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Selective Determination of Catechol in Wastewater at Silver Doped Polyglycine Modified Film Electrode

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A silver doped polyglycine (PGly) modified electrode was prepared by cyclic voltammetry (CV).The electrochemical behavior of catechol (CC) at the modified electrode was studied. A novel method for determination of catechol using cyclic voltammetry was established. The modified electrode showed an excellent electrocatalytical effect on the redox of catechol. In pH=5.0 phosphate buffer solution (PBS), catechol gave an oxidation peak at the modified electrode which can eliminate the interference of resorcin and hydroquinone to the catechol determination. The oxidation peak current versus the concentration of catechol showed a linear relations over the range of 6.0×10^{-7} $mol\cdot L^{-1}$~1.0×10^{-4} $mol\cdot L^{-1}$ with a correlation coefficient as follows: $i_{pa} = 1.19\times10^{-7}+0.036c$ ($mol\cdot L^{-1}$), R = 0.9994; the detection limit was 1.0×10^{-7} $mol\cdot L^{-1}$. The recovery was 97.5.0%~100.5%.The silver and polyglycine compound film modified electrode showed good sensitivity, selectivity, stability, it was applied to the catechol in wastewater with satiafactory results.

Keywords: Glycine, Catechol, Film electrode, Wastewater

1. INTRODUCTION

Catechol (CC) is an important material, which is widely used in tanning, cosmetic, chemical materials and pharmaceutical industries. CC is hazardous to human health occur frequently in the environment. They have been included in the lists of priority pollutants to be monitored in the aquatic environment by international bodies, such as the US Environmental Protection Agency (EPA) and the European Union (EU) [1]. Therefore, it is important to establish a sensitive, rapid and convenient method for the determination of CC. CC, hydroquinone and resorcin are isomers of dihydroxybenzenes with similar molecular structure and they usually coexist. So it is very important to develop selective analysis methods for CC. The established methods for the determination CC are commonly performed after pretreatment and separation [2]. Sample pretreatment and separation, as well as the significant operating complexity, the long times and large volumes of reagents consumed by established techniques make it important to develop a new method capable of selective determination without the need for prior separation of these compounds. CC contains phenolic hydroxy group and possesses excellent electrochemical activity, so various electrochemical methods using different modified electrodes have been reported for the determination of CC [3-6]. However, electrochemical determination of CC using silver (Ag) doped PGly modified film electrode has not been reported. The modified electrode is high selectivity, and has been successfully applied to analyzing CC in wastewater in the presence of hydroquinone and resorcin.

2. EXPERIMENTAL PART

2.1. Apparatus

CHI 660C Electrochemical Workstation was used for electrochemical measurements (Shanghai Chenhua Instrument Corporation, China). A three-electrode system was employed with a bare or modified glassy carbon electrode (GCE or GME) as the working electrode, a platinum wire electrode as the counter electrode, and an Ag/AgCl electrode as a reference electrode.

2.2 Reagent and Chemicals

Catechol, hydroquinone and resorcinol were obtained from sigma-aldrich (Shanghai, China). Phosphate buffer solutions (PBS) were prepared by mixing disodium hydrogen phosphate and citric acid. All other chemicals not mentioned here were analytical reagent grade.

2.3 Preparation of the modified electrode

Prior to electrochemical modification, the bare GCE was polished with gold sand paper and alumina slurry down to 0.05 mm on a polishing cloth. It was rinsed with water and sonicated in1:1 nitric acid, acetone and water for 5 min, respectively. The treated GCE was immersed in containing 0.1 $mol\cdot L^{-1}$ nitric acid, 1.0 $mmol\cdot L^{-1}$ silver nitrate, 0.05 $mol\cdot L^{-1}$ potassium nitrate, 0.015 $mol\cdot L^{-1}$ glycine, and subjected to CV between-1.0~1.9 V at a scan rate of $100mV\cdot s^{-1}$ for 7 cycles. Then the electrode was ready for use after final washing with water.

2.4 Analytical procedure

Under optimal conditions, a series of different concentrations of CC were investigated by CV. A three-electrode system was used, including a GME as the working electrode, a platinum electrode as counter electrode and Ag/AgCl as a reference electrode. Cyclic Voltammograms (CVs) of CC were recorded .The glassy carbon electrode was treated in PBS (pH 5.0) by repetitive scanning so as to no record and used again.

3. RESULTS AND DISCUSSION

3.1 The optimization of electrochemical polymerization

The electrochemical polymerization of silver doped polglycine at electrode is a complex process and is shown in Fig.1. Aminophenol (such as polyglycine) can produce ammonia cation radical by electrochemical oxidation, then the radical cation formed C-N chemical bond on carbon surfaces which creating a stable polymer membrane. Silve particles have a unique electrical, magnetic, optical, thermal properties and catalytic activity. This makes it widely used in optoelectronic devices, electric catalysis and biological sensor [7-9]. Amino acid and silver have synergistic effect; the composite membrane for CC has better catalytic effect. Electrochemical behaviors of the Ag-PGly/GCE were affected by polymerization conditions, such as potential range, cycle and scanning rate. After many experiments by CV, the Ag-PGly/GCE was obtained by CV in the potential range between -1.0 V and 2.0 V for 7 cycles at a scan rate of 100 $mV \cdot s^{-1}$. Silver appears a sharp oxidation peak at 0.509V, which may be due to the deposition of silver on the surface of electrode respectively, There was a wider range oxidation and reduction at 1.55 V and -0.51 V, respectively. The peak potential was constant and the peak currents increased with the scanning frequency increasing. The results showed that the polymer film on the surface tends to be complete with the polymerization reaction.

