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Simple and Efficient Epinephrine Sensor Based on Palladium Doped Poly(L-arginine) Modified Electrode

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A novel palladium doped poly(L-arginine) modified electrode (Pd-PLA/GCE), fabricated by electrochemical immobilization of the palladium doped poly(L-arginine) on a glassy carbon electrode, was used for determination of epinephrine through cyclic voltammetry. The electrochemical properties of epinephrine have been investigated. In phosphate buffer solution (pH 3.0), a pair of redox peaks was observed with potential E_{pa} = 0.500 V and E_{pc} = 0.406 V at a scan rate of 160 mV/s. Epinephrine was determined at the modified electrode under the optimum conditions by both cyclic voltammetry and differential pulse voltammetry. The results show that the peak current and the concentration of epinephrine show good linear relation in a range of $5.00 \times 10^{-7} \sim 1.00 \times 10^{-5}$ mol/L and $1.00 \times 10^{-5} \sim 1.00 \times 10^{-4}$ mol/L with detection limit of 1.0×10^{-7} and 8.0×10^{-8} mol/L. The method was successfully applied to the determination of epinephrine in injection with satisfactory results.

Keywords: Palladium doped, L-arginine, Epinephrine, Modified electrode, Cyclic voltammetry.

INTRODUCTION

Epinephrine (EP), also known as adrenaline, is one of the most important neurotransmitters in mammalian central nervous systems and exists in the nervous tissue and body fluids. Many diseases are related to changes of the epinephrine concentration in mammals[1]. Thus, a quantitative determination of epinephrine concentration is significant for developing nerve physiology, pharmacological research and life science. In recent years, many methods have been reported for the determination of epinephrine, such as high-performance liquid chromatography (HPLC)[2,3], UV spectrophotometry[4], capillary electrophoresis[5-8], fluorescence[9-12], chemiluminescence[13,14] and surface plasma technology[15], *etc*. These methods are very significant due to their importance in separation science and provide low detection limits. However, these methods often require several previous sample preparation steps to obtain a final extract completely compatible with chromatographic determination which makes the procedure more complicated and more expensive. These disadvantages prevent them for routine analysis. Therefore development of a sensitive and rapid method with low cost for determination of epinephrine is necessary.

Because epinephrine is easily oxidized[16], electrochemical methods for epinephrine analysis arouse great interests due to simple operation, on-site monitoring and low-cost instrumentation[17]. Up to now, most epinephrine electrochemical analysis relied on its direct oxidation on the surfaces of various carbon-based electrode materials, such as graphene, ordered mesoporous carbon, carbon nanotubes and graphite[18-21]. However, the poor selectivity of these traditional sensors limited their application in actual samples. Developing novel strategies for fabrication of highly selective electrochemical epinephrine sensors are extremely necessary.

Drawbacks of those electrodes have been overcome by the use of electrodes whose surfaces are modified with specific functionalities, called chemically modified electrodes (CMEs). Modified electrodes with polymer films formed by the electropolymerization of organic monomers have encouraged research in the field of electrochemistry[22,23]. Methods to prepare the modified electrodes by the polymeric films are very simple involving only the immersion of the electrode into the polymer solution. Furthermore, the polymer film modified electrode has important functional groups with high density on the electrode surface and then it can improve the electrochemical activities and stability of the fixed functional groups[24]. These electrodes have been used for the detection of drugs, pesticides and heavy metals[25-28].

Recently, poly amino acid film has been used to fabricate modified electrode which has been used in the determination of biological substances[29]. However, using amino acids solely as modifier to decorate the electrode have not been satisfied people's demand for the convenient and accurate determination.

Doping metal ions, such[30-33] as Fe^{3+}, Pt, Bi, *etc*. on the surface of the electrode is an essential path for improving the efficiency of the modified electrode's electrochemical characters. However, few research using poly amino acid film as modifier and metal ion as doping substances to decorate the electrode has been reported in determining the compounds.

In the present work, a simple, low-cost and easy-to-prepare sensor was obtained by electropolymerization of palladium doped poly-L-arginine (Pd-PLA) at glassy carbon electrode (GCE) and the electrochemical behaviours of epinephrine at the modified electrode were discussed. It is also shown that this sensor is usable to determinate the epinephrine by cyclic voltammetry and differential pulse voltammetry with good linear relation and low detection limits. Due to the palladium doped, the electrochemical response, such as the electron transfer and sensitivity of the modified electrode were enhanced obviously. The proposed method has been applied to determination of epinephrine in injections with simplicity and high selectivity.

