

Research Article

Selective Electrochemical Detection of Epinephrine Using Gold Nanoporous Film

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Epinephrine (EP) is one of the important catecholamine neurotransmitters that play an important role in the mammalian central nervous system. Therefore, it is necessary to determine the change of its concentrations. Nanoporous materials have wide applications that include catalysis, energy storages, environmental pollution control, wastewater treatment, and sensing applications. These unique properties could be attributable to their high surface area, a large pore volume, and uniform pore sizes. A gold nanoporous layer modified gold electrode was prepared and applied for the selective determination of epinephrine neurotransmitter at low concentration in the presence of several other substances including ascorbic acid (AA) and uric acid (UA). The constructed electrode was characterized using scanning electron microscopy and cyclic voltammetry. The resulting electrode showed a selective detection of epinephrine with the interferences of dopamine and uric acid over a wide linear range (from 50 μM to 1 mM). The coverage of gold nanoporous on the surface of gold electrode represents a promising electrochemical sensor with high selectivity and sensitivity.

1. Introduction

Epinephrine (EP) is one of the most important catecholamine neurotransmitters, which plays an important role in the transmission of nerve impulse and is associated with a large variety of physiological processes and illnesses. Monitoring the concentration of EP gains great attention since the changes in its concentrations resulted in many diseases such as Parkinsonism, Schizophrenia, and Huntington's disease as well as drug addiction and HIV infection [1–5] and affects many life phenomena. In biological systems, EP frequently exists with dopamine (DA) and uric acid (UA); therefore, it is necessary to selectively detect EP in the presence of different interferences such as DA and UA [6–9]. For electrochemical sensing, it is important to avoid the overlapping in the electrochemical response of EP and other species due to their close oxidizing potentials. It is difficult to use conventional electrodes for selective determination of EP electrochemically in the presence of DA, UA, and AA, which frequently exist together in biological systems, since at

most solid electrodes they are oxidized at a closed potential producing an overlapping voltammetric response.

Application of electrochemical methods proved to be highly sensitive and selective techniques [10–12] for the detection of biological materials [13, 14]. Many complications face the use of the electrochemical methods such as the influence of many analytes interferences, which may be present at higher concentrations. The use of modified electrodes as biosensors produces several advantages such as the ease of fabrication, the renewable surface, low background current, and also the wide range of potential ranges. Modified electrodes enable the detection of several analytes within different matrices (urine or blood) without separations giving electrical signals at characteristic potentials. Also, the use of these electrodes overcomes the problem of using analytes of a significant electroactivity [15]. In our previous work, we have fabricated several modified electrodes and their applications for detection of many biological targets [16–23]. In recent years, nanomaterials with special physical and chemical properties have been widely applied in chemosensors and

TABLE 1: Comparison of epinephrine sensor based on gold nanoporous film modified gold electrode with other epinephrine sensors.

| Electrode | Method | LOD (μM) | Reference |
|--|--------------|-----------------------|------------|
| Modified carbon nanotubes paste electrode | DPV | 0.09 | [38] |
| Modified gold electrode | CV | 0.1 | [39] |
| Nanodiamond/graphite | LSV | 0.5 | [40] |
| ZnO nanoparticle/modified carbon paste electrode | SWV | 0.05 | [41] |
| Carbon paste electrode modified with iron phthalocyanine | DPV | 0.5 | [42] |
| Penicillamine self-assembled gold electrode | CV | 0.1 | [43] |
| Modified carbon nanotube paste electrode | DPV | 0.035 | [44] |
| Carbon nanotube modified carbon film electrodes | DPV | 0.9 | [45] |
| TTAB modified carbon paste electrode | CV | 0.12 | [46] |
| Molecularly imprinted polymers | Amperometric | 0.03 | [47] |
| MWCNT/dopamine dithiocarbamate modified electrode | Amperometric | 11 | [48] |
| Nanoporous thin Au films | DPV | 2.42 | [49] |
| Gold nanoporous film modified gold electrode | CV | 19 | This study |

biosensors. Nanomaterial-based electrochemical sensing of neurological drugs and neurotransmitters has recently gained great attention [24–26]. Nanomaterials were used as modifiers to fabricate sensors and biosensors [27, 28] due to their novel optical, electrical, and catalytic properties, which result in high selectivity and sensitivity of any detection system [29, 30]. By tuning the surface chemistry of nanostructured materials on the electrode, it could be directed towards the detection and capture of a certain analyte [31]. Presence of nanosized materials enhances electron transfer due to the increase of the electroactive surface area and promotes adsorption of molecules [32–34].

