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Studies on the Electrochemical Behaviors of Epinephrine at a Poly(l-aspartic acid) Modified Glassy Carbon Electrode and Its Analytical Application

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The electrochemical behaviors of Epinephrine (EP) on a poly(l-aspartic acid) membrane are studied by cyclic voltammetry and electrochemical impedance spectroscopy (EIS). The poly(l-aspartic acid) membrane exhibited excellent electrocatalytic activities for the oxidation-reduction reactions of epinephrine, and in eliminating the interference of ascorbic acid (AA) and uric acid (UA). The anodic peak current of EP is linear with its concentration in the range of 1.0×10^{-7}~1.0×10^{-5} mol L^{-1} and 1.0×10^{-5}~1.0×10^{-4} mol L^{-1}. The detection limit is 4.6×10^{-8} mol L^{-1} (S/N=3). Compared with other electrochemical methods, this method has relative low detection limit and broad linear range. The practical application of the proposed method is demonstrated by determining the concentration of EP in pharmaceutical injections and the recovery tests. Some electrochemical parameters involved in the electrode reactions of EP, such as parameters of kinetic $n\alpha$, standard rate constant of the electrochemical reactions k_s and the number of H^+, are also calculated.

Keywords: Epinephrine, l-aspartic acid, ascorbic acid, uric acid, voltammetry

1. INTRODUCTION

Epinephrine (EP) is an important catecholamine neurotransmitter in mammalian central nervous systems[1, 2]. It plays important roles in the function of central nervous, renal, hormonal, and cardiovascular systems. The abnormal concentration level of EP in human body may be symptoms of several diseases,[3] such as schizophrenia and Parkinsonism. Therefore, quantitative determination of EP is significant for studying its physiological functions and aiding diagnosis of some diseases. For this purpose, many methods have been developed for determination of EP, such as high performance

liquid chromatography (HPLC),[4,5] capillary electrophoresis,[6,7] flow injection,[8,9] chemiluminescence ,[10,11 fluorescence,[12] spectrophotometry[13,14] and electrochemical methods.[15,16] Among of these methods, electrochemical methods appear to be the most suitable methods for quantitative determination of EP due to its electroactive nature.[17-19] However, the final oxidation products (epinephrinechrome) of EP would block the electrode surface when it is oxidized directly on a bare electrode.

Another serious problem is the interference of ascorbic acid (AA) and uric acid (UA) which exist in natural environments together with EP and oxidized in almost same potential region.[20, 21] Recently, chemically modified electrodes have been proved to be one of the powerful tools for solving above problems and many chemical materials, such as nanomaterials and polymer materials, are used.[22-27] Among those modified electrodes, amino acids modified electrodes received considerable attentions owing to the easily available materials, easiness of preparation and theirs good biocompatibility.[24-29] To best of our knowledge, using poly(l-aspartic acid) modified electrode for detection of EP and eliminating the interference of AA and UA have not been reported.

L-aspartic acid is one of amino acids which contains two carboxyl groups (-COOH) and one amino group (-NH2). It can be electrochemically polymerized on the GCE by cyclic voltammetry and form a membrane surface rich negative charged. The poly(l-aspartic acid) membrane could catalyze the oxidation of EP and eliminate the interference of AA and UA. The anodic peak currents of EP on the poly(l-aspartic acid) membrane are linear with its concentration, which can be used for determination of EP. Using this method for determination of the content of EP in pharmaceutical injections, the results are satisfactory.

2. EXPERIMENTAL

2.1 Materials and Apparatus

Epinephrine (EP) is purchased from Shanghai Jingchun Reagent Co., Ltd (Shanghai, China). L-aspartic acid (L-Asp) is purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). The EP injections are produced by Chongqing Dikang Yangtze River Pharmaceutical Co., Ltd. (Chongqing, China).

Ascorbic acid (AA) and uric acid (UA) are purchased from Tianjin Kemiou Chemical reagent Co., Ltd. (Tianjin, China) and Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), respectively. Phosphate-buffer saline (PBS, 0.1 mol L^{-1} KH_2PO_4 + 0.1 mol L^{-1} K_2HPO_4 + 0.1 mol L^{-1} KCl, pH 5.0) is used as supporting electrolytes.

The solution of L-Asp is prepared with PBS (pH 5.0) which had been deaerated by bubbling highly pure nitrogen. All chemicals are of analytical grade and used without further purification. Water used in experiments is redistilled water.

