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ORIGINAL PAPER

A novel and simple biosensor based on poly(indoleacetic acid) film and its application for simultaneous electrochemical determination of dopamine and epinephrine in the presence of ascorbic acid

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Abstract A novel and simple biosensor based on poly (indoleacetic acid) film-modified electrode (PIAA/CPE) was fabricated by electrochemical polymerization of indoleacetic acid on a carbon paste electrode (CPE) through cyclic voltammetry. The resulting electrode was characterized by scanning electron microscopy, and the electrochemical behaviors of dopamine (DA) and epinephrine (EP) at the electrode were studied. It was illustrated that PIAA/CPE had excellent electrochemical catalytic activities toward DA and EP. The anodic peak currents (I_{pa}) were dramatically enhanced by about seven-fold for DA and ten times for EP at PIAA/CPE. Thus, the determinations of DA and EP were carried out using PIAA/CPE successfully. The linear responses were obtained in the range of 3.0×10^{-7}~7.0×10^{-4} and 1.0×10^{-6} ~8.0×10^{-4} mol L^{-1} with the detection limits (3σ) of 1×10^{-7} and 4×10^{-7} mol L^{-1} corresponding with DA and EP, respectively. Moreover, the cathodic peaks of DA and EP were well-separated with a potential difference about 325 mV in pH 5.3 phosphate-buffered saline, so simultaneous determination of DA and EP was carried out in this paper. Additionally, the interference studies showed that the PIAA/CPE exhibited excellent selectivity in the presence of ascorbic acid (AA). With good selectivity and sensitivity, the present method has been successfully applied to the determination of DA and EP in pharmaceutical samples.

Keywords Dopamine · Epinephrine · Indoleacetic acid · Chemically modified electrode · Simultaneous determination

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Introduction

Both DA and EP are neurotransmitters belonging to the catecholamine group. Their extremely abnormal levels in biological fluids may lead to several diseases such as Parkinsonism because they play very important roles in physiological and pharmacological functions [1]. However, DA and EP are structurally similar and usually coexist in real biological samples, which complicate their identification. Therefore, to develop sensitive and selective methods for their determination is highly desirable for analytical application and diagnostic research.

A lot of analytical methods can be used to distinguish DA and EP sensitively and selectively, such as fluorescence [2, 3], high-performance liquid chromatography [4–6], spectrophotometry [7], and electrochemistry [8–12]. Among the various methods, voltammetric sensors, especially chemically modified electrodes (CMEs), are becoming more and

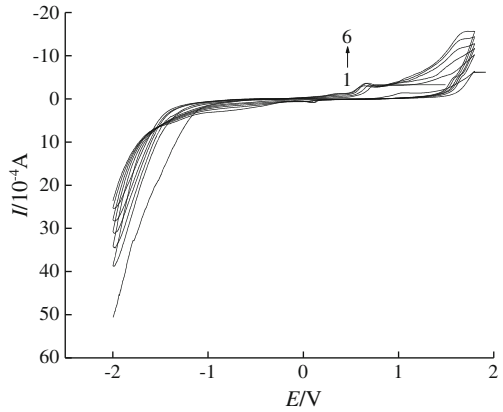

Fig. 1 CVs (six cycles) for eletrochemically polymerization of indole-acetic acid (0.02 mol L^{-1}) on CPE; scan rate 100 mV s^{-1}, pH 4.5 PBS

more popular in scientists because both DA and EP are electroactive. Holding many advantages over conventional CMEs, such as easier fabrication process, more excellent electrochemical catalytic ability, better physical stability, polymer film-modified electrodes (PME) are considered to be favorable alternatives. There have been many reports about determination of DA and EP using PME [13–17]. Wang and Chen [13] modified glassy carbon electrode with poly(taurine), and simultaneous determination of DA and EP was carried out. Zhou et al. [14] modified CPE with poly (isonicotinic acid), thus, DA and EP were successfully distinguished in the presence of ascorbic acid (AA). Zhang et al. [15] casted poly(styrene sulfonic acid) sodium salt/single-wall carbon nanotube on the surface of glassy carbon electrode, and the electrochemical behavior of DA was investigated. Wang et al. [16] combined poly(3-methylthiophene) with Nafion/single-walled carbon nanotubes for highly selective and sensitive determination of DA. Maciejewskaa et al. [17] reported a simple tyrosinase-modified electrode designed through the covalent bonding of the enzyme with poly(indole-5-carboxylic acid) conducting polymer, and the electrode was applied to the amperometric detection of DA. It is well-known that DA and EP exist as cations in biological environment (pH 7.4), therefore, the negatively charged polymer film is considered to be necessary to enhance the enrichment capabilities of the electrode.