EXPERIMENTAL

Epinephrine was purchased from Sigma and were prepared just prior to use. L-Arginine, used in electro polymerization as a monomer, was acquired from Guoyao chemical reagent corporation (Shanghai, China). Phosphate buffer solutions with various pH values (2.0~11.0) were prepared by mixing the stock solutions of 0.1 mol/L H_3PO_4, NaH_2PO_4, Na_2HPO_4 and Na_3PO_4. All chemicals were of analytical grade and were used without further purification. All the solutions were prepared with doubly distilled deionized water and all the experiments were carried out at room temperature.

A BAS100/W electrochemical workstation (BAS group, USA) was used for electrochemical measurements, a conventional three-electrode system was employed with a palladium doped poly-L-arginine (Pd-PLA) modified electrode as a working electrode, a saturated Ag/AgCl as a reference electrode and a Pt wires as an auxiliary electrode. All pH measurements were performed by a digital pH/mV meter (pHS-3C, Shanghai, China).

Preparation of the Pd-PLA/GCE electrode: The bare glassy carbon electrode was polished with 0.05 μm alumina slurry and a polishing cloth to obtain a mirror surface. After each polishing, it was rinsed with 1:1 HNO_3, ethanol and ultrasonicated in doubly distilled deionized water for 5 min to remove any adhesive substances on the electrode surface, respectively. After cleaning, the bare glassy carbon electrode was modified with palladium chloride and L-arginine (Pd-PLA) by cyclic sweeping from 2.2 to -0.7 V at a scan rate of 160 mV/s for 8 cycles in solution containing 1.6 mol/L HNO_3 (0.8 mL), 5×10^{-3} mol/L L-arginine (3.5 mL), 0.010 mol/L $PdCl_2$ (1.5 mL), 1.0 mol/L KNO_3 (3.0 mL). Finally, the electrode's surface was rinsed by doubly distilled deionized water. The obtained modified electrode is denoted as Pd-PLA/GCE.

The experiments were performed by cyclic voltammograms from 0.1 to 0.7 V at 160 mV/s in pH 3 phosphate buffer solutions with the quiet time of 8 s. The differential pulse voltammetric measurements were recorded between 0.1 and 0.7 V at pulse increment of 3 mV, pulse amplitude of 50 mV, pulse width of 0.06s and pulse period of 0.2s. After each sweep, the electrode was put into the blank solution until the peak faded away.

RESULTS AND DISCUSSION

Electropolymerization of palladium doped poly-L-arginine (Pd-PLA) film at the glassy carbon electrode surface: Fig. 1 shows the cyclic voltammograms of polymerization under optimum conditions. As shown in Fig. 1, in the first potential sweep, an oxidation peak, appeared at the peak potential of 0.0 V, can be assigned to the oxidization of deposited palladium and an obscure wide oxidation peak, appeared at the peak potential of 1.7 V, was attributed by the polymerization of L-arginine, together with a reduction peak, appeared at the peak potential of -0.3 V, can be ascribed by the reduction of Pd^{2+}. With the increase of sweep cycles, the peak potential was almost unchanged and the current response increases somewhat till the eighth scan. The results show that the passivation is related to the grafting of Pd-PLA onto glassy carbon electrode. This binding process is almost complete after 8 cycles.

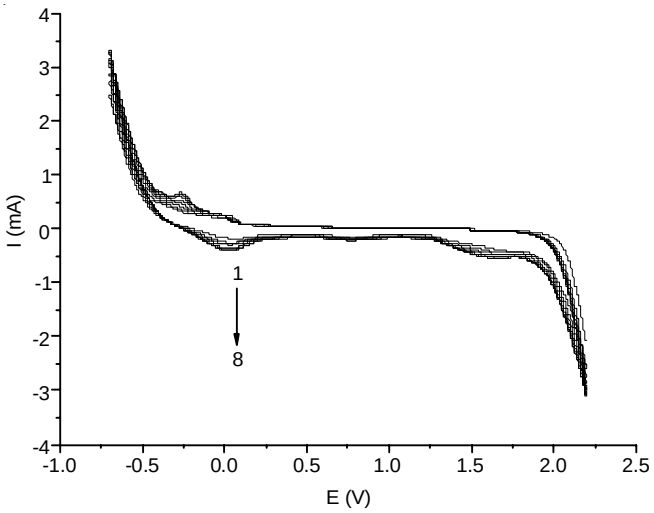

Fig. 1. Cyclic voltammetric curves of the palladium doped L-arginine in the polymerization process at scan rate of 160 mV/s. From 1 to 8 indicate the total number of sweeps