All electrochemical experiments are performed on a CHI 660 C electrochemical workstation (Shanghai CH Instruments Co., China), which is in connection with a GCE (Φ = 3.0 mm) or modified GCE working electrode, a platinum wire auxiliary electrode and a saturated calomel reference

electrode (SCE). The pH values of all solutions are measured by a model pHS-25 digital acidometer (Shanghai Leici Factory, China).

2.2 Preparation of the PL-Asp modified electrode

Prior to modification, the GCE is pretreated as follows: first, the GCE is polished to a mirror-like with wet $4^{\#}$ and $6^{\#}$ metallographic sandpapers and 0.05 μm α-Al_2O_3 slurry on a polishing cloth, then the electrode is sonicated for 5 min in nitric acid, ethanol and redistilled water in sequence, finally, the electrode is treated by cyclic scan in the potential range of -0.50~1.80 V in 0.5 mol L^{-1} H_2SO_4 solution until a stable signal is obtained, followed by rinsing with water and ethanol, and dried at room temperature. The pretreated electrode is immersed into the solution of PBS (pH 5.0) containing 2.0×10^{-3} mol L^{-1} L-Asp. Then the L-Asp is polymerized on the electrode surface by cyclic sweeping from -0.80 to +2.40 V for eight cycles at a scan rate of 100 mV s^{-1}. Taking out the electrode and rinsing with ethanol, water and 0.1 mol L^{-1} PBS (pH 5.0), to remove any physisorbed, unreacted materials from the electrode surface, the modified electrode is prepared and is denoted as PL-Asp/GCE.

2.3 Electrochemical detection

The electrochemical determination of EP is carried out in PBS (pH 4.0) with cyclic voltammetry in the range of 0.0-0.6 V at the scan rate of 100 mV s^{-1}. All solutions are deaerated by bubbling highly pure nitrogen prior to measurements and a nitrogen atmosphere is maintained during the whole course of determination.

Electrochemical impedance spectroscopy (EIS) measurements are performed in PBS（pH 4.0）solution containing 1.2×10^{-5} mol L^{-1} EP. The experiments conditions are as follows: the amplitude is 5 mA, and the range of frequency is from 0.1 Hz~100 kHz with open circuit potential.

3 RESULTS AND DISCUSSION

3.1 Electrochemical polymerization of L-Asp on GCE

In this work, the electrochemical polymerization of L-Asp on the GCE is performed with cyclic voltammetry by consecutive cyclic sweep from -0.8 to +2.4 V at scan rate of 100 mV s^{-1} in 0.1 mol L^{-1}PBS solution (pH 5.0) containing 2.0×10^{-3} mol L^{-1} l-aspartic acid. The results are shown in Figure 1. The L-Asp had one cathodic peak (a) and two anodic peaks (b and c). The cathodic peak currents (peak a) increased with the number of scan cycles and then maintained constant at 8 cycles. Taking out the electrode and ishing with distilled water, a gray color poly(L-Asp) film could be seen at the electrode surface obviously, indicating that an electroconductive polymer film is formed on the electrode surface.

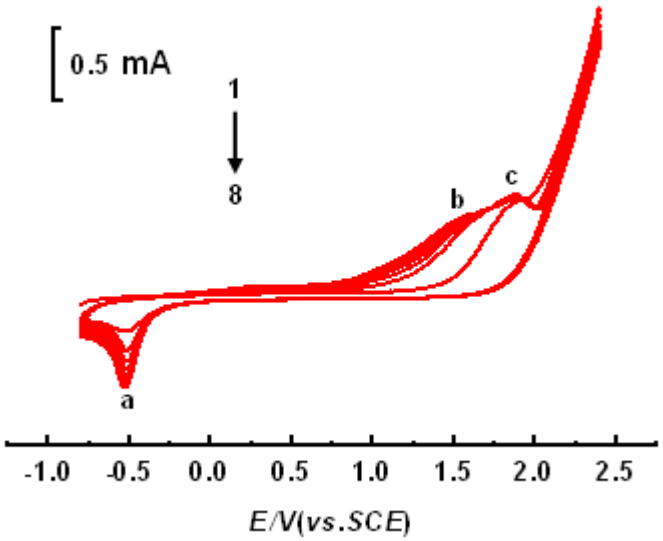

Figure 1. Cyclic voltammograms of 1.2×10^{-3} mol L^{-1} L-aspartic acid in polymerization process from 1 to 8 cycles on glassy carbon electrode in the potential range of -0.8~2.4 V at the scan rate of 100 mV s^{-1}.