Recently, conducting porous layers modified electrodes were reported to improve the mass transport character from planar diffusion to thin layer; this change could shift the potential under which the target species undergo oxidation or reduction from that required to electrolyse the interfering species that facilitate the differentiation between species which oxidize or reduce at similar potentials under planar diffusion conditions [5, 6, 35]. Moreover, gold (Au) nanoporous has been attracting interest due to the wide range of applications that require inertness, conductivity, or increased surface area [7]. The immersion of nanoporous modified material in an electrolyte induces charges on the surface of a material because a potential is applied across the electrolyte/material interface, forming a capacitive double layer [8]. Recently, we have reported the development of nanoporous Au film modified Au electrodes and their applications for monitoring DA as well as cell-based chip [36, 37].

In the present work, we focus on developing nanoporous Au layer on Au electrode and its application as a sensor for selective electroanalytical detection of EP. The biosensor was fabricated based on electrochemical deposition of Au nanoporous layer onto Au electrode. The capability of nanosensor to selectively detect EP is evaluated in the presence of different interferences such as DA and UA. Herein, using nanoporous Au layer modified Au electrode in electrochemical detection of EP within a range from 1 mM to 50 μM . The detection limit of our developed EP sensor in comparison with some examples of electrochemical sensors

of EP based on modified electrodes was presented in Table 1, in addition to the detection of different concentrations of EP in the presence of DA and UA; the fabricated sensor was also applied to detect and quantify the mixture of EP and UA in human serum sample as real sample applications. Characteristics of the developed biosensor were investigated using cyclic voltammetric, SEM, calibration curves, and limit of detection of EP.

2. Experimental

2.1. Chemicals. Chloroauric acid tetrahydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$), trisodium citrate dehydrate, EP, DA, and UA were obtained from Sigma-Aldrich (3050 Spruce St, St. Louis, MO 63103, USA). Phosphate buffer solution (PBS) was prepared by using 0.1M Na_2HPO_4 and NaH_2PO_4 and its pH was adjusted with H_3PO_4 or NaOH solutions.

2.2. Equipment. All electrochemical measurements were performed using micro-Autolab, potentiostat/galvanostat instrument (Netherlands) connected to a three-electrode cell; Metrohm Model 663VA stand was controlled by Autolab Nova software at room temperature. A three-electrode system consisted of a platinum wire as a counter electrode, Ag/AgCl as the reference electrode, and modified Au substrate as a working electrode. The surface morphology was analyzed by SEM (ISISDS 130C, Akashi Co., Tokyo, Japan).

2.3. Electrochemical Measurements. The electrochemical measurements were carried out by immersing the fabricated modified Au electrode together with the reference and counter electrodes in the different concentrations of epinephrine ranging from 1 mM to 50 μM ; the solutions were prepared in different phosphate buffer solutions buffered (pH 4, 6, and 9). Experiments were carried out to optimize all conditions in order to obtain the best cyclic voltammogram.

2.4. Fabrication of Mesoporous Gold Film. A 5 nm thick titanium layer and a 43 nm thick Au film were patterned one after the other on a glass substrate by DC magnetron

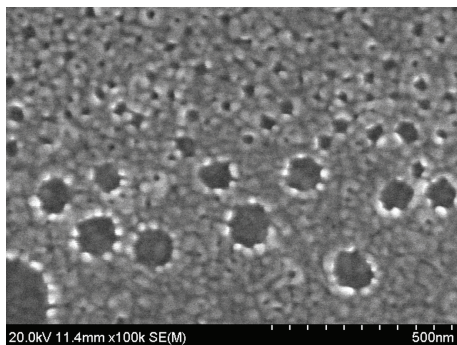


FIGURE 1: SEM image of Au nanoporous layer modified Au electrode.