Electrochemical impedance characterization of the modified electrode: To investigate the binding of Pd-PLA on the surface of glassy carbon electrode, electrochemical impedance measurements (EIS) was used to characterize the fabricated Pd-PLA/GCE. Fig. 2 shows the EIS results for glassy carbon electrode and Pd-PLA/GCE in 0.1 mol/L $[Fe(CN)_6]^{3-/4-}$ solution containing 0.1 mol/L KCl. As can be seen, the bare glassy carbon electrode exhibited a small semicircle at high frequencies and a linear part at low frequencies, which implied the characteristic of a kinetic control process of the electrochemical process (Fig. 2 a). After the Pd-PLA film was electrodeposited on the bare glassy carbon electrode, the EIS of the resulting film showed a lower Ret (Fig. 2b), which indicated that Pd-PLA is beneficial to the electrons transfer.

Electrochemical behaviour of epinephrine at the Pd-PLA/GCE: In order to study the electrochemical behaviour of the modified electrode, the cyclic voltammograms at the

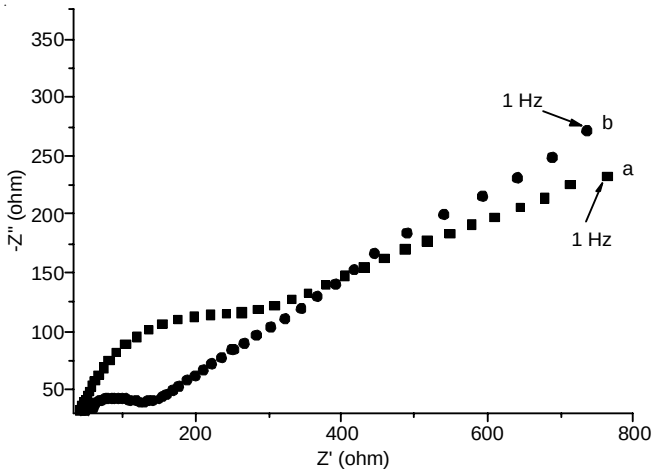

Fig. 2. Nyquist impedance plots of the bare glassy carbon electrode (a) and Pd-PLA/GCE (b) in 0.1 mol/L $[Fe(CN)_6]^{3-/4-}$ solution containing 0.1 mol/L KCl

bare glassy carbon electrode (1), Pd/GCE (2), PLA/GCE (3) and Pd-PLA/GCE (4) were obtained in 2.50×10^{-5} mol/L epinephrine (pH = 3.0). As shown in Fig. 3, epinephrine shows a pair of redox peaks with a weak peak current at a bare glassy carbon electrode within a scanning range of 0.1 to 0.7 V. While at Pd/GCE and PLA/GCE, the oxidation peak current gradually increased with reduction peak current approximately constant. Compared with other modified electrodes, there is an obvious pair of redox peaks with highest peak current at the Pd-PLA/GCE, showing an obvious catalytic effect of the modified Pd-PLA film.

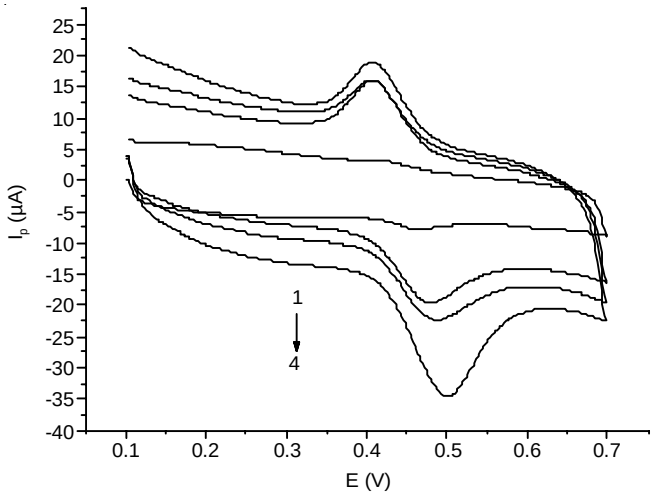

Fig. 3. Cyclic voltammograms of 2.50×10^{-5} mol/L epinephrine at glassy carbon electrode (1), Pd/GCE (2), PLA/GCE (3) and Pd-PLA/GCE (4); PBS: pH = 3; scan rate: 160 mV/s; epinephrine concentration: 2.50×10^{-5} mol/L

Optimization of the experimental conditions: In order to obtain ideal analytical data for the determination of epinephrine, some of the important factors were optimized systematically.