The influence of the potential region on performance of the electropolymerization is investigated. The potential range from -0.8 to +2.4 V is chosen in this work. If the positive potential is lower than +1.8 V, no polymer film could be obtained. This could be attributed to the lack of the radical cation at the oxidative potential lower than +1.8 V. According to the literature of,[24-26] the L-Asp monomer is oxidized first at a higher positive potential to form α-amino free radical, which could be linked on an electrode surface, and then the poly(L-Asp) films are formed(Figure 2).

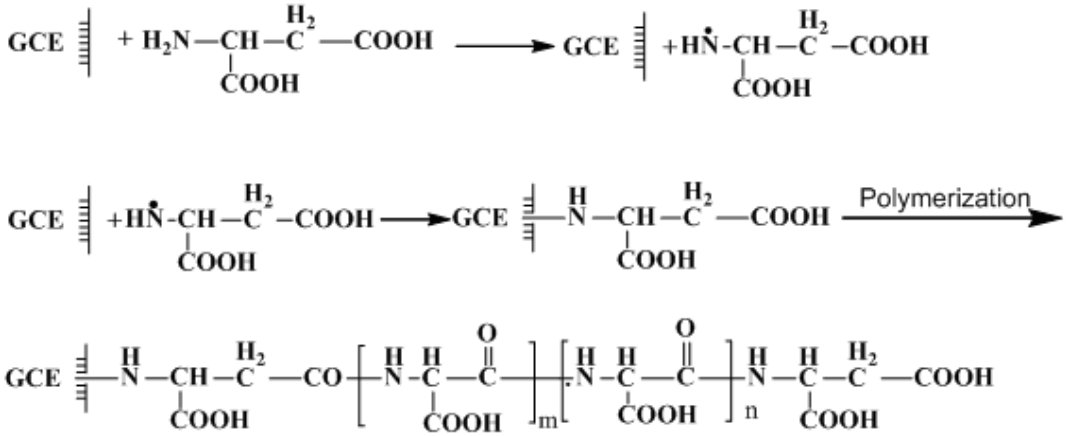

Figure 2. The proposed process of the electropolymerization of L-Aspartic acid.

3.2 Electrochemical response of EP on PL-Asp/GCE

The electrochemical responses of 1.2×10^{-5} mol L^{-1} EP are recorded by cyclic voltammetry in the potential range of 0.0-0.6 V at the scan rate of 100 mV s^{-1}. The results are shown in the Figure 3.

Curve a is the cyclic voltammogram of EP on the bare electrode, EP had no obvious peak currents. However, on the PL-Asp/GCE, EP had a couple of well-defined redox peak currents (curve b). Curve c is the cyclic voltammogram of PL-Asp/GCE in PBS (pH 4.0), no obvious peak currents are found. The results demonstrated that the PL-Asp membrane had good properties in electro-catalyzing the oxidation–reduction reactions of EP and facilitating electron transfer, which could be attributed to the membrane's three-dimensional structure and the rich carboxyl groups on the membrane surface. The carboxyl groups could combine with the hydroxyl groups in EP to form hydrogen bond. The formation of hydrogen bond weakened the bond energy of hydroxyl in EP and enriched amount of the EP on the electrode surface. Therefore, the rate of electron transfer is accelerated and the current is increased.

The cathodic peak and anodic peak of EP at the PL-Asp/GCE are at 0.310 V and 0.362 V, respectively. The formal potential (E^0) for EP on the PL-Asp/GCE is calculated to be 0.336 V and the i_{pa}/i_{pc} is approximate to 1, which showed that the electrochemical reactions of EP at the modified electrode are a quasi-reversible reaction process.

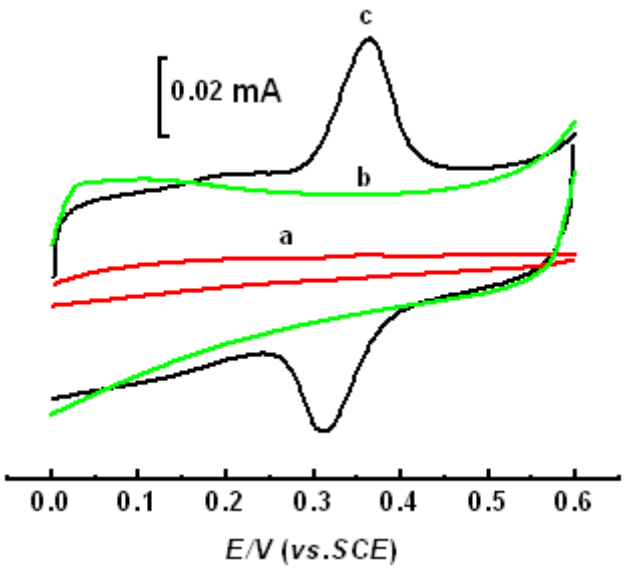

Figure 3. The cyclic voltammogram curves of the bare GCE (a) and the PL-Asp/GCE (c) in 1.2×10^{-5} mol L^{-1} EP solution, and the PL-Asp/GCE (b) in blank solution. The blank solution is PBS (pH = 4.0) solution without EP. The scan rate of 100 mV s^{-1}.