In this work, we prepared a novel poly(isonicotinic acid) film-modified electrode, with which the electrochemical behaviors of DA and EP were carefully investigated, including the coexisted AA. Satisfying results that the modified electrode had different electrochemical response toward these species were obtained, and an effective analytical method for simultaneously detect DA and EP in the presence of AA was set up for routine analysis.

Experimental

Apparatus

All electrochemical measurements were performed with a CHI-832 electrochemical workstation (CHI Instruments,

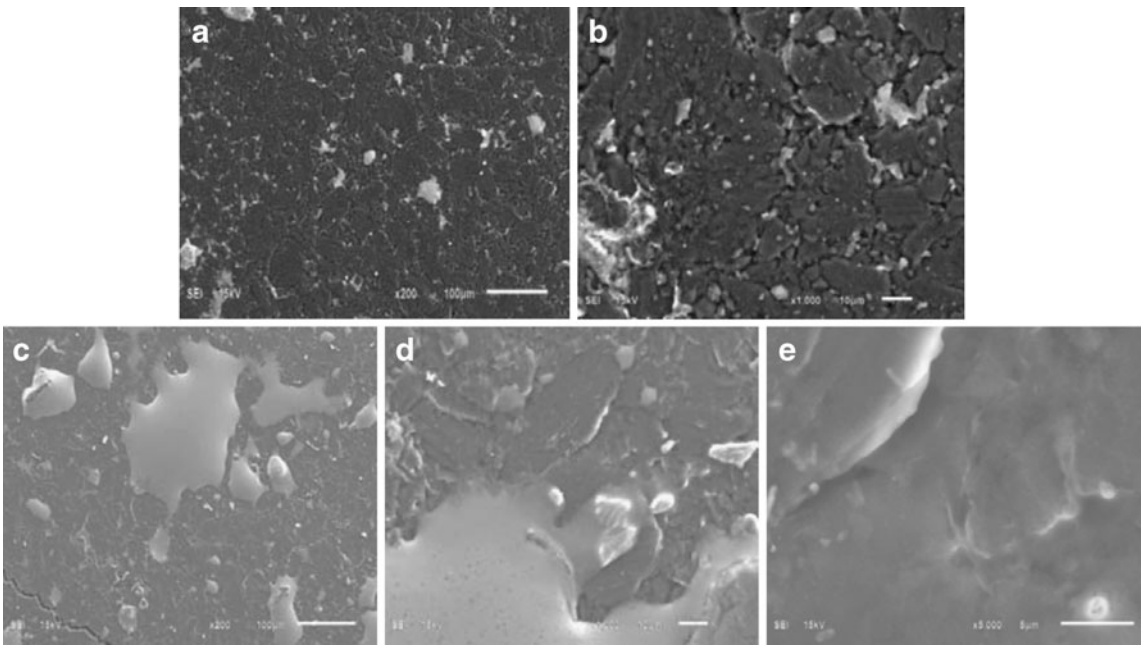

Fig. 2 SEM images of bare CPE (**a** ×200, **b** ×1,000) and PIAA/CPE (**c** ×200, **d** ×1,000, **e** ×5,000)

Chenhua Corp, China). A conventional three electrode system was used for all electrochemical experiments, which consisted of a platinum wire as auxiliary electrode, a saturated calomel electrode (SCE) as reference electrode, and a bare or modified CPE as working electrode. All potentials were referenced to SCE, and all the values of pH were adjusted by a Model SA 720 pH meter (Orion Research, USA). The morphologies of the resultant electrodes were observed with scanning electron microscopy (SEM) (model: JEOL JSM-2000) operated at an accelerating voltage of 15 kV.

Chemicals and solutions

DA and EP hydrochloride injection were obtained from Sigma (USA). Indoleacetic acid was purchased from Shanghai Chemical Regent Company (China). All the reagents used were of analytical reagent grade. Phosphate-buffered saline (PBS) was prepared with 0.1 mol L^{-1} Na_2HPO_4–KH_2PO_4, and 0.1 mol L^{-1} H_3PO_4 and 0.1 mol L^{-1} NaOH were used to adjust the value of pH when necessary. Additionally, 1.0 mol L^{-1} NaCl was used to balance the ionic strength, double-distilled water was used throughout the experiments, and all experiments were conducted at room temperature.

