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Electrochemical Behaviors of Norepinephrine on the Silver Doped Poly Aminosulfonic Acid Composite Membrane Modified Electrode and its Determination

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The Ag-poly aminosulfonic acid composite membrane modified glassy carbon electrode (GCE) was fabricated by cyclic voltammery. The membrane had excellent properties for catalyzing the redox of norepinephrine (NE) and excluding the interference of ascorbic acid for the reductive of NE. The reductive peak currents of NE were linear with its concentrations in the range of 8.49×10^{-7} ~ 7.55×10^{-6} mol/L and 7.55×10^{-6} ~10^{-4} mol/L. The detection limit was 5.66×10^{-8} mol/L (S/N = 3). The conditions, such as pH values, scan rates and the influence of foreign substances, that affected the determination of NE were investigated. The proposed method had wide linear range, high sensitivity and good selectivity and was used for detecting the content of the NE in injections with satisfied results.

Keywords: Silver; poly aminosulfonic acid; norepinephrine; glassy carbon electrode; cyclic voltammetry

1. INTRODUCTION

Norepinephrine (NE) is one of important catecholamine neurotransmitters in mammalian central nervous systems which secreted and released by the adrenal glands. The concentration level change caused by the metabolic hindrance can induce many physiological functions disorder, such as the regulation of cardiovascular function, analgesia, affective disorders, and thermoregulation. Therefore, it is very necessary to develop fast, accurate and sensitive methods for the direct detection of NE. Many methods, such as spectrophotometry[1,2], ion chromatography[3], gas chromatography[4], high-performance liquid chromatography[5] and fluorescence spectroscopy[6]

were employed for the determination of NE. However, most of these methods have their shortcomings, such as comparatively high detection limit, time-consuming, low sensitivity and complicated processes. In recent years, the polymer membrane modified electrode has been extensively used in analyzing various biomaterials[7-10] due to its good stability and biocompatibility. Among of these modified electrodes, the poly amino acid modified electrode has excellent electrocatalytic activities for the redox reduction reactions of catecholamine neurotransmitters[11-13]. When the poly amino acid membrane was doped with metal particles by electrodeposition, the electrochemical properties of the membrane was improved significantly. To best of our knowledge, using this kind of modified electrode to determine the content of NE has not been reported.

In this paper, the silver was doped into the poly aminosulfonic acid (pASA) membrane by cyclic voltammetry to modify the glassy carbon electrode (GCE). The modified electrode was used to study the behaviors of NE and set up a novel method for determination of NE. The results showed that peak currents of NE increased significantly after the silver particles were doped into the pASA membrane and on the membrane, the ascorbic acid had no interference for the determination of NE. This modified electrode had many advantages, such as the facile of fabrication, good reproducibility and stability. The proposed method has good prospect for using in practical.

2. EXPERIMENTAL

2.1. Materials and Apparatus

Norepinephrine (NE) and ascorbic acid were purchased from National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China); Aminosulfonic acid (ASA) were purchased from Runjie chemicals Ltd. (Beijing, China); Phosphate-buffer saline (PBS, 0.1 mol/L KH_2PO_4 + 0.1 mol/L K_2HPO_4 + 0.1 mol/L KCl) were adjusted with H_3PO_4 or NaOH to appropriate pH values. All chemicals were of analytical grade and used without further purification. Water used in experiments was quartz sub-boiling redistilled water.

All electrochemical experiments were performed on a CHI 660 C electrochemical analyzer (Shanghai CH Instruments, China) with a three-electrode arrangement consisting of a glassy carbon electrode (GCE) (Φ = 3.0 mm) or film-coated GCE working electrode, a Ag/AgCl reference electrode and a platinum wire auxiliary electrode. The pH values of all solutions were measured by a model pHS-25 digital acidometer (Shanghai Leici Factory, China).

