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Preparation of Poly(erythrosine) Modified Electrode and Its Application in Determination of Catechol

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A poly(erythrosine) chemical modified electrode (P-Ery/GCE/CME) was fabricated by electrochemical immobilization of erythrosine on a glassy carbon electrode through cyclic voltammetry. The modified electrode had good electrocatalytic oxidation function to catechol and it significantly increased the catechol oxidation peak currents. The effect of acidity of electrolytes and scan rates on electrocatalytic oxidation function of the P-Ery/GCE/CME of catechol was also studied. The linear response were obtained in the range of 6×10^{-6} to 7×10^{-4} mol/L and the detection limit was 8×10^{-7} mol/L for catechol. The modified electrode has exhibited satisfactory stability and selectivity and strong antiinterference. It was successfully used to determine catechol in wastewater samples with recoveries between 99.1 and 103.2 %.

Keywords: Poly(erythrosine) modified electrode, Catechol, Electrocatalytic.

INTRODUCTION

Catechol (CAT) is an important organic chemical raw materials and used in rubber, pharmaceuticals, pesticides, dyes, photographic materials, spices and other industries of basic organic ingredients or intermediates. Because of catechol of the high toxicity and low degradation, there is a large toxicity for organ¹⁻³ and an environmental pollutant⁴. Therefore, it is important to establish a rapid, simple, sensitive and accurate method for the determination of catechol. Several methods for the determination of phenolic compounds are HPLC^{5,6} gas chromatography, spectrophotometry⁷. However, these methods are mostly procedures cumbersome, time-consuming and most of them required expensive large equipment. Compared with other methods, electrochemical methods have been received great attentions due to its simple, rapid, low cost and high sensitivity.

Recently, polymer film modified electrode in chemical sensors is concerned. Electro-polymerization in the determination and analysis of substances has many advantages, because the electrochemical deposition of the polymer is strongly adsorbed on the electrode surface to form a stable polymer film, which has a fine sensitivity, selectivity and uniformity⁸⁻¹⁰. The molecular structure of the polymer organic of dye has a large π -conjugated system to be conducive to adsorption of molecules on the electrode surface, the molecule itself has

excellent electrochemical activity and is a better medium body¹¹. In this paper, poly(erythrosine) modified electrode is prepared by polymerization of erythrosine into glassy carbon electrode; determination of catechol modified electrode has effective catalytic activity. This modified electrode can be used to simulate the determination of catechol in water samples. Currently, erythrosine not been used in modified electrode.

EXPERIMENTAL

Erythrosine (Ery) was obtained from Tianjin Guangfu Fine Chemical Research Institute (China), catechol and other analytical chemicals were purchased from the Sinopharm Chemical Reagent Co. Ltd (China). 0.10 mol/L phosphate buffered solution (PBS, NaOH-KH₂PO₄) was prepared in our laboratory.

Electrochemical experiments were recorded on LK2005 A Electrochemical Workstation. Acidity adjustment were obtained from a PHS-3C pH meter and Cleaning of the electrode were deal with a KQ 3200 E ultrasonic cleaner.

Preparation of copper doped poly(erythrosine)/GCE/CME modified electrode: GCE ($\Phi = 3$ mm) was polished on a wet metallographic sand paper (size 1000) and then was sequentially polished with 0.3 and 0.05 μm alumina/water slurry on a polishing cloth to a mirror-like finish, followed by sonication and then rinsed with distilled water.

The treated GCE was immersed in PBS buffer solution containing 1×10^{-3} mol/L erythrosine and subjected to CV in the range of -0.8-2.3 V at a scan rate of 100 mV/s for 10 cycles. P-Ery /GCE/CME modified electrode was cleaned with distilled water and ready to use the determination of catechol.

General procedure: All electrochemical experiments were carried out at LK2005 A electrochemical workstation. A conventional three-electrode system was used where glassy carbon electrode or P-Ery/GCE/CME, a platinum wire and an Ag/AgCl electrode were used as working, counter and reference electrodes, respectively. Cyclic-voltammetry and differential pulse voltammetry were carried out in PBS (0.1 mol/L, pH = 7.0) medium. Cyclic voltammetry was carried out on the electrolytic cell without stirring at a scan rate of 100 mV/s in a voltage range of -0.4 to 0.6 V at room temperature. Differential pulse voltammetry was obtained by scanning the potential from 0 to 0.4 at room temperature.