Preparation of the modified electrode

Firstly, CPE was prepared by mixing graphite powder and mineral oil at the ratio of 5: 0.7 (*w*/*w*) carefully, and then the paste was packed into a plastic tube (Ø=3.0 mm). The electric conduction was provided by a copper wire connected to the paste in the inner hole of the tube. Importantly, a well-prepared CPE must be polished successively with sulfate paper to obtain a mirror surface, rinsed with double-distilled water, and then treated in pH 7.0 PBS by repetitive scanning in the potential range of −0.4 and +0.8 V at a scan rate of 100 mV s^{-1} until a stable background was obtained before modification.

Cyclic voltammetry (CV) was used to form polymerization film. The polymeric film was deposited on the CPE by cyclic sweeping from −2.0 to +2.0 V at 100 mV s^{-1} for six cycles in pH 4.5 PBS containing 0.02 mol L^{-1} indoleacetic acid. Prior to use, the modified electrode was rinsed with double-distilled water and then treated in pH 7.0 PBS by repetitive scanning in the potential range of −0.4 and +0.8 V at a scan rate of 100 mV s^{-1} to obtain a stable background.

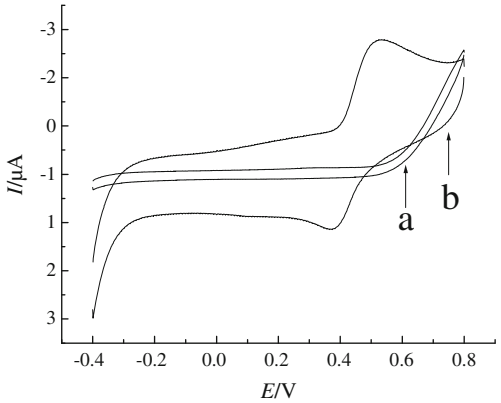

Fig. 4 CVs of EP at bare CPE (*curve a*) and PIAA/CPE (*curve b*), pH 3.0 PBS, scan rate 100 mV s^{-1}, C_{EP} 4.0×10^{-5} mol L^{-1}

Results and discussions

Eletrochemically polymerization of indoleacetic acid on the CPE surface

Figure 1 shows the CVs of electrochemical polymerization of indoleacetic acid. The voltage range plays a decisive role

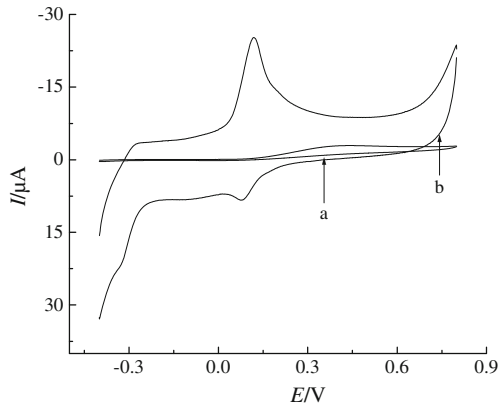

Fig. 3 CVs of DA at bare CPE (*curve a*) and PIAA/CPE (*curve b*), pH 7.4 PBS, scan rate 100 mV s^{-1}, C_{DA} 4.0×10^{-5} mol L^{-1}

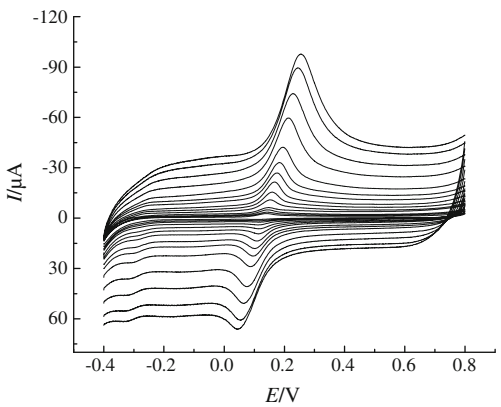

Fig. 5 CVs of DA with different scan rates at PIAA/CPE, scan rates 20~5,000 mV s^{-1}, C_{DA} 1.0×10^{-5} mol L^{-1}, pH 7.4 PBS

