. Nyquist plots of 1.0 mM $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ solution in 0.1 M of KCl of (a) bare GCE, (b) GCE/EG-Ni(NPs), (c) GCE/EG-Ni-Au(NPs). Frequency range is from 0.05 to 75,000 Hz, the modulation amplitude is 10 mV, working electrode potential is 215 mV and the Equivalent circuit applied for calculations [(R(Q[RW])].

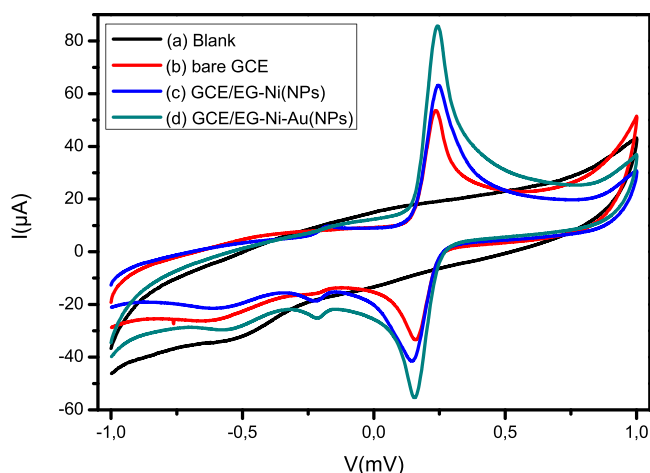


Figure 6. Cyclic voltammograms of modified electrodes performed with dopamine 1 mM in PBS pH = 6. At potential sweep rate of 100 mV s^{-1} vs Ag/AgCl/(sat. KCl). (a) Blank (modified electrode in PBS) (b) bare GCE, (c) GCE/EG-Ni(NPs), (d) GCE/EG-Ni-Au(NPs).

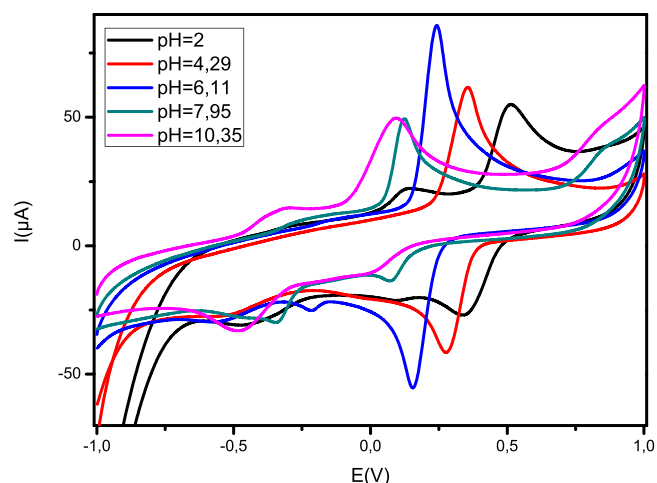


Figure 7. Cyclic voltammograms of dopamine 1 mM in 0.1 M PBS buffer solution at various pHs at GCE/EG-Ni-Au(NPs). The scan rate is 100 mV s^{-1} vs Ag/AgCl/(sat. KCl).

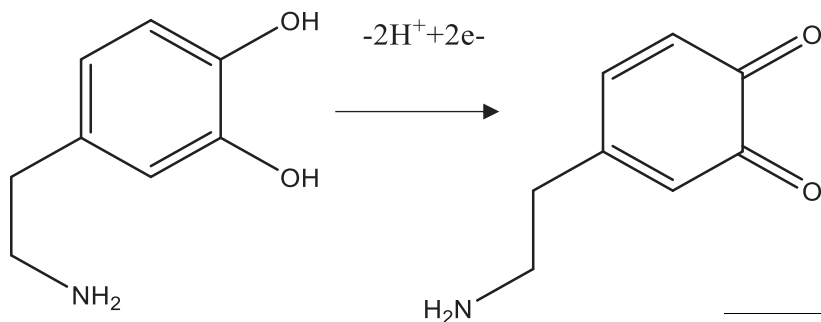
anodic peak potentials (E_a) of DA have a good linear relationship with the solution pH in the range from 2.0 to 8.0. The linear regression equations of DA is $E_a(\text{DA}) = -0.065 \text{ pH} + 0.641$, the slope of 65 (DA) represented in equations is close to the

anticipated Nernstian value defined as 59 mV per pH at 25 °C, indicating that the number of electron and transferred proton involved in the electrochemical reaction is equal. The reaction is exhibited as follow ²⁹:

Table III. Comparison of the proposed modified GCE with other electrochemistry methods in the detection of dopamine.