2.2 Preparation of the Modified Electrode

Prior to modification, the GCE was pretreated as follows: first, the GCE was treated to a mirror-like by polishing with wet 4# and 6# metallographic sandpapers and 0.05 μm α- Al_2O_3 slurry

on a polishing cloth, then the electrode was sonicated for 5 min in nitric acid (1:1, V/V), absolute ethanol and redistilled water in sequence for 2 min in each step. Thereafter, used the pretreated electrode as working electrode, the fabrication of the silver doped poly aminosulfonic acid composite membrane were performed with cyclic voltammetry in the aqueous solution containing 0.100 mol/L nitric acid, 0.003 mol/L silver nitrate, 0.002 mol/L aminosulfonic acid and 0.15mol/L potassium nitrate in the potential range of -0.8 ~ 2.0 V for ten cycles at the scan rate of 60 mV/s. The result of electrode were rinsed with redistilled water and dried, and donated as Ag-pASA/GCE. As control modified electrode, the poly aminosulfonic acid modified GCE (pASA/GCE) were fabricated as above procedures except without 0.003 mol/L silver nitrate.

2.3 Electrochemical detection

The appropriate amount of NE was added into 50 mL cell and diluted with PBS of pH 5.0, then the NE was enriched on the Ag-pASA/GCE working electrode for 60 s with stir, and thereafter, the cyclic voltammograms were recorded on the CHI 660 C electrochemical analyze in the potential range of 0~0.6 V at the scan rate of 100 mV/s. After each of detection, the electrode could be regenerated by scanning with cyclic voltammetry in PBS (pH 5.0) until the peak currents of NE disappeared. The regenerated electrode was rinsed with redistilled water and dried with filter paper and it could be used again.

3. RESULTS AND DISCUSSION

3.1 Optimal Conditions for the Polymerization

The electrochemical parameters of cyclic voltammetry for the polymerization that could affect the performance of the polymer membrane, such as the range of potential, the scan rate and the sum of the scan cycles were optimized, and the results showed that the biggest peak currents of NE were obtained on the polymer membrane which was fabricated with the potential range of -0.8~2.0 V for ten cycles at the scan rate of 60 mV/s.

The cyclic voltammograms of the silver and aminosulfonic acid under the optimal conditions were showed in Fig.1. The results showed that the solution of 0.100 mol/L nitric acid, 0.003 mol/L silver nitrate, 0.002 mol/L aminosulfonic acid and 0.15 mol/L potassium nitrate had four peak currents on the GCE, and the peak currents increased with the sum of the scan cycles and almost reached constant after ten cycles, indicating that a uniform membrane was formed on the surface of the electrode.

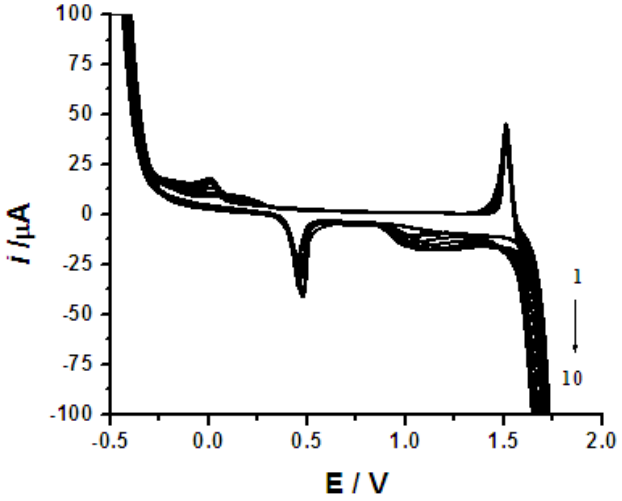

Figure 1. The successive cyclic voltammograms of 0.100 mol/L nitric acid, 0.003 mol/L silver nitrate, 0.002 mol/L aminosulfonic acid and 0.15 mol/L potassium nitrate on the GCE. The scan rate is 60 mV/s.

3.2 Electrochemical Behaviors of NE on the Ag-pASA/GCE

In order to study the electrochemical behaviors of NE on the Ag-pASA/GCE, the cyclic voltammograms of NE were recorded on the bare GCE, the pASA/GCE and the Ag- pASA/GCE, respectively, and the results were showed in Fig.The results showed that only very faint electrochemical responses of NE were obtained on the bare GCE (curve 1).