RESULTS AND DISCUSSION

Fig. 1 shows the cyclic voltammograms of polymerization process of poly(erythrosine). As can be seen from the Fig. 1, there is a oxidation peak at 1.6 V and a reduction peak at -0.6 V, respectively. The peak potential was constant and the peak currents increased with the scanning frequency increasing, but the amplitude decreased with the scanning frequency increasing. Which indicated that the polymer film on the surface of electrode tended to be complete with the polymerization reactions and polymerization and the deposition rate slows down.

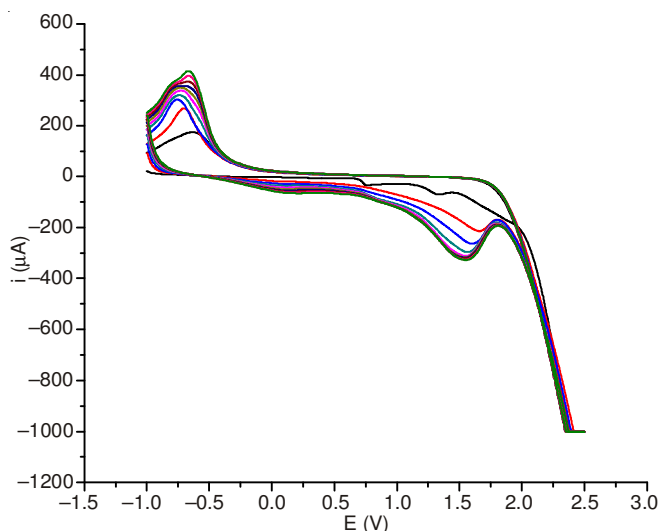


Fig. 1. Cyclic voltammograms of P-Ery/GCE/CME in the polymerization process

P-Ery/GCE/CME electrical catalysis: Fig. 2 shows the cyclic voltammetry curves of catechol at the unmodified GCE (curve 1) and P-Ery/GCE/CME (curve 2). At the unmodified GCE, an oxidation peak is observed at 0.23 V during the anodic sweep from -0.4 to 0.6 V. On the reverse scan, a corresponding reduction peak appears at 0.09 V. So, the peak potential separation ($\Delta E_p = E_{pa} - E_{pc}$) is as large as 140 mV at the unmodified GCE, indicating that the electron transfer is slow. The response of catechol shows great difference at the P-Ery/GCE/CME in

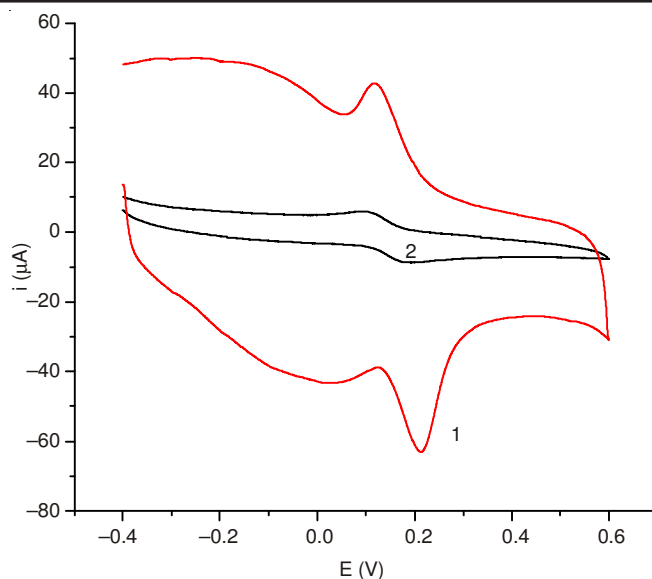


Fig. 2. Cyclic voltammetry curves of 1×10^{-4} mol/L catechol at different electrode in PBS (7.0) (1: P-Ery/GCE/CME ;2: GCE)

identical conditions. Firstly, the oxidation peak potential shifts negatively to 0.21 V, while the reduction peak potential shifts positively to 0.12 V. Therefore, the ΔE_p is 90 mV at the poly(erythrosine) modified GCE, suggesting that the electrode process of catechol becomes more reversible. Secondly, the oxidation and reduction peak currents significantly increases, revealing that the P-Ery/GCE/CME can greatly improve the determining sensitivity of catechol.

Fig. 3 shows cyclic voltammetric response of the P-Ery/GCE/CME to catechol solutions of different concentration. It appeared clearly that the oxidation peak current of modified electrode increased rapidly with the concentration of catechol increasing and the peak current presents a good linear relationship with the concentration of catechol in a certain range, indicating that P-Ery/GCE/CME has high catalytic performance for catechol and can be used for the trace detection of catechol.