sputtering. Bare Au electrodes were freshly cleaned using acidic piranha solution ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$, 7:3 v/v) and then rinsed thoroughly with deionized water (DIW) and dried under N_2 gas. Then, the freshly cleaned Au electrodes ($2\text{ cm} \times 1\text{ cm}$) were immersed in 5 mL of 1 mM aqueous solution of HAuCl_4 containing PEG ($20\ \mu\text{L}/\text{mL}$) [13]. Au nanoporous layer was electrochemically deposited at negative potential of -1.3 V (Ag/AgCl). Finally, the residue surfactant that might be adsorbed on the modified surface was removed by rinsing the substrates with DIW and then sonicated for 5 min with isopropyl alcohol. The surface morphologies were analyzed by scanning electron microscopy (SEM) (ISI DS-130C, Akashi Co., Tokyo, Japan).

2.5. Selectivity of the Developed EP Sensor. The selectivity of the prepared electrode towards EP was studied by using a mixture of EP solutions with different concentrations of dopamine and uric acid as interferences, which are commonly present in urine.

3. Results and Discussion

3.1. Characterization of Gold Modified Electrode. Morphology of the Au nanoporous film modified Au electrode that was fabricated based on electrodeposition method was characterized by using SEM as shown in Figure 1. The SEM demonstrated the deposition of monolayer nanoporous Au film with two sets of pore diameters; one has a pore diameter of about 40 nm and the other sets have a pore diameter of about 100 nm.

3.2. Detection of Epinephrine Using Gold Modified Electrode. The cyclic voltammetry study for 10^{-5} M of EP solution (supporting electrolyte is sodium phosphate buffer of pH 7.0, 0.01 M) at Au nanosensor is presented in Figure 2. The voltammetric measurements were performed by scanning the potential within a range from -0.7 to $+0.7\text{ V}$. The interaction of EP on the surface of the Au nanosensor resulted in an oxidation peak at $+0.2\text{ V}$ and a reduction peak at -0.2 V due to the reduced quinone species as shown in Figure 3 [38]. The results obtained state the ability of the Au nanoporous monolayer immobilized on the Au electrode to efficiently catalyze the oxidation of EP. The use of Au modified electrode accelerates

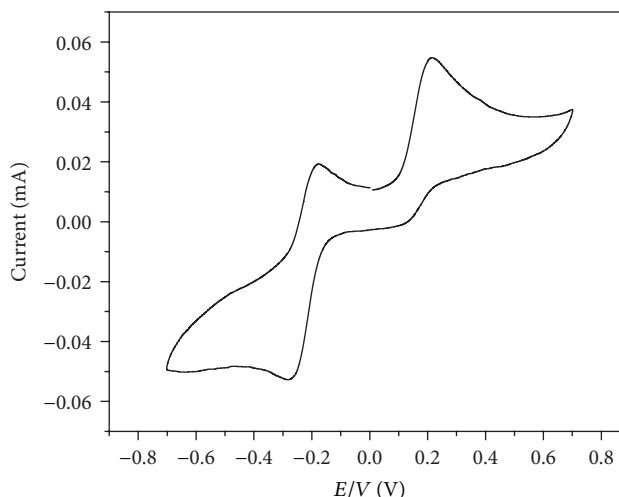


FIGURE 2: Cyclic voltammogram of epinephrine.

the electron transfer giving rise to sharp oxidation and reduction peaks and also the high intensity as presented in Figure 2.

3.3. Effect of Different Epinephrine Concentrations. Cyclic voltammograms of different concentrations of epinephrine ranging from 1 mM to $10\ \mu\text{M}$ at the Au nanoporous modified Au electrode are shown in Figure 4(a), which demonstrated that the redox current peaks were increased with increasing the concentration of EP. A linear response is obtained between the oxidation-reduction electrochemical peaks and the concentration of epinephrine where both of the electrochemical peaks increased with the increase of the concentration of epinephrine as presented in Figure 4(b). The limit of detection of the developed sensor was found to be $19\ \mu\text{M}$ that is in the same range of the detection limit for several reported sensors as shown in Table 1.