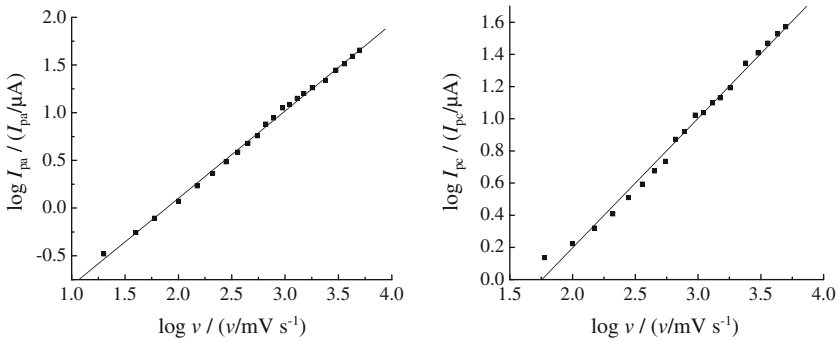

Fig. 6 Effects of the scan rate on peak current of DA at PIAA/CPE

in the polymeric process. It has been reported that there was an optimum voltage range for the anodic peak potentials (E_{pa}) which led to the polymerization of indole monomers [18]. Our experimental results showed that a potential window from −2.0 to 2.0 V did generate the polymerization of indoleacetic acid. Such a behavior could be explained according to the stability or reactivity of the radical cation intermediate in the region of the electrode surface [18]. Furthermore, the other polymeric conditions were optimized by varying scan rates, pH and the contents of indoleacetic acid, and then applying the obtained modified electrode to catalyze DA. Either the higher scan rate or acidity or content of indoleacetic acid would lead to the crack of polymer and decrease the catalytic power. The dense and compact film with excellent electrocatalysis toward DA was obtained when deposited in the range of −2.0~2.0 V at 100 mV s^{-1} for six cycles in pH 4.5 PBS containing 0.02 mol L^{-1} indoleacetic acid. During the polymerization process, an obvious anodic peak was observed at about 0.70 V, which may be attributed to the formation of a radical cation and dication forms of indoleacetic acid [19], and no obvious cathodic peak appeared. The peak currents increased continuously with incessant scans and trended to be stable after six cycles. This observation indicated that poly(indoleacetic acid) film was successfully deposited on the surface of CPE. After polymerization, adherent black polymeric film can be observed on the CPE surface.

In order to further confirm the formation of poly(indoleacetic acid) film on the surface of CPE, the SEM technique was employed. Figure 2 shows the surface morphologies of different electrodes. A much rougher surface was observed for irregularly shaped flakes of graphite on the CPE surface (images a and b). However, a layer of smoother and compact thin film was obtained on the surface of PIAA/CPE (images c, d, and e). The obvious differences on the surface morphologies confirmed that the CPE was coated by poly(indoleacetic acid) film.

Electrochemical behavior of DA and EP at the PIAA/CPE

Figure 3 shows the typical CVs of DA at bare CPE and PIAA/CPE. As can be seen, DA appears a broad oxidation peak and no obvious reduction peak at bare CPE (curve a), while a couple of well-defined redox pair is obtained at PIAA/CPE, accompanied with a seven-fold enhanced I_{pa}. The E_{pa} and cathodic peak potential (E_{pc}) were at 119 and 76 mV, respectively, with the peak potentials separation ($\Delta E_p = E_{pa} - E_{pc}$) of 43 mV. Greatly enhanced peak current and smaller peak separation strongly indicated excellent catalytic ability of poly(indoleacetic acid) film and the faster electron transfer of DA. It is well-known that DA exists as cations in biological environment (pH 7.4) with a positively charged amino group (pK_a 8.9) [1], while indoleacetic acid (pK_a 4.8) was nonprotonated in pH 7.4 PBS. Therefore, the possible reason for the excellent catalytic ability and the accelerated electron transfer could be explained as the electrostatic interaction between DA cations and the negatively charged poly(indoleacetic acid) film, which would lead to a