Effects of pH on the peak current and peak potential of epinephrine: To investigate the effect of pH on the response of epinephrine, cyclic voltammograms at the Pd-PLA/GCE were recorded (Fig. 4). All the peak potential for epinephrine shifted to negative potential by increasing the pH value of solution. Based on $E_p = (E_{pa} + E_{pc})/2$, the relationship between E_p and pH can be described using the following equations: $E_{pa} = 0.6814\text{-}0.05925$ pH, R = 0.9930 (pH = 2.0~11.0) and E_{pc}(V) = 0.5931-0.05962 pH, R = 0.9991 (pH = 2.0~6.5), respectively. According to the Nernst equation, the slope of 59 mV·pH^{-1} reveals that protons have taken part in the electrode reaction process and the proportion of electrons and protons involved in the reactions was 1:1. Therefore, a mechanism for epinephrine oxidation can be proposed in eqn. 1. This conclusion is in accordance with the known electrochemical reactions of epinephrine[34]. The pH of epinephrine solutions changed from pH 2 to 11 and the potential was scanned in the range of -0.1 to 0.7 V. The results showed that the redox peak current of epinephrine increased with increasing pH value until the highest peak current and the best peak shape were obtained at pH 3, while the peak current decreased dramatically when the pH value exceeded 3. Thus, a buffer solution of pH 3 was chosen as the supporting electrolyte in this work.

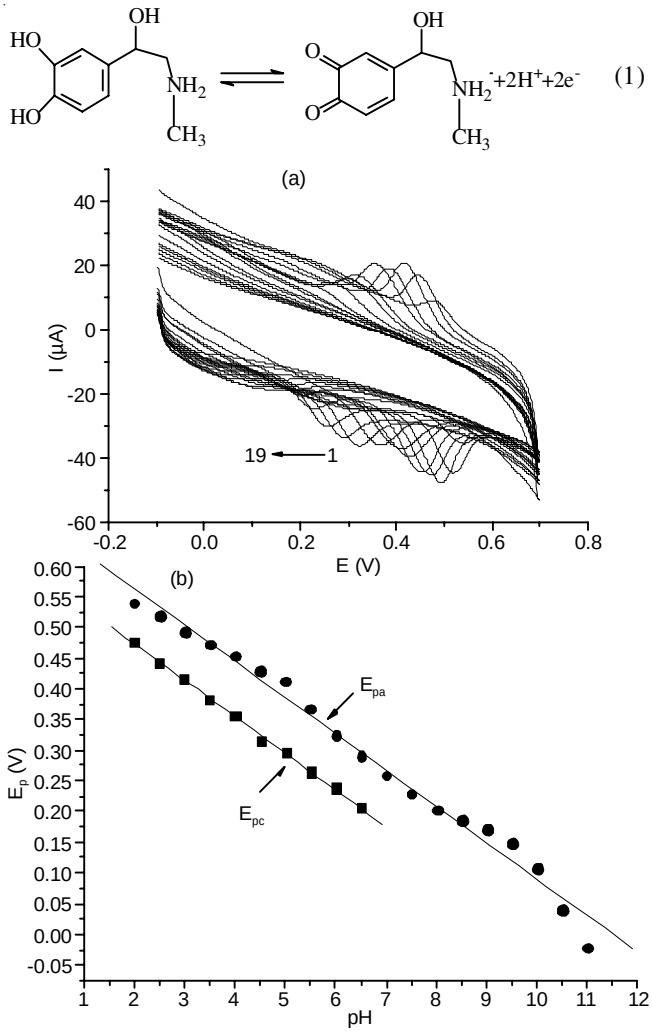

Fig. 4. Cyclic voltammograms of epinephrine at Pd-PLA/GCE at different effects of solution pH (a) and the relationship curve between the peak potential and pH (b); pH from 1 to 19: 2.0, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7, 7.5, 8, 8.5, 9, 9.5, 10, 10.5, 11; Scan rate: 160 mV/s; epinephrine concentration: 2.50×10^{-5} mol/L