3.4. Dependence of pH. The electrochemical behavior of epinephrine was reported to be influenced by the acidity or alkalinity of the solution [50]. Effect of solution pH on the electrochemical behaviors was analyzed in PBS solutions of different pH (4, 7, and 9). A marked change is noticed in the electrochemical response of EP at Au nanosensor with the increase of pH value as in Figure 5. Figure 5 shows the important influence of change of the pH value on the redox reaction of EP at Au nanoporous modified Au electrode, which indicated that the redox peak was negatively shifted with increasing the pH value of the pH solution, which could be attributed to the uptake of electrons by an equal number of protons [51–53]. These results indicated the high dependence of the cyclic voltammograms response of EP on the pH of the solutions used as was shown in Figure 5.

3.5. Simultaneous Determination of Epinephrine and Uric Acid. Several chemically modified electrodes have been applied in the electrochemical and biological fields [6, 54–59]. It is always of great importance to achieve the highest

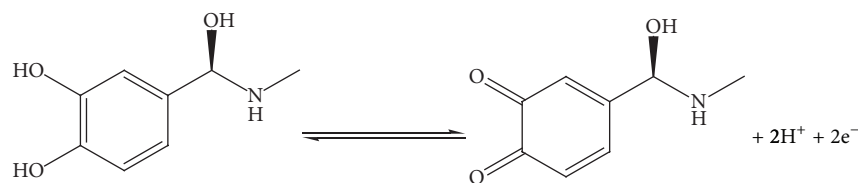


FIGURE 3: Oxidation mechanism of epinephrine.

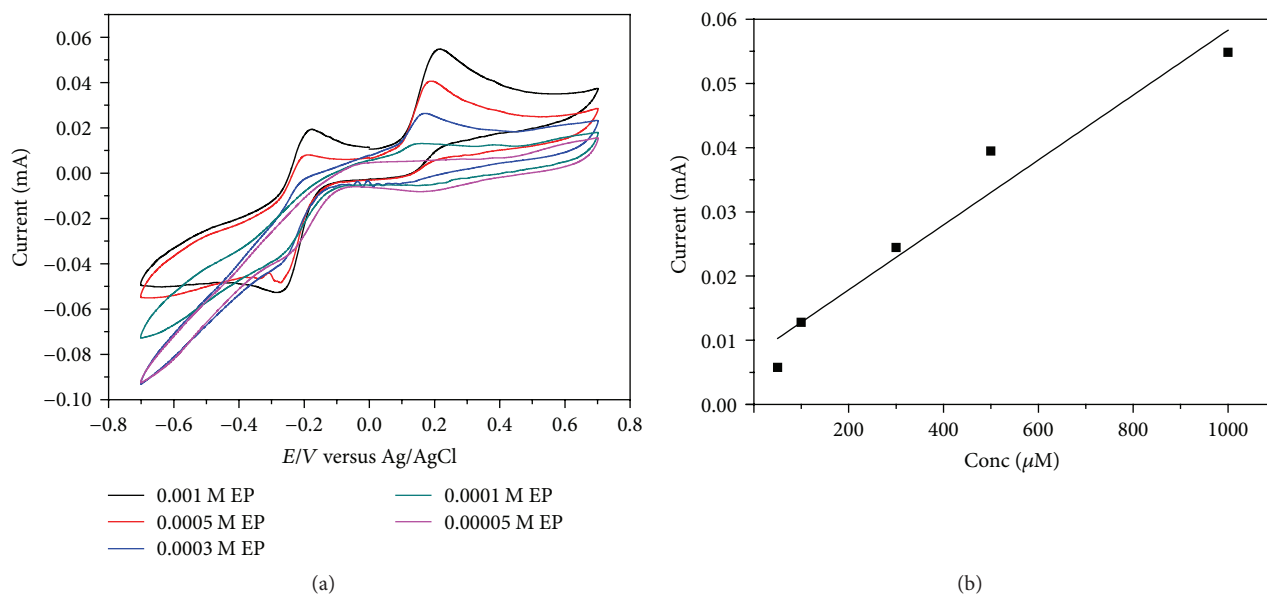


FIGURE 4: (a) Cyclic voltammogram of different concentrations of epinephrine and (b) linear relation between current and epinephrine concentrations.