Methods	Linearity	Detection limit	References
Gold nanoparticles–cyclodextrin–graphene-modified electrode with SWV	0.5–150 μM	0.15 μM	22
Graphene-diamond electrode with DPV	5 μM –2mM	200 nM	30
GO/GCE with DPV	1.0–15 μM	0.27 μM	31
Electrochemically reduced GO/GCE with DPV	0.5–60 μM	0.50 μM	32
rGO/AuNPs with DPV	1–60 μM	20 μM	33
$\text{Fe}_3\text{O}_4/\text{r-GO}/\text{GCE}$	0.4–3.5 μM	0.08 μM	34
Au/rGO/GCE	6.8–41 $\text{M}\mu\text{M}$	1.4 μM	35
Colorimetric based on salt-induced AuNP aggregation	33 nM –3.33 mM	33 nM	36
Colorimetric based on the aggregation of AuNPs induced by copper ions	0.5–10 μM	200 nM	37
Electrochemiluminescence sensor CdSe quantum dots	0.20–12 μM	0.5 μM	38
Fluorescence method based on BSA-Au NCs quenching	0–6 nM	0.622 nM	39
GCE/EG-Ni-Au(NPs) with SWV	0.2–100 μM	0.1 μM	This work

GO: graphene oxide.
rGO: reduced graphene oxide.



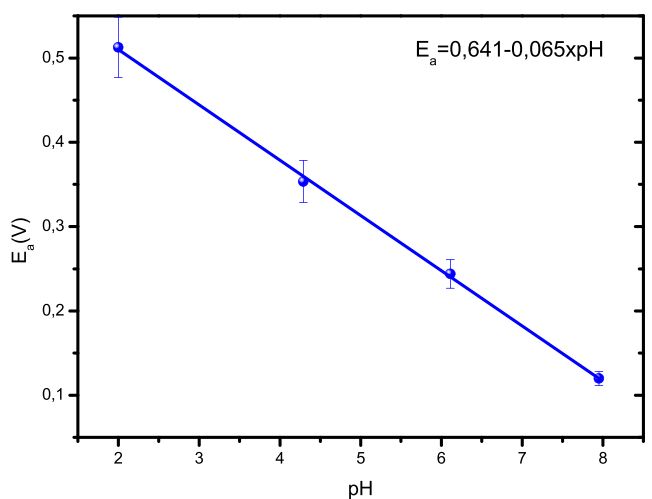
Electrochemical detection of DA.—In order to investigate the electrode performance for dopamine sensing, the Square wave voltammetry (SWV) method was carried out using GCE/EG–Ni–Au (NPs) modified electrode. As shown in Fig. 9, the characteristic peak current of dopamine in 0.1 M PBS increases with the increase of the added concentrations from 1 nM to 1 mM. As depicted in Fig. 9, the oxidation peak currents shows an enhancement with the increase of

DA concentrations. The relationship of the peak current as a function of dopamine concentration is plotted in Fig. 10 and it shows a good linearity with a linear equation:

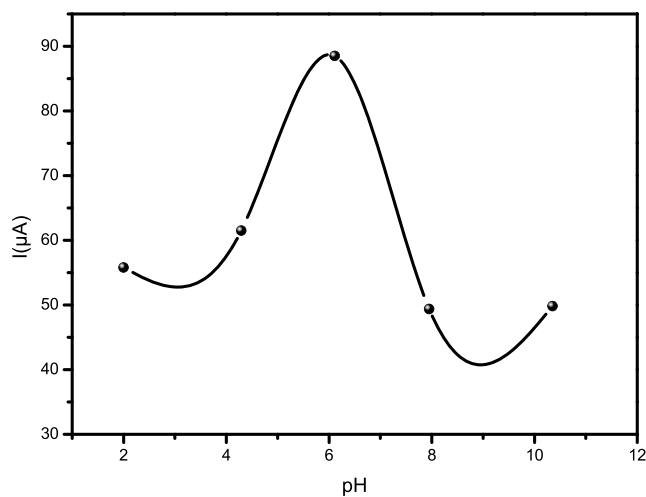
$$I(A) = 0.641 \times x + 1,559E - 5 (R^2 = 0,9872)$$