Effect of scan rate on the peak current and determination of the diffusion coefficient (D): Scan rate (n) can influence the current responses of epinephrine and the

corresponding electrochemical parameters could be deduced from the relationship between the scan rate of potential sweep and current responses of epinephrine oxidation. Fig. 5 shows a cyclic voltammogram of the Pd-PLA/GCE modified electrode at various scan rates obtained in phosphate buffer (pH 3) containing 2.50×10^{-5} mol/L epinephrine. As shown in Fig. 5, the peak potentials E_{pa} and E_{pc} shifted towards positive and negative values linearly and the redox peak currents increased, with the scan rates range from 20 to 600 mV/s. The linear-regression equations of I_{pa} and I_{pc} with the scan rates are expressed as $\log I_{pa} = -0.5319 + 0.8195 \log \nu$, $R = 0.9968$ and $\log I_{pc} = -0.5191 + 0.7358 \log \nu$, $R = 0.9980$, respectively (Fig. 5b). The slope is between 0.5 and 1, indicating that the electrochemical behaviors of epinephrine on Pd-PLA/GCE are the combination of diffusion and adsorption. The symmetry of the potential becomes worse with the scan rates ranging after 160 mV/s. Therefore, 160 mV/s was used as the scan rate.

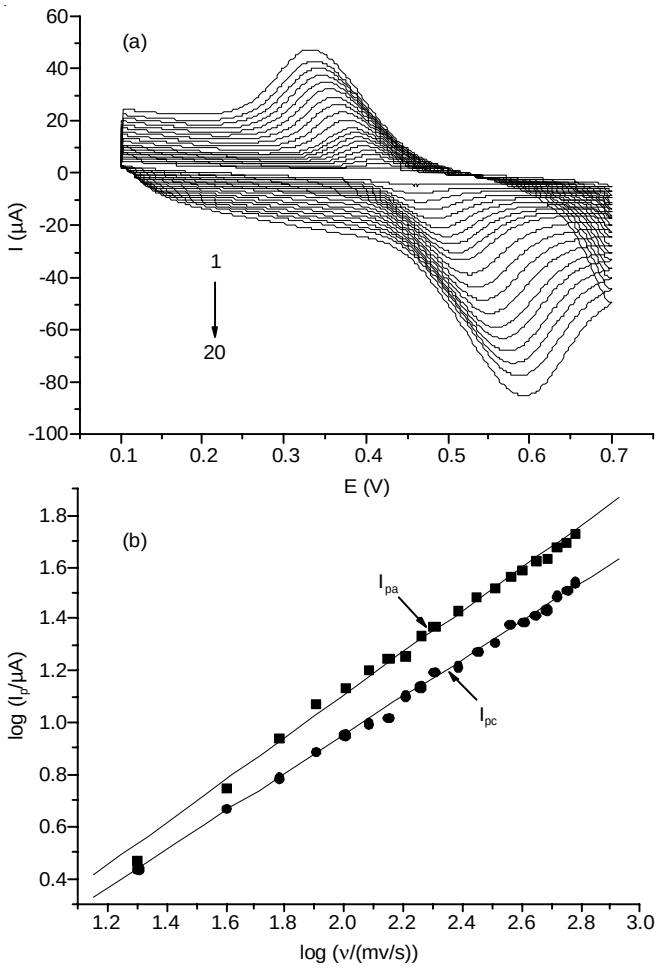

Fig. 5. Cyclic voltammograms of epinephrine at different scan rates (a) and the relationship curve between log I_p and log ν (b); scan rate from 1 to 20: 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 240, 280, 320, 360, 400, 440, 480, 520, 560 and 600 mV S^{-1}; epinephrine concentration: 2.50×10^{-5} mol/L

Fig. 6 shows the peak potentials E_{pa} and E_{pc} as a function of the potential sweep rate. The values of E_p were proportional to the logarithm of the scan rate over the range of 100 to 600 mV/s. The regression equations were acquired as $E_{pa} = 0.1930 + 0.1416 \log \nu$, $R = 0.9927$ and $E_{pc} = 0.5882 - 0.09007 \log \nu$, $R = 0.9906$.