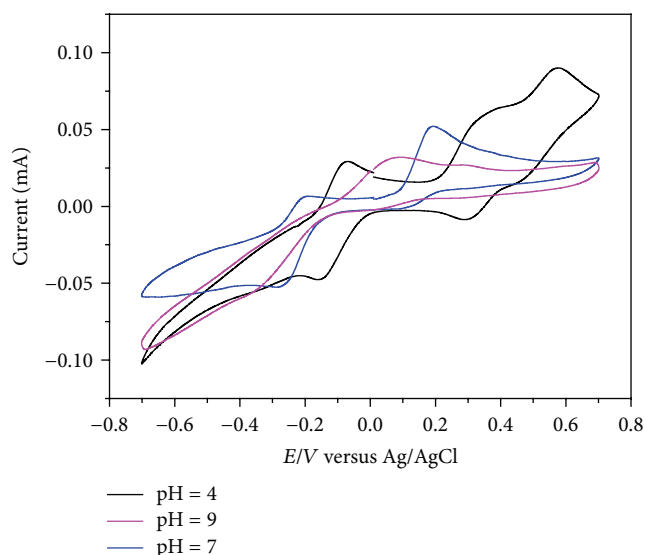


FIGURE 5: Cyclic voltammogram of the pH dependence of epinephrine.

selectivity and sensitivity towards neurotransmitters in presence of different interferences. Many difficulties have often faced the simultaneous detection of epinephrine, dopamine,

and uric acid [7–9, 60]. Studies have been often developed towards the determination of a single component [61–63] due to overlapping of the voltammetric response of both DA and EP as a result to the similarities in their chemical structures. Our study is focused on the selective detection of EP in presence of uric acid which are frequently present together in biological systems and have no reduction peak. Figure 6 represented the CV of a mixture of EP and uric acid; a separation between the two cathodic peaks at 0.3 V and 0.5 V is obtained, respectively, which is enough to avoid any interference. According to the obtained results, the selective detection of epinephrine in presence of uric acid is applicable with sensitivity.

3.6. Application of Au Nanoporous Modified Au Electrode for Monitoring Epinephrine in Real Samples. In order to investigate the performance of the developed modified electrode to detect epinephrine in real samples, we have used human serum as a complex matrix. The application of the developed epinephrine sensor was studied by analyzing different concentrations of epinephrine in human serum that have been obtained from a healthy donor. Different epinephrine concentrations (250, 375, and 500 μM) were spiked into 1% human serum and the mixed samples were analyzed. Figure 7(a) shows the cyclic voltammograms of different epinephrine concentrations (250, 375, and 500 μM) spiked

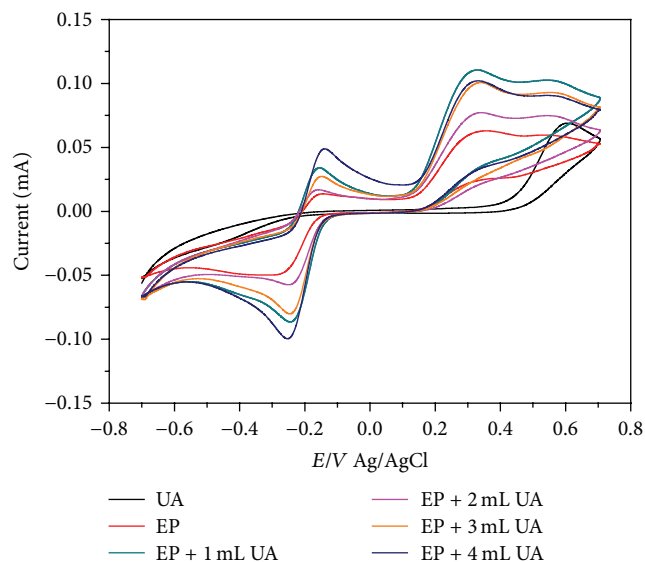


FIGURE 6: Cyclic voltammogram of epinephrine in presence of uric acid.