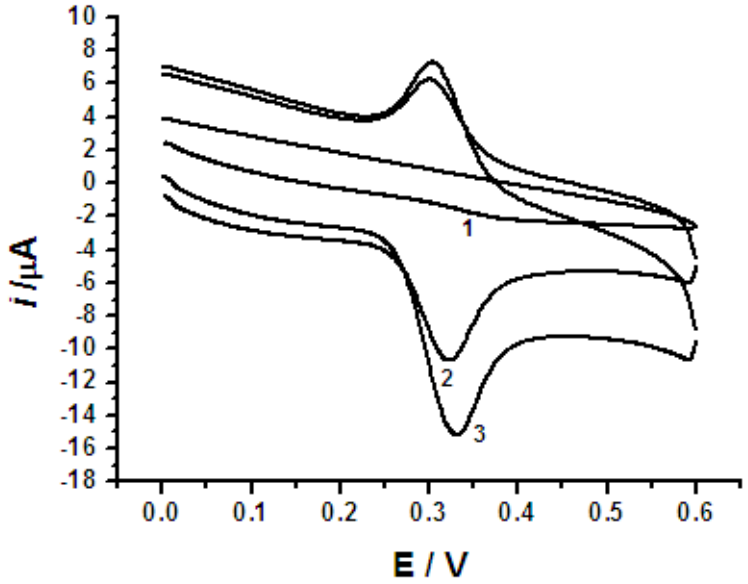

Figure 2. Cyclic voltammograms of 3.0×10^{-5} mol/L NE at the bare GCE (curve 1), the pASA/GCE (curve 2) and the Ag-pASA/GCE (curve 3). Supporting electrolyte solution: PBS of pH 5.0, Scan rate: 100 mV/s.

However, on the pASA/GCE, a pair of redox peak currents appeared, and the anodic peak potentail (E_{pa}) and cathodic peak potetential (E_{pc}) were at 0.324 V and 0.305 V, respectively, and corresponding, the anodic peak current (i_{pa}) and cathodic peak current (i_{pc}) were -6.54 μA and 4.31 μA, respectively (curve 2). When the membrane of poly aminosulfonic acid was doped silver particles, i.e. on the Ag- pASA/GCE (curve 3), the E_{pa} (0.330 V) and E_{pc} (0.305 V) of NE had almost no changes compared with that on the pASA/GCE. However, the i_{pa} and i_{pc} of NE increased to -11.99 μA and 6.89 μA, respectively. They almost were two times of that on the pASA/GCE. The results indicating that the doped silver could improve the electrochemical properties of the pASA membrane.

3.3 Influence of pH Values

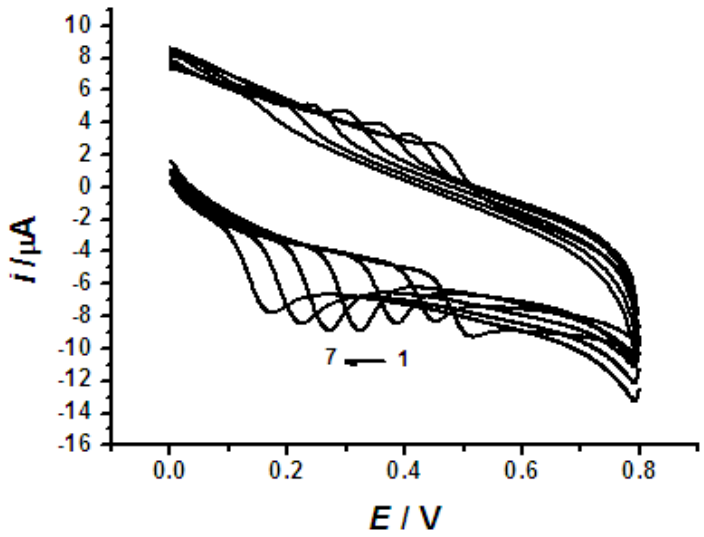

Figure 3. Cyclic voltammograms of 2.0×10^{-5} mol/L NE at the Ag- pASA/GCE in PBS of different pH values. Scan rate:100 mV/s; pH of curve 1 to 7 · 2.2, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, respectively.

The pH values of PBS had significant influence on the redox of NE on the Ag-pASA/GCE. The cyclic voltammograms of NE were recorded on the pASA/GCE in the PBS of different pH values and the results were showed in Fig. 3. The results showed that, in the pH range of 2.2 ~ 8.0, the anodic peak currents increased with the increase of the pH values and reached the maximum at the pH 5.0, then decreased. So the pH 5.0 was selected as the optimal pH values. Both the E_{pa} and the E_{pc} negatively shift with the increase of the pH values, and the further study showed that the E_{pa}s were linearly with the pH values and the regressive equation E_{pa} (V) = -0.056 pH + 0.62 with r = -0.9966 (Fig. 4), indicating that the protons took part in the redox reactions of NE on the modified electrode.