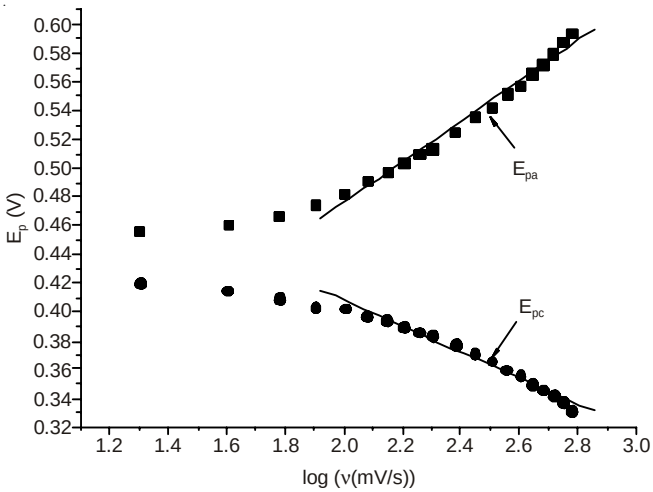

Fig. 6. Relationship curve between E_p and log ν of epinephrine

Based on the eqns. 2 and 3[35], where α is the transfer coefficient, n_α is the number of electrons transferred, ν is the scan rate, α can be calculated from the slope of the equation and was found to be 0.61 (close to the theoretical value of 0.5), indicating the electrode process is quasi-reversible in the range of 100 to 600 mV/s. When $\upsilon = 400$ mV/s, $\Delta E_p = 202$ mV and $n\Delta E_p > 200$ mV, the standard rate constant k_s could be calculated to be 1.04/s by using eqn. (4)[35]. This result is much bigger than that reported in the literature[36].

$$E_{pa} = A + \left(2.303RT/\left(1-\alpha\right)n_\alpha F\right)\log \upsilon \quad (2)$$

$$E_{pc} = B - \left(2.303RT/\alpha n_\alpha F\right)\log \upsilon \quad (3)$$

$$\log k_s = \alpha \log\left(1-\alpha\right) + \left(1-\alpha\right)\log \alpha - \log \frac{RT}{n_\alpha F \upsilon} - \frac{\alpha\left(1-\alpha\right)n_\alpha F \Delta E}{2.3RT} \quad (4)$$

The diffusion coefficient D of epinephrine was determined by chronocoulometric method[37]. According to the formula given by Anson:

$$I(t) = I_d(t) = \frac{nFAD^{1/2}C_0}{(\pi t)^{1/2}} \quad (5)$$

where I_d is the limiting diffusion current (A), A is the surface area of the studied electrode (cm^2), C_0 is the bulk concentration of epinephrine (mol/cm^3), n is the electron transfer number, F is the faraday coefficient (C/mol), t is time (s). At a diffusion limited rate condition, a plot of I_d *vs.* t will be linear and the value of D can be calculated from the slope of this line. The obtained experimental plots for different modified electrodes were shown in Fig. 7b and the corresponding D value was listed in Table-1. The results show that the diffusion coefficient D increases with the modified electrodes.

Calibration plot: Epinephrine was determined at the modified electrode under the optimum conditions by both cyclic voltammetry and differential pulse voltammetry, because differential pulse voltammetry has higher current sensitivity and better resolution than cyclic voltammetry. The results were shown in Fig. 8. Fig. 8 showed that the peak currents increased with the increasing concentration of epinephrine. The peak current and the concentration of epinephrine show good linear

TABLE-1
DIFFUSION COEFFICIENT OF EPINEPHRINE (EP) AT DIFFERENT MODIFIED ELECTRODES

Analyte	Electrode	Regression equation	Correlation coefficient	Diffusion coefficient (cm^2/s)
Epinephrine	Pd-PLTE/GCE	$I = -1.131 \times 10^{-4} + 6.252 \times 10^{-5} t^{-1/2}$	0.9978	2.564×10^{-7}
	PLA/GCE	$I = -2.111 \times 10^{-4} + 6.188 \times 10^{-5} t^{-1/2}$	0.9990	2.512×10^{-7}
	Pd/GCE	$I = -1.939 \times 10^{-4} + 5.354 \times 10^{-5} t^{-1/2}$	0.9982	1.881×10^{-7}
	GCE	$I = -1.752 \times 10^{-4} + 4.578 \times 10^{-5} t^{-1/2}$	0.9986	1.375×10^{-7}