Electrochemical impedance spectroscopy (EIS) is an important means to study the kinetics of electrode reactions and electrode surface phenomena. The Nyquist diagrams of 1.2×10^{-5} mol L^{-1} EP on the bare GCE and PL-Asp/GCE are shown in the Figure 4. Curve a and c are the Nyquist diagrams of EP, which are recorded with electrochemical workstation on the bare GCE and PL-Asp/GCE, respectively. The Nyquist diagrams of b and d are obtained by the Equivalent software according to the equivalent circuit (Figure 4, Insert) on the bare GCE and PL-Asp/GCE, respectively. Curve a and b, c and d are almost completely overlap. Therefore, the equivalent circuit could reflect the factual characteristics of the frequency response of the reaction systems. The values of the charge transfer resistance (R_{ct}) are obtained on the bare electrode (6823 Ω) and PL-Asp/GCE (132 Ω) according to the

equivalent circuit. The results indicated that the PL-Asp membrane had unique properties in facilitating electron transfer.

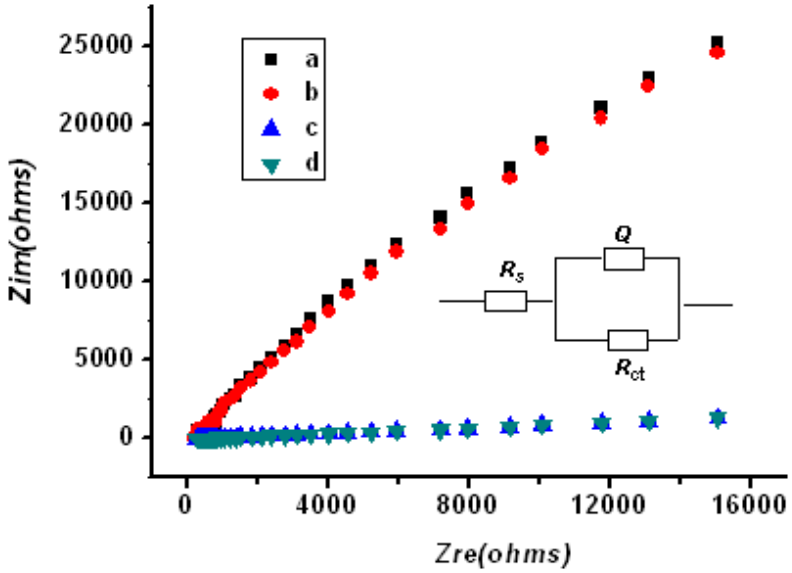

Figure 4. Nyquist diagrams of 1.2×10^{-5} mol L^{-1} EP on the bare GCE (a,b) and the PL-Asp/GCE (c,d). Insert: the equivalent circuit is used to fit Nyquist diagrams.

Curve a and c are obtained by measurements; Curve b and d are obtained by the Equivalent software according to the equivalent circuit. R_{ct} is charge transfer resistance; R_s is solution resistance; Q is constant phase element.

3.3 Effects of scan rates on the oxidation of EP on PL-Asp/GCE

Figure 5 is the cyclic voltammograms of 1.2×10^{-5}mol L^{-1} EP on the PL-ASP/GCE at different scan rate. It showed that both cathodic and anodic peak currents increased with the scan rate, and the peak-to-peak separation (ΔE_p) become bigger and bigger simultaneously, which indicated that the reversibility of the reactions on the PL-ASP/GCE is getting worse.