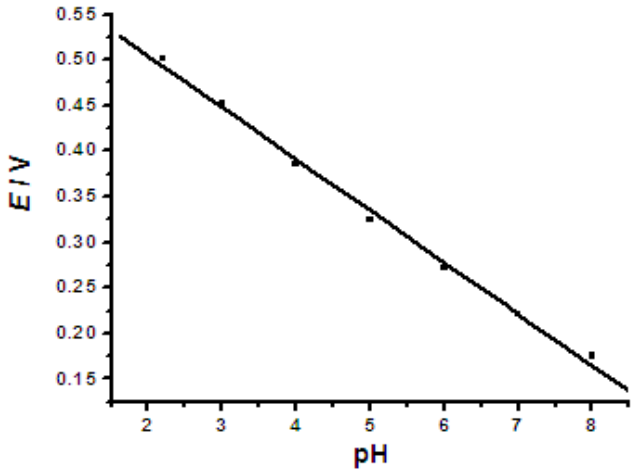

Figure 4. Cyclic voltammograms of 2.0×10^{-5} mol/L NE at the Ag- pASA/GCE in PBS of different pH values. Scan rate:100 mV/s; pH of curve 1 to 7 · 2.2, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, respectively.

3.4 Influence of Scan Rates

The influence of the scan rate on the electrochemical behaviors of NE was studied in the scan rate range of 40 ~ 400 mV/s and the results were shown in Fig. 5. It was found that the peak to peak separation increase with the scan rates, and the peak currents were linearly with the scan rates. The linear regressive equation was i_{pc} (A) = $4.84 \times 10^{-6} + 1.57 \times 10^{-7}$ ν (mV/s) with r = 0.9964 (Fig. 6), indicating that the reaction process of NE on the modified electrode was controlled by adsorption. Considered the shape of the curves and the reversibility, the scan rate of 100 mV/s was used in the determination.

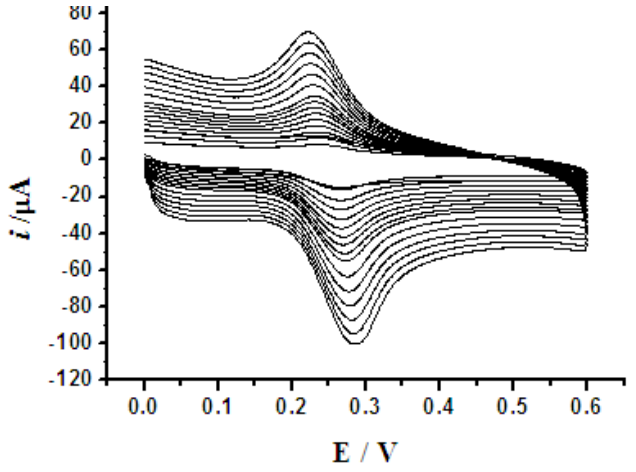

Figure 5. Cyclic voltammograms of 2.0×10^{-5} mol/L NE on the Ag- pASA/GCE at different scan rates. Scan rate (from inner to outer): 40, 60, 80, 100, 120, 140, 160, 180, 200, 220, 240, 260, 280, 320, 360, 400 mV/s.

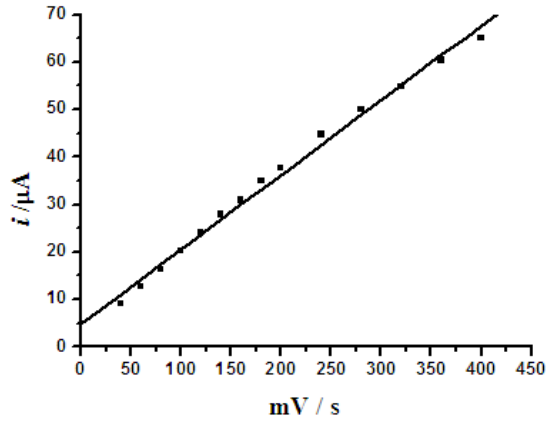

Figure 6. Plot of E_{pa} *vs.* scan rate.