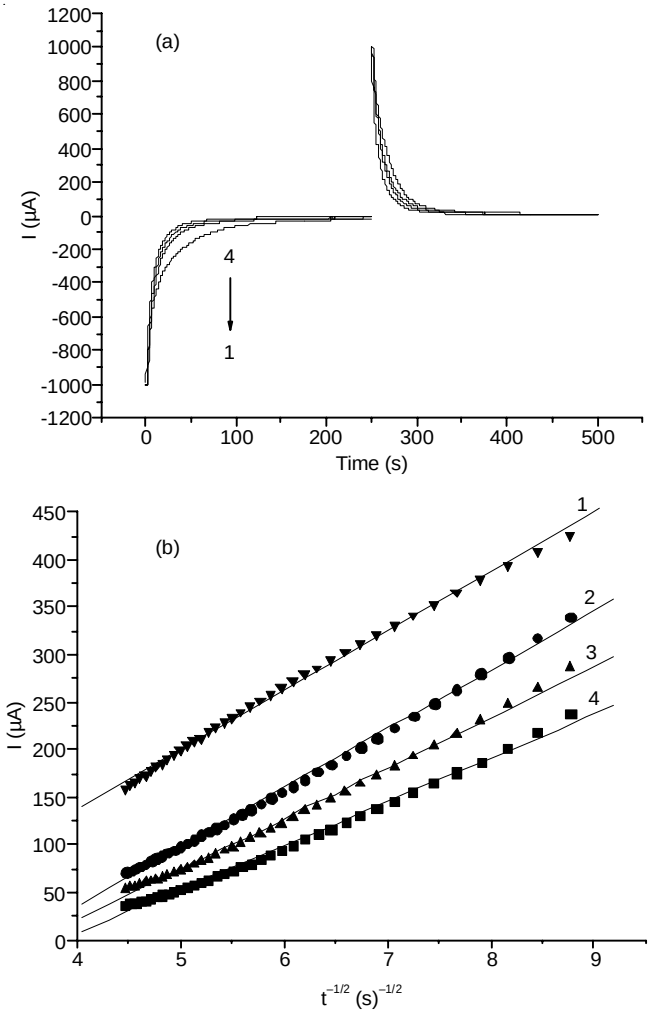

Fig. 7. Chronoamperograms of epinephrine at the different modified glassy carbon electrode (a) and the relationship curve between I and $t^{-1/2}$ (b); Pd-PLA/GCE (1); PLA/GCE (2); Pd/GCE (3) and GCE (4); PBS: pH 3; epinephrine concentration: 2.50×10^{-5} mol/L

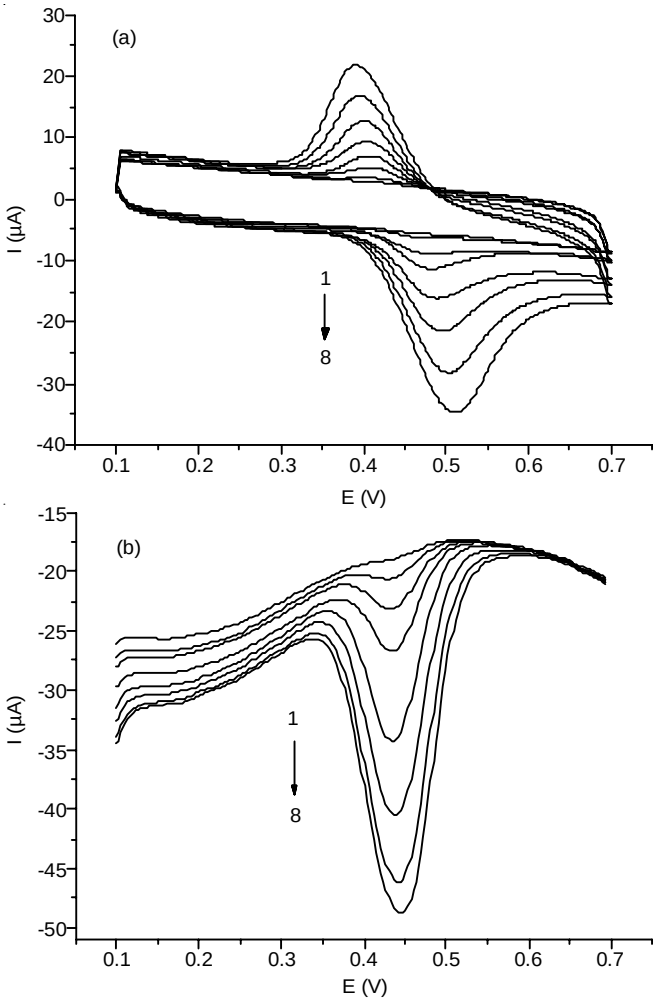

Fig. 8. Cyclic voltammetrys curve of epinephrine with different concentrations at Pd-PLA/GCE (a) and differential pulse voltammetrys curve of epinephrine with different concentrations at Pd-PLA/GCE (b); epinephrine concentrations (from 1 to 8): 5×10^{-7}, 1×10^{-6}, 5×10^{-6}, 1×10^{-5}, 3×10^{-5}, 5×10^{-5}, 8×10^{-5}, 1×10^{-4} mol/L

relation in a range of $5.00 \times 10^{-7} \sim 1.00 \times 10^{-5}$ and $1.00 \times 10^{-5} \sim 1.00 \times 10^{-4}$ mol/L with detection limit of 1.0×10^{-7} and 8.0×10^{-8} mol/L. The linear regression equations, the correlation coefficients and the detection limit are listed in Table-2.