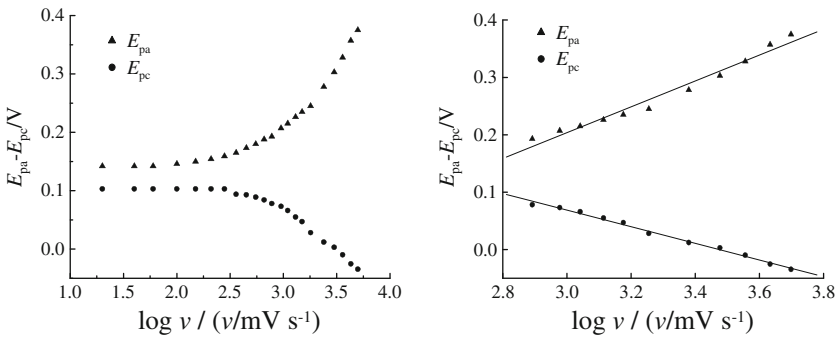

Fig. 7 Effects of the scan rate on peak potentials of DA at PIAA/CPE

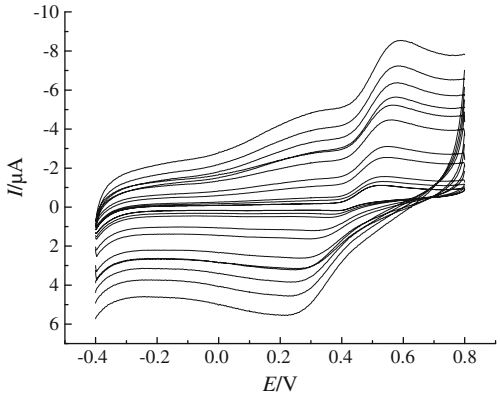

Fig. 8 CVs of EP with different scan rates at PIAA/CPE, scan rates 20~5,000 mV s^{-1}, C_{EP} 2.0×10^{-5} mol L^{-1}, pH 3.0 PBS

higher concentration of DA around the surface of the electrode. Figure 4 shows that EP exhibits a poor electrochemical response at bare CPE, whereas at PIAA/CPE, a couple of definite oxidation and reduction peak is obtained at 350 and 550 mV, respectively, which is largely contributed to the catalytic activity of poly(indoleacetic acid) film.

Effects of scan rates on the electrochemical response of DA and EP

The effects of the scan rate on the electrochemical behavior of DA were investigated at the PIAA/CPE in pH 7.4 PBS, as is shown in Fig. 5. I_{pa} and cathodic peak current (I_{pc}) increased with the increased scan rate. The logarithm of the peak current of DA was leaner with the logarithm of scan rate within the range of 20~5,000 mV s^{-1} (Fig. 6). The linear regression equations can be expressed as log I_{pa} (I_{pa}/μA)=0.8055 log v (v/mV s^{-1})−1.414 (R=0.9957) and log I_{pc} (I_{pc}/μA)=0.9148 log v (v/mV s^{-1})−1.727 (R=0.9994), respectively. It can be inferred from the slopes of the equations that the contribution of adsorption plays a more important role in the oxidation and reduction processes both [20].

Figure 7 presents us the changes of peak potentials as the scan rates vary. As can be seen, E_{pa} and E_{pc} of DA almost kept constant in the range of 20~780 mV s^{-1}, while shifted linearly toward positive and negative values when the scan rate increased within 780~5,000 mV s^{-1}. The linear regression equations were E_{pa} (V)=0.2254 log v (v/mV s^{-1})−0.4725 (R=0.9861) and E_{pc} (V)=−0.1448 log v (v/mV s^{-1})+0.5033 (R=0.9963). Hence, according to the Laviron theories [20], the transfer coefficient α_a and α_c could be calculated from the slopes of the equations and were found to be 0.8688 and 0.2043. While v=780 mV s^{-1}, ΔE_p=115 mV, and then $n\Delta E_p$>200 mV. The standard rate constant (K_s) for oxidation process could be calculated to be 3.68 s^{-1} according to Eq. 1 [20], indicating that poly(indoleacetic acid) has obvious catalysis for the redox reaction of DA at the electrode.

$$\log K_s = \alpha_a \log(1-\alpha_a) + (1-\alpha_a)\log\alpha_a - \log\frac{RT}{nFv} - \frac{\alpha_a(1-\alpha_a)nF\,\Delta E}{2.3RT} \quad (1)$$

When it came to term with EP, it was demonstrated that both of anodic and cathodic processes were largely controlled by diffusion within 150~3,000 mV s^{-1} with linear regression equations as following: log I_{pa} (I_{pa}/μA)=0.5311 log v (v/mV s^{-1})−1.088 (R=0.9989) and log I_{pc} (I_{pc}/μA)=0.1138 log v (v/mV s^{-1})−0.4515 (R=0.9936), respectively (Figs. 8 and 9).