Table 1. Slopes and intercepts of the plot of logi_{pa} ~ log$v$ at different epinephrine concentrations on PL-Asp/GCE modified electrode (Sweep rate range: 60~200 mV s^{-1})

Concentration of EP C (10^{-5} mol L^{-1})	slopes of logi_{pa}~log$v$	Intercept of logi_{pa}~log$v$	Coefficient (γ)
500	0.4075	-3.4141	0.9977
49.3	0.6563	-3.2992	0.9990
4.93	0.7562	-3.5694	0.9955
0.493	0.8313	-4.0624	0.9901
0.049	0.9793	-4.5453	0.9955

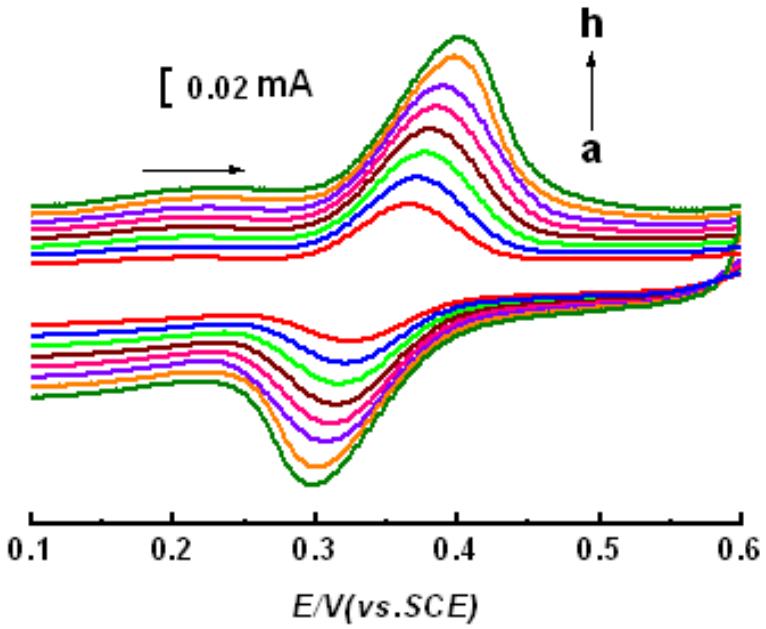

Figure 5. Cyclic voltammograms of 1.2×10^{-5} mol L^{-1} EP on PL-ASP/GCE at different scan rate v / (mV s^{-1}) a. 60; b. 80; c.100; d. 120; e.140; f.160; g. 180; h. 200.

The further study showed that the reaction on the modified electrode is controlled by different modes for different concentration of EP. Table 1 is the slope and the intercept values of the plot of logi_{pa} vs. log$v$ for different concentration of EP. The slopes decreased with the concentrations of EP. It is approximate to 0.5 at high concentration and is approximate to 1 at low concentration, which demonstrated that the reactions on the modified electrode is controlled by diffusion at high concentration and controlled by adsorption at low concentration.

When the concentration of EP is 1.2×10^{-5} mol L^{-1}, the reaction on the electrode is an adsorption-controlled quasi-reversible reaction. The relationship between E_{pa} and ln$v$ in the cyclic voltammgrams could be expressed in Eq. (1) by Laviron.[30]

$$E_p = E^0 + [RT/(\alpha nF)] \ln[(RTk_s)/(\alpha nF)] - [RT/(\alpha nF)]\ln v \quad (1)$$

Where, k_s is the rate constant of the electrochemical reactions; n, F, α, R and T have their usual significance. According to the Eq. (1), k_s = 154.4 s^{-1} and αn = 0.917 are calculated from the slope and intercept of E_{pa} (V) = 0.028 ln$v$ + 0.377. In most systems α turns out to lie between 0.3 and 0.7, and it can usually be approximated by 0.5 in the absence of actual measurements.[31] So the number of the electron (n) involved in the reaction is estimated to be 2.

3.4 Effects of pH on the oxidation of EP on PL-Asp/GCE

In the range of pH 2.0~9.0, the influences of pH on the redox reaction of EP are investigated. The results showed that the cathodic and anodic peaks potential are all negatively shift with pH values

increasing and the cathodic peaks disappeared at the pH 6.0, which showed that the H^+ took part in the electrode reactions. The peak currents increased with value of pH at first, and then decreased. So the pH 4.0 is adopted as the optimum pH.