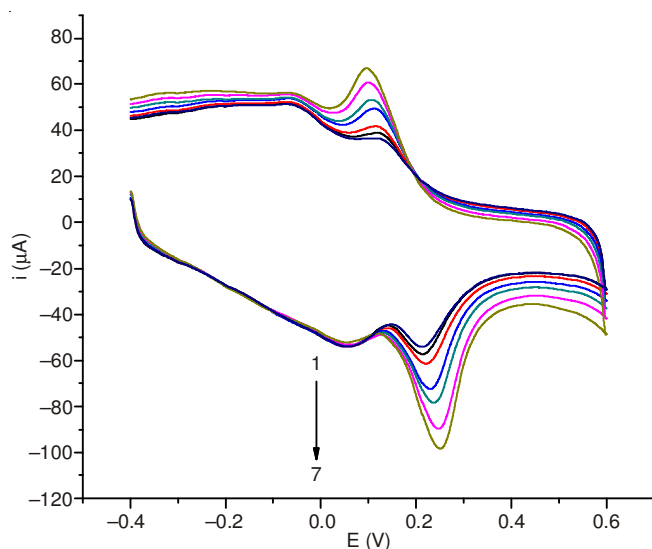


Fig. 3. Cyclic voltammetry curves of Fig. 3 shows CV response of catechol solutions of different concentration at P-Ery/GCE/CME in PBS (7) (a→f: 20, 30, 40, 100, 140, 200, 300 $\mu\text{mol/L}$)

Selection of the acid: The effects of the solution pH on electrochemical processes for 1×10^{-4} mol/L catechol were also studied using cyclic voltammetry in NaOH-KH₂PO₄ buffer in the pH range 5.8-8 at catechol sensor. The experimental results showed that the cathodic and anodic peak potentials for catechol shifted negatively as the pH was increased from 5.8 to 7.8. It can be seen that the redox peak currents for catechol increased as the pH is increased from 5.8 to 7. But at a pH higher than 7, the redox peak currents decreased with increasing pH. Catechol was easily oxidized by air at higher pH (pH = 8) and temperature value, so redox peaks of catechol did not appear at pH = 8. Overall, the NaOH-KH₂PO₄ buffer (pH 7) was chosen as the determination electrolyte (Fig. 4).

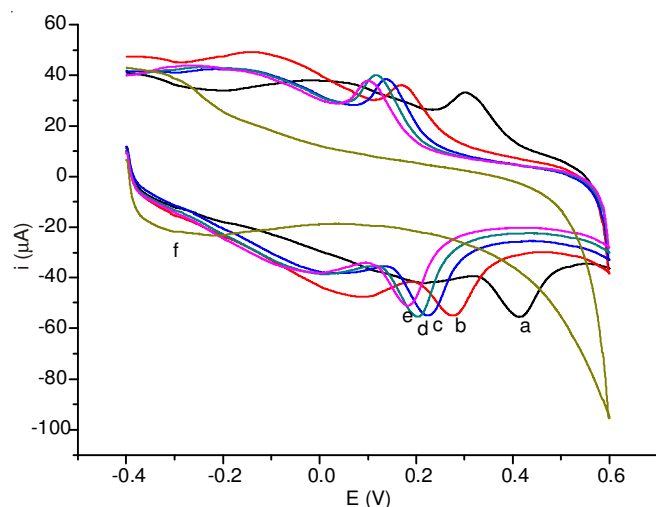


Fig. 4. Cyclic voltammograms of the P-Ery/GCE/CME in solution of varying pH levels in 1×10^{-4} mol/L catechol in 0.1 M PBS (a→f: 5.8, 6.2, 6.6, 7, 7.4, 8)

Effect of scan rates: The effect of scan rates were 50-200 mv/s at P-Ery/GCE/CME, which was investigated by the cyclic voltammetry and the results showed in Fig. 5a. From the Fig. 5a, as the scan rate increases, the redox peak current increases. Catechol redox peak current and the scan rate showed a good linear relationship. The oxidation and reduction peaks current of catechol present a good linear relationship with the scan rate in the Fig. 5b. The regression equations is: $I_{pa} (\mu A) = -0.472 - 13.95 v (mV/s)$ ($R = 0.997$), $I_{pc} (\mu A) = 0.343 + 7.963v (mV/s)$ ($R = 0.998$) and it indicated that the electrode reaction of catechol at P-Ery/GCE/CME was a typical adsorption-controlled process.