3.6 Linear range and detection limit

Under the optimal conditions, the studies showed that the reductive peak currents of NE at the Ag-pASA/GCE were linearly with its concentration in the range of $8.49 \times 10^{-7} \sim 7.55 \times 10^{-6}$ mol/L and $7.55 \times 10^{-6} \sim 2.36 \times 10^{-4}$ mol/L. The linear regressive equations were $i_{pc} = 5.402\ C + 9.2 \times 10^{-6}$ with r = 0.9951 and $i_{pc} = 5.012\ C + 9.7 \times 10^{-6}$ with r = 0.9924, respectively. The detection limit was 5.66×10^{-8} mol/L (S/N = 3).The linear range is much wider than the results of literatures [14-22] and the detection limit is lower than the results of literatures [14-19, 23].

3.7 Tolerance of foreign substances

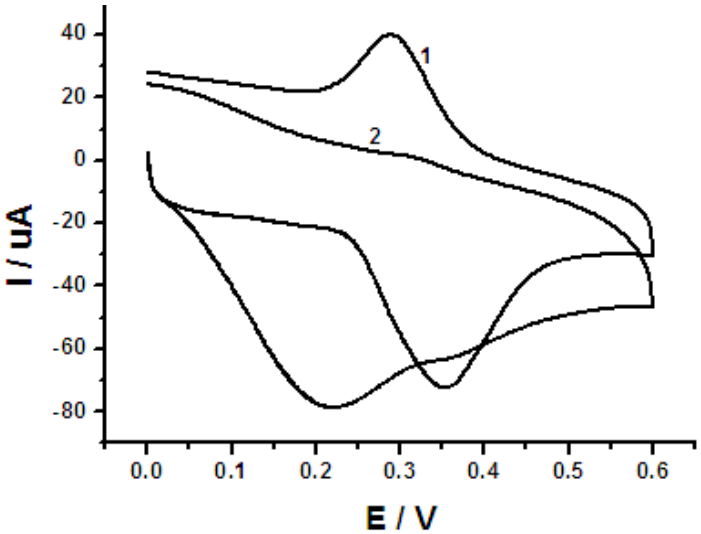

Figure 7. Cyclic vatammograms of 2.0×10^{-5} mol/L norepinephrine (curve 1) and 2.0×10^{-4} mol/L ascorbic acid (curve 2) on the Ag-pASA/GCE. Supporting electrolyte solution: PBS of pH 5.0, Scan rate: 100 mV/s

The interference of many foreign substances with the determination of 2.0×10^{-5} mol/L NE was investigated under the optimal conditions. It was found that 100 times of amino acids, 100 times of metallic ions, such as K^+, Na^+, Ca^{2+}, 100 times of Cl^- had no obvious influence on the results of a determination error within ± 5% allowed. The cyclic voltammogram of 2.0×10^{-4} mol/L ascorbic acid was recorded on the Ag-pASA/GCE and the results were showed in the Fig.7. Ascorbic acid had only a wide reductive peak at 0.22 V and almost no oxidative peak was observed. The reductive peak of NE was at 0.324 V. Therefore, ascorbic acid did not interfere with the determination of NA.

3.8 Recovery test

Table 1 Results of determination of NE in injection samples

Samples	Content ($\times10^{-6}$ mol/L)	R.S.D (%)	Added ($\times10^{-6}$ mol/L)	Found ($\times10^{-6}$ mol/L)	Recovery (%)
1	14.50	2.8	29.5	43.2	97.3
2	6.62	3.1	29.5	37.4	104.3
3	4.20	3.6	29.5	34.3	102.1

The proposed system was applied to the analysis of NE in injections. The content of NE and the recoveries were calculated according to the linear regressive equations mentioned above. The results were listed in Tab.1. They are in excellent agreement with the labeled values. The recoveries varied from 97.3% to 102.1%. These results indicate that the method provides a potential tool for the separated determination of NE in the presence of AA.

4. CONCLUSIONS

A novel composite membrane of silver doped poly aminosulfonic acid was fabricated by cyclic voltammetry. This membrane had excellent properties for catalyzing the redox of NE. Compared with the membrane of poly aminosulfonic acid without silver, the peak currents of NE had significant increase and the ascorbic acid had no influence for the determination of NE. The proposed method had broad linear range, high sensitivity and good selectivity. It was used to determine the content of NE in injections with satisfied results. The recovery test showed that the recoveries varied from 97.3% to 102.1%.

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