Effects of pH on the electrochemical response of DA and EP

Since protons took part in the electrode reaction processes of DA and EP, the effects of pH were studied. As is shown in Fig. 10, the peak currents of DA increase with the increasing pH from 3.0 to 7.4 so that the maximum peak current is obtained at pH 7.4, and then it decreases when pH increases from 7.4 to 9.2. E_{pa} and E_{pc} for DA linearly shifted to negative potential with regression equations of E_{pa} (V)=0.5791−0.0623 pH (R=0.9942) and E_{pc} (V)=0.5376−0.0634 pH (R=0.9931), respectively. The slopes of 0.0623 and 0.0634 V pH^{-1} (close to the theoretical value of 0.0585 V pH^{-1}) showed that the uptake of electrons was accompanied by an equal number of protons. Figure 11

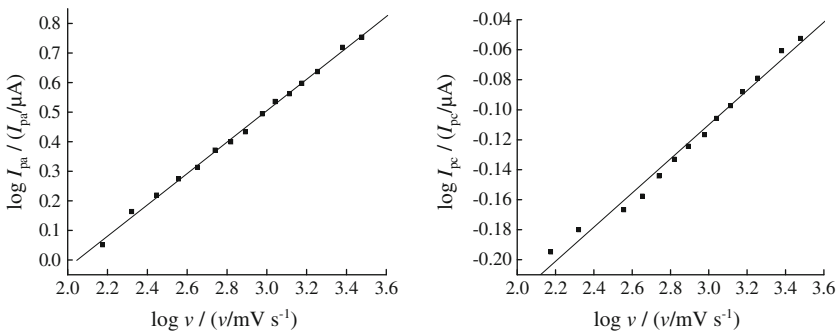

Fig. 9 Effects of the scan rate on peak current of EP at PIAA/CPE

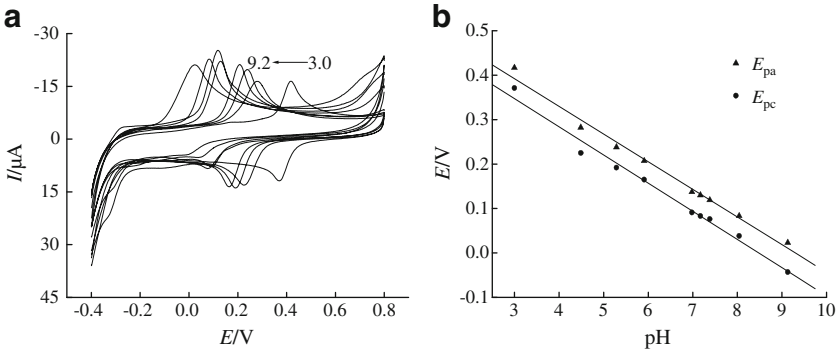

Fig. 10 CVs of DA in different pH solutions (**a**) and effects of pH on peak potentials (**b**) at PIAA/CPE, C_{DA} 3.0×10^{-5} mol L^{-1}, scan rate 100 mV s^{-1}

shows that the peak currents of EP increase with the increasing pH from 3.0 to 8.0 so that the maximum peak current is obtained at pH 8.0, and then it decreases when pH further increases from 8.0 to 9.2. E_{pa} and E_{pc} for EP linearly shifted to negative potential with regression equations of E_{pa} (V)= 0.6936−0.6762 pH (R=0.9924) and E_{pc} (V)=0.1329− 0.0557 pH (R=0.9979) within the range of pH 3.0~8.0, indicating that the proportion of the electrons and protons involved in the redox process of EP were 1:1.

Determination of DA and EP

According to the experimental results discussed above, PIAA/CPE showed good electrocatalytic activity for the redox reactions of DA and EP in a wide pH range, so the determinations of DA and EP were successfully carried out in pH 7.4 PBS and pH 5.3 PBS, respectively. The leaner responses were obtained in the range of 3.0×10^{-7}~7.0×10^{-4} mol L^{-1} for DA and 1.0×10^{-6}~8.0×10^{-4} mol $L^{-1}$for EP with the regression equations: I_{pa} (μA)=0.09696−0.05788 C_{DA} (μmol L^{-1}) (R=0.9950) and I_{pa} (μA)=−1.276−0.4064 C_{EP} (μmol L^{-1}) (R=0.9962), respectively. The detection limits (3σ) for DA and EP were 1×10^{-7} and 4×10^{-7} mol L^{-1}, respectively.