Linear range and detection limit: In different concentrations of catechol solution, P-Ery/GCE/CME as the working electrode was investigated by DPV in Fig. 6a. under the optimal conditions, the anodic peak current was linear with the value of catechol concentration ranging from 6×10^{-6} mol/L to 7×10^{-4} mol/L. The regression equation is $I_{pa} (\mu A) = -0.002c - 0.753 (\mu mol/L)$ ($R^2 = 0.996$) and the detection limit was 8×10^{-7} (S/N = 3).

Reproducibility and interference: Under the optimized conditions, P-Ery/GCE/CME was used to determine 1×10^{-4} mol/L catechol solution for ten times. The RSD is calculated to be 2.5 %, revealing that this method for the determination

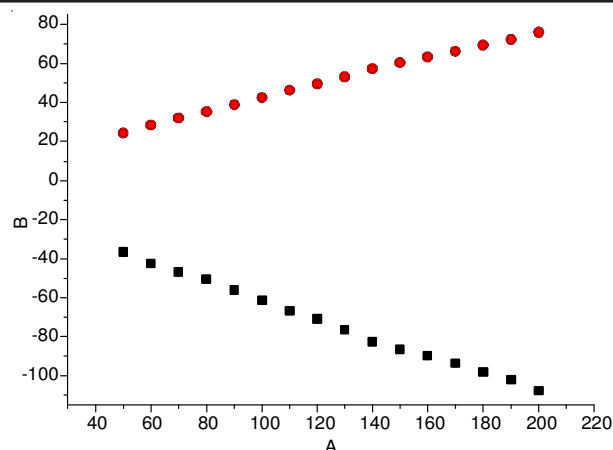


Fig. 5. Cyclic voltammograms of 1×10^{-4} mol/L catechol at P-Ery/GCE/CME with different sweep rate; (a) Sweep rate: 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200 mV/s; (b) linear relationship of I_p vs. v at P-Ery/GCE/CME

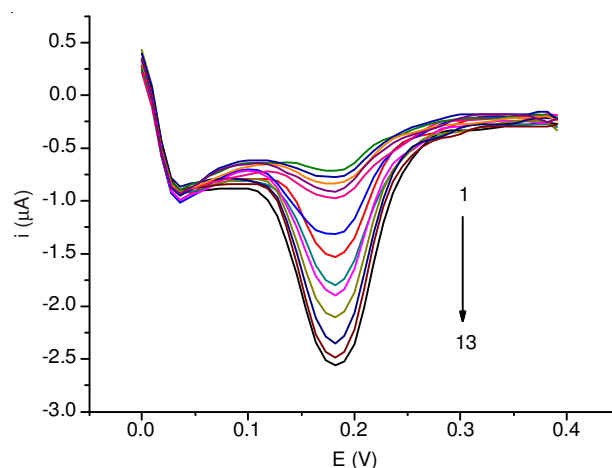


Fig. 6. Differential pulse voltammograms of P-Ery/GCE/CME in PBS(7.0). (c/µmol/L, 1→13: 6, 30, 40, 60, 70, 200, 280, 380, 420, 500, 600, 680, 700)

of catechol has excellent reproducibility. The interferences of other species on the determination of catechol were examined. It was found that 100-fold NO_3^- , K^+ , Ba^{2+} , Cl^- , Mg^{2+} , SO_4^{2-} , Na^+ , Cu^{2+} , CrO_4^{2-} , Fe^{2+} , NH_4^+ ; 20-fold Pb^{2+} , Br^- ; virtually did not interfere with the oxidation signal of 4×10^{-5} mol/L catechol at the P-Ery/GCE/CME (peak current change < 5 %).

Analytical applications: In order to investigate the applications of the developed method for determination of catechol, simulated water samples (containing: 5×10^{-4} mol/L Mg^{2+} , Pb^{2+} , Ba^{2+} , Na^+ , NO_3^- , Cl^-) were selected for analysis using the standard adding method. The results are listed in Table-1, the recovery rate was in the range of 99.1-103.2 %, which clearly indicated the applicability and reliability of the modified electrode.

TABLE 1
DETERMINATION RESULTS OF CATECHOL
IN WASTE WATER SAMPLES

Sample No.	Added (µM)	Found (µM)	Recovery (%)
1	10	10.32	103.2
2	50	50.55	101.1
3	80	80.43	100.5
4	120	118.94	99.1

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