(Linear range: $2 \times 10^{-7} - 10^{-4}\text{M}$)

The detection limits of DA is found to be $0.1 \mu\text{M}$. Various nanocomposites based non-enzymatic dopamine sensors are summarized in Table III. Compared with others reported nanocomposites based dopamine sensors, the GCE/EG–Ni–Au(NPs) electrode shows comparable sensitivity and linear range. Also, if we compare between our elaborated method and the standard methods like Colorimetric methods for detection of dopamine (Table III) we can consider that our sensor has a good response. After the step of DA detection, the modified electrode can be regenerated after 45 min immersion in deionized water under stirring (Fig. 11). It is clear that all the DA molecules were removed from the surface of the modified electrode. The influence of various substances like UA, AA and glucose as potential interference compounds on the determination of dopamine was studied under the optimum conditions with 10^{-5} M DA at pH = 6.0. The results given in Fig. 12 show that the peak current of DA is not significantly affected by the studied potential interfering species. Therefore, ascorbic acid showed interference in determination of DA if its concentration is 100 times higher than DA concentration. Human serum samples were used for analysis of DA. For evaluation of the analytical performance of our sensor, a known amount of dopamine was added to real samples and results are depicted in Table IV. The appreciable found and recovery results revealing that our modified GCE is promising for the determination of DA present in real samples.



(A)



(B)

Figure 8. (A) Anodic peak potentials against pH and (B) Relationship between the anodic peak current and pH values in the presence of 1 mM DA.

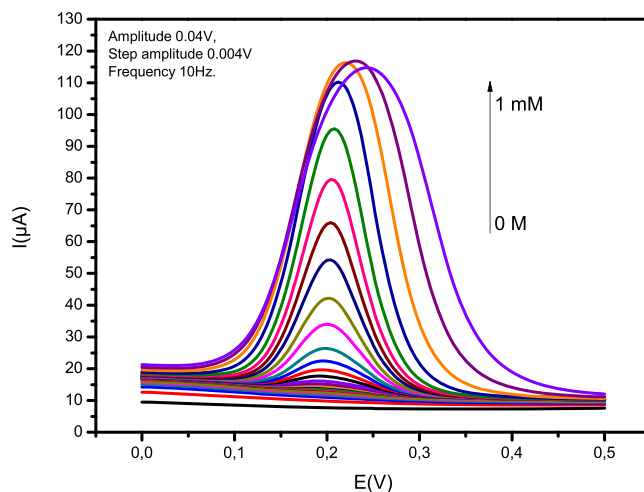
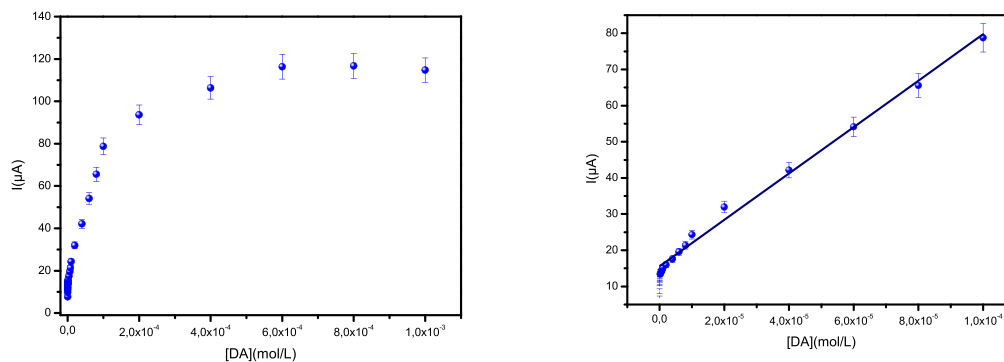


Figure 9. Anodic square wave voltammograms spectra of GCE/EG–Ni–Au (NPs) in the presence of dopamine in PBS (0.1 M) pH = 6. Amplitude 0.04 V, Step amplitude 0.004 V and frequency 10 Hz.



$$I(A) = 0.641 \times x + 1,559E - 5 (R^2 = 0,9872)$$

Figure 10. Plots of oxidation peak currents vs the concentrations of DA from 0 to 10^{-3} M.