In pH 5.3 PBS, two well-separated reduction peaks are observed at +0.168 V and −0.157 V corresponding with DA and EP, as is shown in Figure 12. The reduction peak potential difference of DA and EP was 325 mV, so the simultaneous determination of DA and EP was carried out successfully in their mixture. Figure 13a illustrated the CV responses of DA and EP at PIAA/CPE while the concentrations of DA and EP increased synchronously. It can be seen from Fig. 13b that the I_{pc} of DA and EP increased linearly with their increasing concentrations in the range of 2.0×10^{-5}~7.0×10^{-4} and 1.0×10^{-5}~5.0×10^{-4} mol L^{-1}, respectively. The linear regression equations were I_{pc} (μA)=0.006840 C_{DA} (μmol L^{-1})+0.7966 (R=0.9981) and I_{pc} (μA)=0.00396 C_{EP} (μmol L^{-1})+0.3676 (R=0.9988) corresponding with DA and EP. The simultaneous determination limits (3σ) for DA and EP were 7×10^{-6} and 4×10^{-6} mol L^{-1}, respectively.

Interferences of other foreign compounds

Since AA, DA, and EP are structurally similar and usually coexist in real biological samples, the interference of AA has been studied carefully. Figure 14 demonstrates that there is no reduction peak of AA obtained in pH 5.3 PBS when the concentration of AA is 50 times higher than DA and EP. The possible reason was that AA existed as anion (pK_a 4.2) in pH 5.3 PBS, and there must be a repulsion interaction between AA and the negatively charged polymer, so we can hardly observe any obvious electrochemical response of AA. Furthermore, the influences of various foreign species on the determination of 4.0×10^{-5} mol L^{-1} DA and 4.0×10^{-5} mol L^{-1}EP

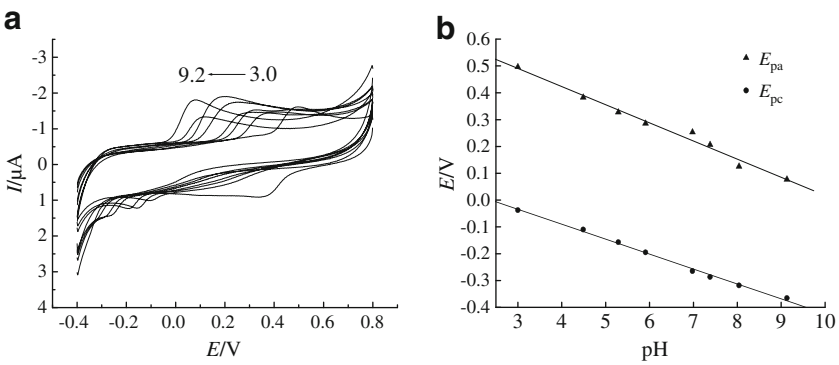

Fig. 11 CVs of EP in different pH solutions (**a**) and effects of pH on peak potentials (**b**) at PIAA/CPE, C_{EP} 2.0×10^{-5} mol L^{-1}, scan rate 100 mV s^{-1}

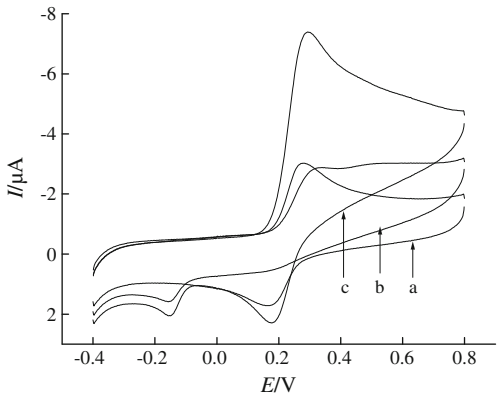

Fig. 12 CVs of DA, EP, and the mixture of DA and EP in pH 5.3 PBS, **a** 4.0×10^{-5} mol L^{-1} DA, **b** 4.0×10^{-5} mol L^{-1} EP, **c** 4.0×10^{-5} mol L^{-1} DA and 4.0×10^{-5} mol L^{-1} EP, scan rate 100 mV s^{-1}