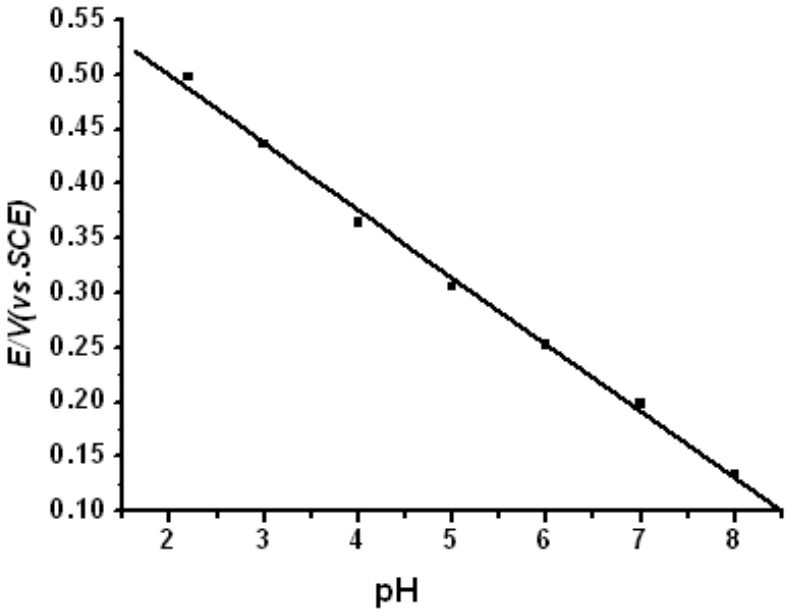

Figure 6. The plot of oxidation potential vs. pH.

The concentration of EP is 1.2×10^{-5} mol L^{-1}

3.5 Linear regression equation, linear range and detection limit

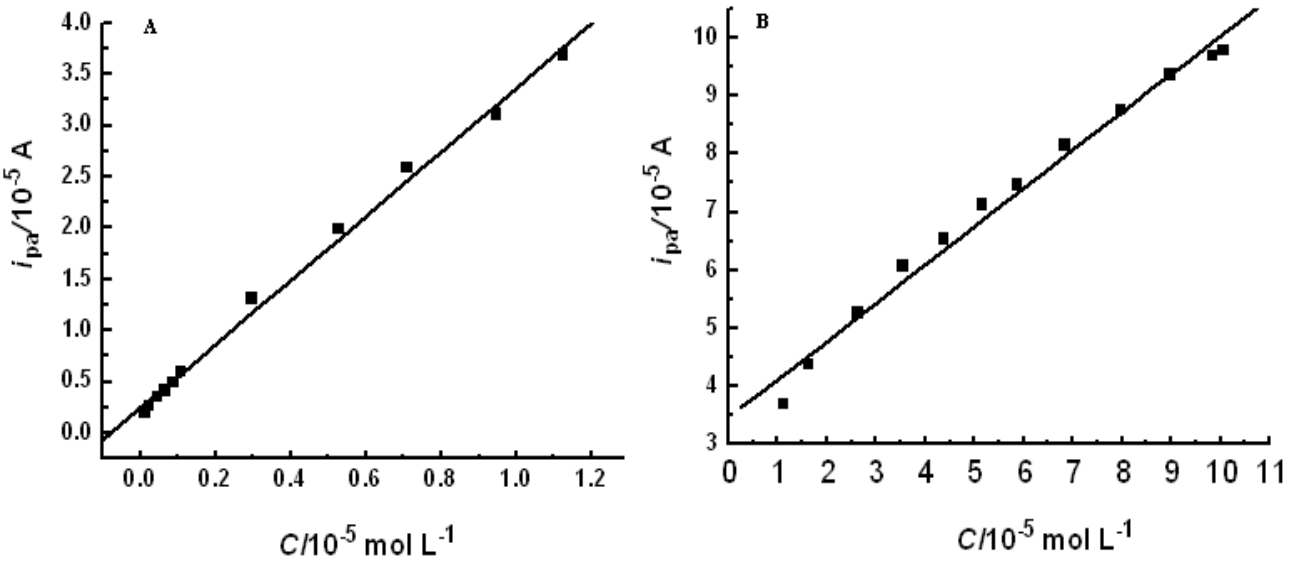

Figure 7. Relationship of oxidation peak currents with the concentrations of EP (A: the concentration range from 1.0×10^{-5} to 1.0×10^{-4} mol L^{-1}; B: 1.0×10^{-7}~1.0×10^{-5} mol L^{-1}) at PL-Asp/GCE in PBS (pH = 4.0).

Figure 6 is the plot of the oxidation potential vs. pH. Based on E_{pa} = -0.0612 *pH* + 0.6204 (γ= 0.9980) and the Eq. (4) [32], the number of H^+ taking part in the electrode reaction is calculated to be *m* = 2.07 ≈ 2.

$$E_{pa} = E^0 - 2.303\,(mRT/nF)\,\log H^+ \quad (4)$$

Where, E^0 is the formal potential, m the number of the protons involved in the reaction and *n* is 2 (see above). Other terms have their usual significance.