Reproducibility and stability of the modified electrode: Reproducibility is one of the most important properties of the modified electrode. To ascertain the reproducibility of the modified electrode, the oxidation peak currents of two parallel

TABLE-2
LINEAR EQUATIONS, REGRESSION EQUATIONS CORRELATION COEFFICIENTS AND DETECTION LIMITS

Method	Linear ranger (mol/L)	Regression equation (mol/L)	Correlation coefficient (R)	Detection limit (mol/L)
Cyclic voltammetry	5.00×10^{-7}-1.00×10^{-5}	$I_{pa} = -0.8427 - 6.011 \times 10^5 C$	0.9915	1.0×10^{-7}
		$I_{pc} = 0.6901 + 5.859 \times 10^5 C$	0.9941	
	1.00×10^{-5}-1.00×10^{-4}	$I_{pa} = -3.402 - 2.538 \times 10^5 C$	0.9962	
		$I_{pc} = 3.644 + 1.585 \times 10^5 C$	0.9859	
Differential pulse voltammetry	5.00×10^{-7}-1.00×10^{-5}	$I_{pa} = -0.1355 - 6.920 \times 10^5 C$	0.9935	8.0×10^{-8}
	1.00×10^{-5}-1.00×10^{-4}	$I_{pa} = -6.004 - 2.257 \times 10^5 C$	0.9929	

experiments, which were repeated 40 times and 50 times, respectively, in 2.50×10^{-5} mol/L epinephrine solution at the Pd-PLA/GCE were investigated. The relative standard deviations were 3.4 and 1.3 % for the determination of epinephrine solution, indicating that the modified electrode has good reproducibility. When the modified electrode was stored at room temperature for 15 days or determined successively for 50 times, the same shape of the voltammetric curves of epinephrine could be maintained, indicating that the modified electrode is stable and does not suffer from surface fouling by oxidation products during the voltammetric measurements.

Interference study: Cations, anions and organics are widely coexisted with epinephrine in real biological matrices and therefore, avoiding those interferences is an important target for epinephrine analytical methods. The influence of those various foreign species on the determination of 2.50×10^{-5} mol/L epinephrine solution was investigated. The tolerance limit was taken as the maximum concentration of the foreign substances which caused a relative error of approximately ± 5 % in the determination. According to the results, the following compounds has no interference (mg/10 mL): glucose, L-proline, L-valine, L-threonine, L-aspartic acid, L-glutamate, vitamin C, uric acid, Na^+, K^+, HCO_3^-, CO_3^{2-}, Zn^{2+}, Ca^{2+}, Mg^{2+}, Mn^{2+}, Zr^{4+}, NH_4^+, Cl^-, SO_4^{2-}, Ba^{2+}, Ag^+, Sr^{2+}, Co^{2+}, Pb^{2+}, NO_3^- (≤ 1), Cu^{2+} (0.8 for oxidation peak, 0.5 for reduction peak), L-cysteine (0.4 for oxidation peak and 0.5 for reduction peak); I^- (0.5); F^- (0.5 for oxidation peak and no interference in reduction peak), dopamine (0.2), Bi^{3+}, Fe^{2+}, Cr^{3+} (0.1). Therefore, it is possible to determine epinephrine in the sample at the Pd-PLA/GCE modified electrode.

Sample analysis: The developed method was applied to the determination of epinephrine in two different batch numbers epinephrine hydrochloride injection. The determination results are listed in Table-3. The recoveries were 98.7 and 100.7 %, respectively. The recovery and relative standard deviations were acceptable, showing that the proposed method could be efficiently used for the determination of epinephrine in injections.

TABLE-3
ANALYTICAL RESULTS OF
EPINEPHRINE (EP) INJECTION SAMPLES (n = 6)

Sample	Recommended (μg/mL)	Found (μg/mL)	RSD (%)	Added (m/μg)	Recovery (%)
EP injection I	1	0.983	1.9	10	100.7
EP injection II	1	1.021	2.5	10	98.7

Conclusion

As a summary of this work, a sensitive electrochemical sensor has been developed using electropolymerization of palladium doped poly-L-arginine (Pd-PLA) at a glassy carbon electrode electrode under the optimum conditions. The detection limits were obtained from cyclic voltammetry and differential pulse voltammetry investigations and showed the lowest concentration of epinephrine that could be measured. The advantages of this electrode include a wide liner range, high sensitivity, selectivity and good reproducibility of the voltammetric responses, which makes the proposed modified electrode very useful to the detection of epinephrine in injection solution with satisfactory results. It is hope that the modified electrode will be a good application for further sensor development.

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