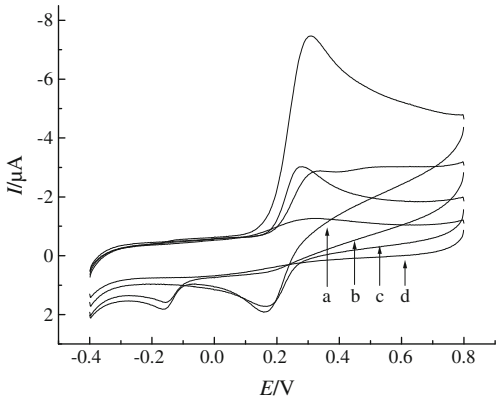

Fig. 14 CVs of different analytes. **a** 2.0×10^{-4} mol L^{-1} AA, **b** 4.0×10^{-5} mol L^{-1} EP, **c** 4.0×10^{-5} mol L^{-1} DA, **d** 2.0×10^{-4} mol L^{-1} AA+ 4.0×10^{-5} mol L^{-1} EP+4.0×10^{-5} mol L^{-1} DA, scan rate 100 mV s^{-1}

were investigated. An approximately ±5% relative error caused by the foreign substances was taken as the tolerance limit in the determination. The results revealed that glucose, citric acid, tartaric acid (>100-fold) and K^+, Na^+, Ca^{2+}, Mg^{2+}, Zn^{2+}, Fe^{3+}, Cr^{2+}, SO_4^{2-}, NO^{3-}, and Cl^- (>100-fold) had no interferences on the detection of DA and EP.

Reproducibility and stability

Eight repeated measurements of 4×10^{-5} mol L^{-1} DA and 4×10^{-5} mol L^{-1} EP in the presence of 2×10^{-3} mol L^{-1} AA produced a relative standard deviation (RSD) of 3.36%. For four electrodes prepared in the same way, an acceptable reproducibility with RSD of 4.28% was obtained for the determination of 4×10^{-5} mol L^{-1} DA and 4×10^{-5} mol L^{-1} EP, indicating a good reproducibility of the fabrication method. Also, there were no obvious changes in the response of the PIAA/CPE electrode after its storage in the air at room temperature for 2 weeks, which displayed a good stability.

Application to samples

The developed method was applied to determine DA and EP in their mixed pharmaceutical samples by the calibration curve method. Specified contents of DA and EP are 10.00 and 1.00 mg mL^{-1}, respectively. The proposed CV method was used to detect DA and EP simultaneously in their mixture. The average determination results were 9.78 and 0.966 mg mL^{-1} corresponding with DA and EP, with relative errors of 2.2% and 3.6% when compared with the injection specifications (10.00 and 1.00 mg mL^{-1}), indicating that the determination results were quite correspond with the values given by injection specifications. The analytical application results implied favorable features to apply the PIAA/CPE in the direct determination of DA and EP in real samples.

Conclusions

In conclusion, the simple and efficient biosensor based on PIAA/CPE has excellent electrochemical catalytic activity toward DA and EP. The anodic peak currents for DA and EP were dramatically enhanced at PIAA/CPE. So, it can be used to detect DA and EP simultaneously in their mixed solution containing large excess of AA by CV technique. Many outstanding advantages, such as wide leaner ranges, low detection limits, excellent sensitivity, selectivity, and stability confirmed that the proposed method can be used to analyze real samples.

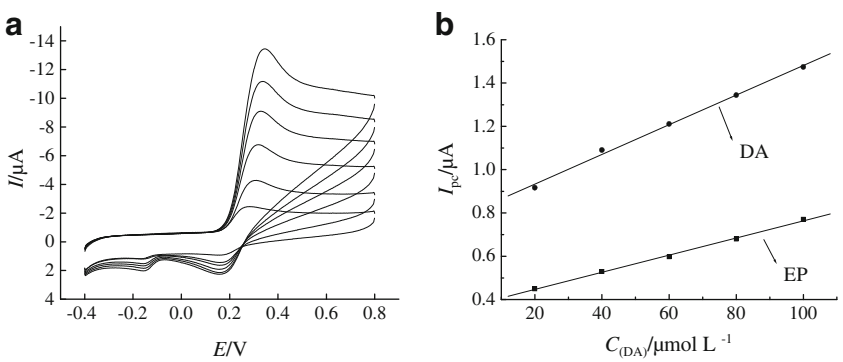

Fig. 13 CVs of the mixture containing DA and EP with different concentrations at PIAA/CPE (**a**), the relationship between cathodic peak currents and concentrations (**b**), scan rate 100 mV s^{-1}; pH 5.3 PBS

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