Under the optimal conditions, using the anodic peak currents as the detection signals, two linear calibration ranges of 1.0×10^{-7}~1.0×10^{-5} mol L^{-1} and 1.0×10^{-5}~1.0×10^{-4} mol L^{-1} are obtained for EP determination. The plots of i_{pa} vs. C_{EP} are demonstrated in figure 7. The two linear regression equations are i_{pa}(A) = $0.6571C_{EP}$ + 3.4616×10^{-6} (γ = 0.9964) (Figure 7 A) and i_{pa}(A) = $3.133C_{EP}$ + 2.404×10^{-6} (γ = 0.9978) (Figure 7 B), respectively. The detection limit is 4.6×10^{-8} mol L^{-1} (S/N=3). The two linear calibrations might be related to the different reaction modes for different concentration of EP.

By comparing with other electrochemical methods, this method had higher sensitivity, wider linear range and better stability. The comparison of the proposed method with other electrochemical methods is listed in Table 2.

Table 2. Comparison of the proposed method with other electrochemical methods for determination of EP.

Modified electrode	Linear range (mol L^{-1})	Detection limit (mol L^{-1})	Ref.
Poly(taurine)	2.0×10^{-6}~6.0×10^{-4}	3.0×10^{-7}	3
Layered double hydroxide	0.5×10^{-6}~0.3×10^{-3}	0.13×10^{-6}	18
Gold nanoparticles	0.1×10^{-6}~0.75×10^{-6}	0.82×10^{-7}	22
Poly(l-arginine)	5.0×10^{-7}~5.0×10^{-5}	5.0×10^{-7}	24
L-cysteine self-assembled monolayers	1.0×10^{-7}~5.0×10^{-6}	1.0×10^{-8}	29
Overoxidized dopamine film	2.0×10^{-6}~8.0×10^{-4}	3.0×10^{-7}	33
Poly L-aspartic acid	1.2×10^{-7}~1.1×10^{-5} and 1.1×10^{-5}~1.1×10^{-4}	4.6×10^{-8}	This work

3.6 Reproducibility and stability of PL-Asp/GCE

The regeneration, reproducibility and stability of the biosensor are investigated by determination of 1.2×10^{-5} mol L^{-1} EP on the modified electrode. After a time of determination is finished, the poly(L-Asp) membrane could be removed from the electrode surface by cyclic scanning from 0.0 V to 0.6V at the scan rate of 100 mV s^{-1} in PBS solution (pH 5.0) until no redox peaks appear, then the electrode could be coated with poly(L-Asp) again. After this course is repeated for 8 times, the detection signal is about 97 % of the first measurement signal. To ascertain the

reproducibility of electrode-to-electrode, a batch of 7 modified electrodes prepared in the same way are used to determine 1.2×10^{-5} mol L^{-1} EP with the RSD of 3.2%. The results indicated that this electrode had a good reproducibility. After measurements, the electrode is kept in PBS solution (pH 5.0). The long-term stability study is performed by detecting a time every 10 days in 30 days. The current response for 1.2×10^{-5} mol L^{-1} EP decreased about 4.6 %, 6.8 % and 14.6 % in sequence, which showed that the modified had long-term stability.