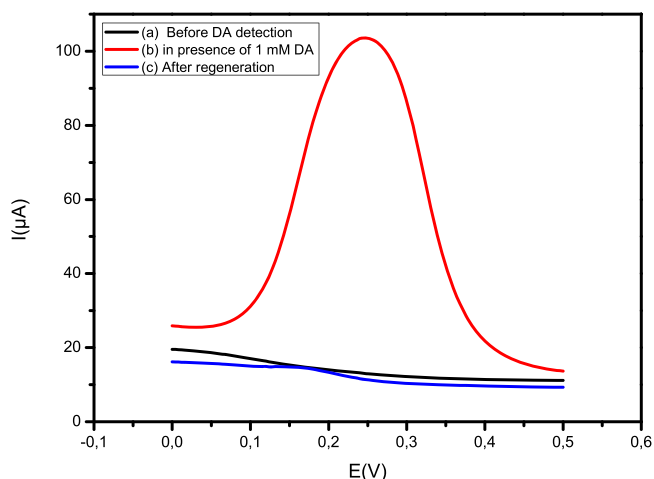


Figure 11. Square Wave Voltammetry of a modified glassy carbon electrode in phosphate buffer pH = 6, before and after regeneration with deionized water solution. (a) Before DA detection, (b) in presence of 10^{-3} M DA and (c) After regeneration.

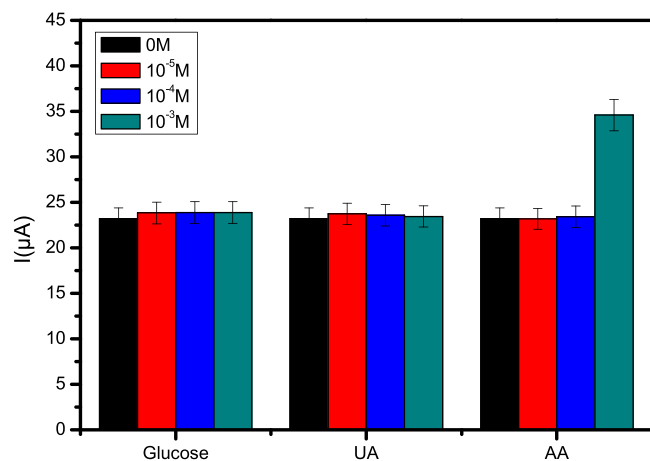


Figure 12. Effect of interfering molecules UA, AA and glucose in presence of 10^{-5} M dopamine (various concentrations of interfering species from down to up: 10^{-5} – 10^{-3} M). Supporting electrolyte was 0.1 M phosphate buffer (pH = 6).

Table IV. Application of the proposed method for determination of dopamine.

Human serum samples	Added	Found	RSD%	Recovery%
Samples 1	10^{-6}	0.98×10^{-6}	2.79	98
Samples 2	5×10^{-5}	4.8×10^{-5}	1.08	96
Samples 3	10^{-4}	0.98×10^{-4}	2.33	98

Conclusions

In this work, a highly performing detection of dopamine compound was performed using modified glassy carbon electrode with EG-Ni-Au(NPs). The modified electrode with EG-Ni-Au(NPs) showed better electrochemical properties than bare and EG-Ni(NPS), in terms of reducing peak-to-peak separation and intensity of the peak for DA characterized by a reversible behavior. The SWV analysis using a portable instrument highlighted the advantages of using EG-Ni-Au(NPs), this sensor is able to detect DA with high sensitivity and large linear range.

Acknowledgments

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