in serum, which exhibited similar electrochemical behavior epinephrine in PBS solution. This result indicated that the developed modified electrode could be applied for monitoring of epinephrine in real samples without interferences. Moreover, in biological environments, uric acid is commonly present with epinephrine and may be oxidized at similar potentials as epinephrine [64, 65]. Cyclic voltammograms of 2.5×10^{-4} epinephrine mixed with 2.5×10^{-4} uric acid and spiked in human serum sample were recorded as shown in Figure 7(b), which showed the ability of the electrode to distinguish epinephrine from uric acid in real sample since the oxidation peak of epinephrine was not affected by uric acid.

4. Conclusions

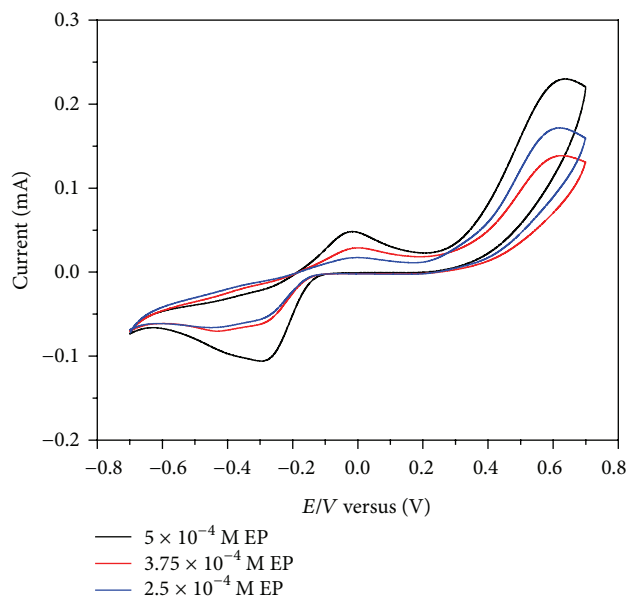
A new Au nanoporous modified Au electrode has been developed for epinephrine determination. The detection was performed by electroanalytical techniques by immersing the prepared electrode together with the reference and counter electrode in different epinephrine solutions and recording the cyclic voltammograms, which presented high sensitivity and low detection limit. The sensors show good reproducibility and excellent stability for more than six months. One important advantage is the marked peak separation between uric acid and epinephrine using Au nanoporous Au electrode indicating high selectivity. Application to real samples gave high sensitivity and selectivity of epinephrine.

Competing Interests

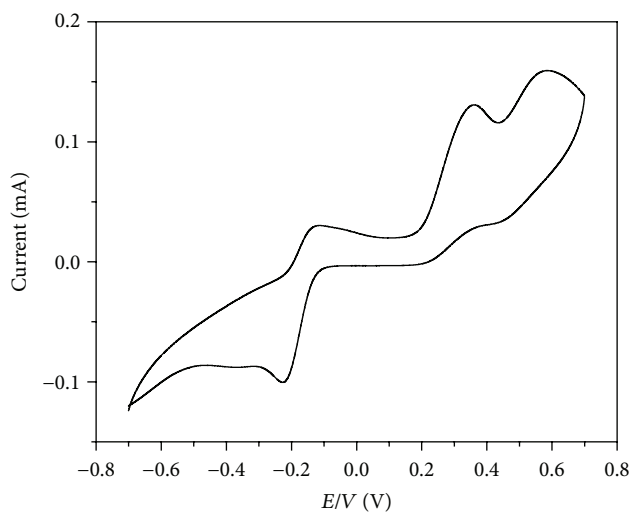
The authors declare that they have no competing interests.

Acknowledgments

This work was supported by Assiut University.



(a)



(b)

FIGURE 7: Cyclic voltammogram of (a) different concentrations of epinephrine in serum and (b) epinephrine in presence of uric acid in serum samples.

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