3.7. Tolerance of foreign substances

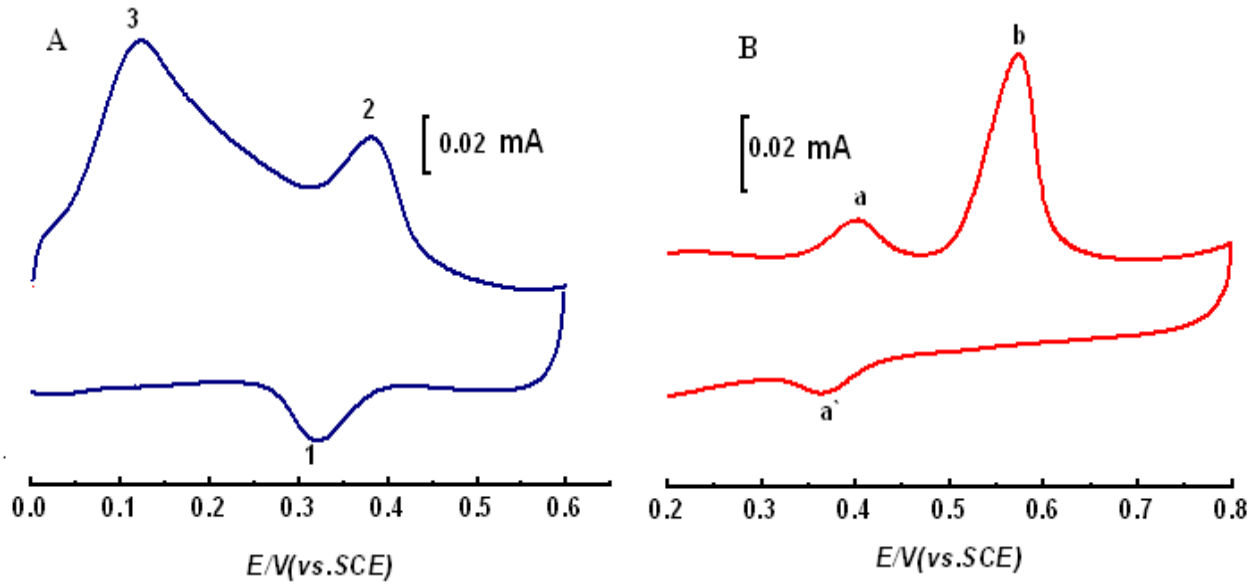

Figure 8. Cyclic voltammograms of 1.2×10^{-5} mol L^{-1} EP in the presence of 2.4×10^{-3} mol L^{-1} AA (A) and 3.6×10^{-3} mol L^{-1} UA (B)

The influences of AA or UA on the determination of EP are investigated by cyclic voltammetry. Figure 8 is the cyclic voltammograms of 1.2×10^{-5} mol L^{-1} EP on the PL-Asp/GCE in the presence of 2.4×10^{-3} mol L^{-1} AA (Figure 8A) and 3.6×10^{-3} mol L^{-1} UA (Figure 8B). The results showed that AA had only an anodic peak at about 0.12 V at the modified electrode (Figure 8A, peak 3) and no cathodic peaks appear. UA had an irreversible anodic peak is at about 0.56 V (Figure 8B, peak b). The anodic peak potential of EP is at about 0.38 V (Figure 8A, peak 2 and Figure 8B, peak a). By comparing the differences of the anodic potential values of AA and EP, UA and EP, the conclusion that AA and UA had no influence on the determination of EP is obtained naturally.

The interference of foreign substances, such as metallic ions, anions and amino acids, on the determination of 1.2×10^{-5} mol L^{-1} EP is also investigated under the optimal conditions. The results showed that 200 times of amino acids, such as d, l-aspartic acid, d-threonine, l-serine, l-alanine, l-glycine, l-cysteine, l-phenylalanine and l-glutamic acid; 100 times of metallic ions, such as Fe^{3+}, Fe^{2+}, Ca^{2+}, Cu^{2+}, Mg^{2+}, Co^{2+}, Zn^{2+} and Ni^{2+}, had no obvious influence on the results of the determination within ±5 % error allowed.

3.8 Analytical application

The practical application of the PL-Asp modified electrode is tested by measuring the concentration of EP in injections which are produced in different batches. The amounts of EP in injection are calculated from the calibration equation and the results are listed in Table 3.

Table 3. Determination results of EP in injections

Injections	Label claimed (mg)	Found (mg) average	RSD (%, *n=7*)	Recovery (%)
Sample Ⅰ	1.0	0.99	1.2	99.0
Sample Ⅱ	1.0	0.98	2.8	98.0
Sample Ⅲ	1.0	1.01	3.1	101

Table 4. The results of recovery determination

Sample	Adding concentration (mg mL^{-1})	Detect concentration (mg mL^{-1})	Recovery (%)	R.S.D. (%, *n=7*)
1	0.5	1.49	98.0	2.13
2	1.0	2.08	108.0	1.36
3	2.0	3.05	103.0	1.27
4	3.0	3.99	99.7	2.51

The recovery of this method is studied as follows: 0.5, 1.0, 2.0, 3.0 mL solutions of 1.0 mg mL^{-1} EP are added into four 10 mL tubes, respectively, and diluted to 10 mL with PBS solution containing 1.0 mg mL^{-1} EP injections. The are listed in Table 4. The recovery is from 98 ~ 108%, indicating the applicability of the proposed method.

4. CONCLUSION

In this paper, the L-Asp is electropolymerized on a GCE by cyclic voltammetry, and the electrochemical behaviors of EP are studied on this modified electrode. Based on the relationship of the anodic peak currents of EP and its concentrations, a simple method for determination of EP is developed. The membrane of L-Asp had excellent properties in excluding the interference of AA and UA. Compared with other electrochemical methods, the proposed method had high sensitivity, wide linear range and good stability. This method could be used for determination of the content of EP in real samples.

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