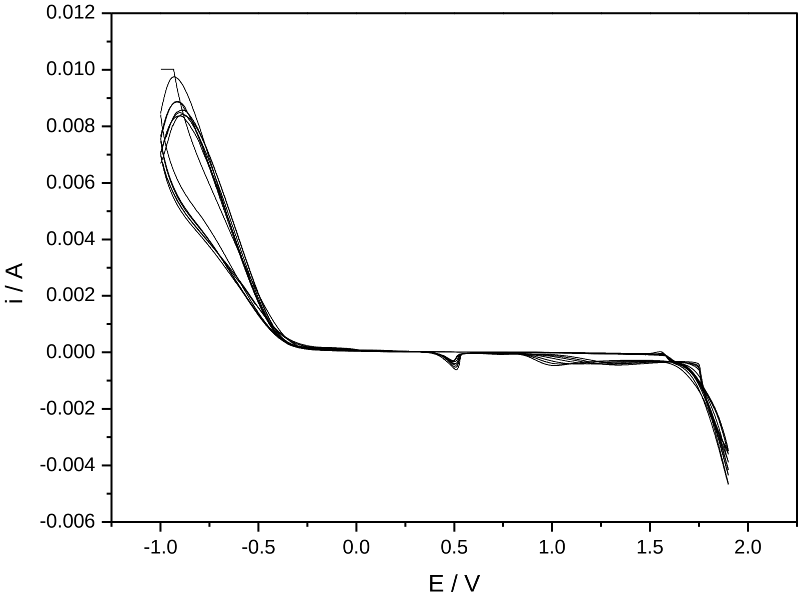


Figure 1. CVs of silver and glycine in polymerization process

3.2 Electrochemical behaviors of CC on electrode

Fig.2 shows the CVs of 2.50×10^{-5} mol·L^{-1} CC in 0.1 mol·L^{-1} PBS (pH5.0) at a GCE, PGly /GCE and Ag-PGly /GCE. The peak current intensity was zero at the GCE .The peak current intensity was increased at the PGly /GCE and Ag-PGly/GCE. Ag-PGly film electrochemical sensor showed an excellent performance for detecting CC. The redox peak currents was $i_{pa}=-2.319\times10^{-6}$A and $i_{pc}=1.971\times10^{-6}$A at the Ag-PGly/GCE, which was 2.6~3.0 times than the redox peak currents at the PGly/GCE with $i_{pa}=6.054\times10^{-6}$A and $i_{pa}=5.922\times10^{-6}$A. This unique and excellent performance shows that Ag-PGly/GCE is a simple, sensitive, and quantitative electrochemical sensor for detecting CC.

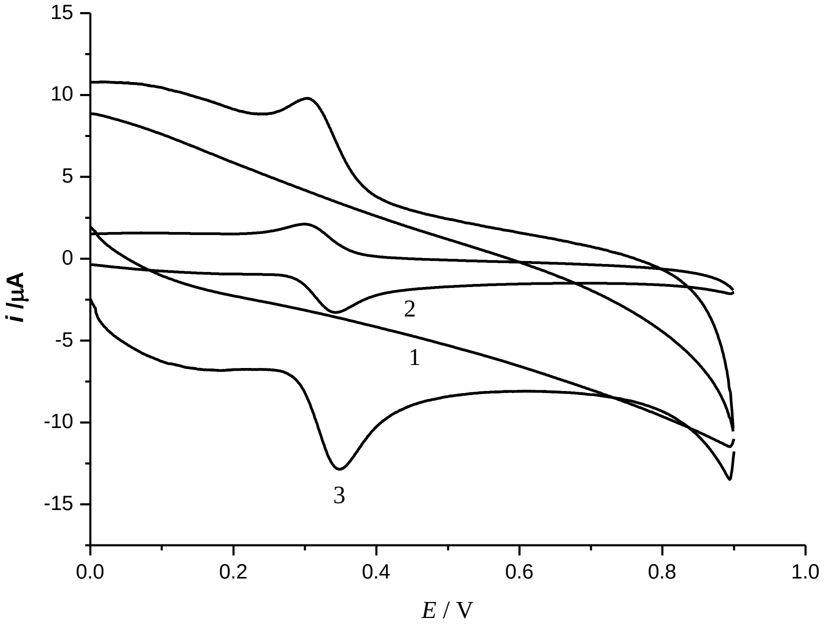
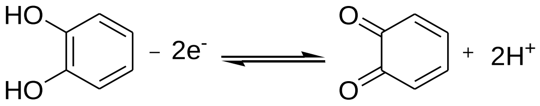


Figure 2. CVs of CC at a GCE (1), PGly/GCE (2), Ag-PGly/GCE (3) PBS (pH5.0), scan rate: 100 mV·s^{-1}

3.3 Optimization of the experimental conditions

3.3.1 Effect of Solution pH

Effect of solution pH (2.2~9.0) on the electrochemical signal was analyzed. Figure 3 showed important influence of pH on the redox reaction of CC at Ag-PGly/GCE. It can be seen that the redox peak negatively shifted with increasing the pH value of solution.The relationship between oxidation potential (Ea) and pH can be described using the following equation: Ea=0.56 –0.055pH, R=0.9951. According to the Nernst equation, the slope of -55mV·pH−1 reveals that the proportion of the electron and proton involved in the reactions is near 1: 1. As CC oxidation is a two-electron process, the number of protons involved is also predicted to be two. Therefore, a mechanism for the CC oxidation can be proposed in Scheme 1. This is in agreement with the previous report [10].



Scheme 1. The mechanism of CC

The redox peak currents increased as the pH changing from pH 2.2~5.0, and then decreased after pH>5.0. A solution of pH 5.0 was chosen as the supporting electrolyte.

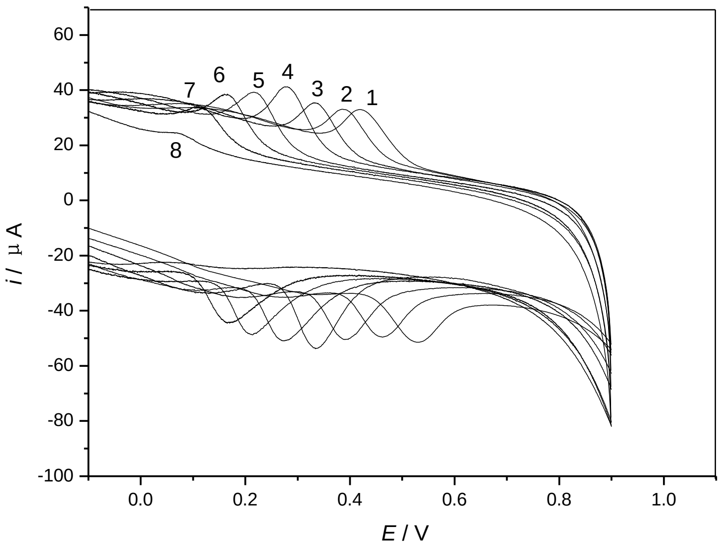


Figure 3. CVs of CC at different pH levels. pH（1-8：2.2, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0）

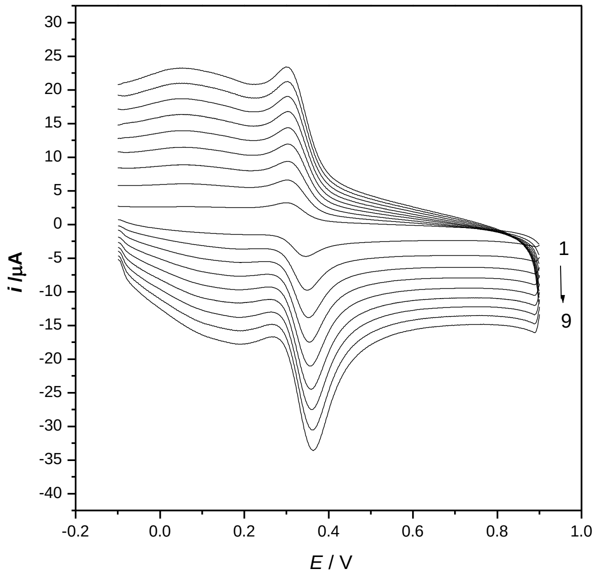


Figure 4. CVs of CC at the Ag-PGly/GCE（A）and its variation with scan rates (B).Scan rates: 1-9:40, 80,120,160,200,240,280,320, 360 mV·s^{-1}

Figure 4 was the CVs of CC at Ag-PGly/GCE with different scan rates. We can see that E_a slightly shifted in the positive direction with the increase of scan rate. The redox peak currents linearly increased with the scan rates ranging from 40 to 360 mV·s^{-1}. The linear regression equations of the i_{pa} and i_{pc} for the scan rates are expressed as $i_{pa}(A) = -2.23\times10^{-6}-7.49\times10^{-8}v(mV)$, R = 0.9996; $i_{pc}(A) = 2.74\times10^{-6}+6.06\times10^{-8}v$ (mV), R = 0.9912 respectively, suggesting that the electrochemical behaviors of CC on the Ag-PGly/GCE was an adsorption process. Scan rate of 100 mV·s^{-1} was chosen in this experimentation.

3.4 Linearity and Detection Limit

The i_{pa} was linearly related to the CC concentration in the range of 6.0×10^{-7}~1.0×10^{-4} mol·L^{-1}.The linear regression equation was $i_{pa}=1.19\times10^{-7}+0.036c$ (mol·L^{-1}), R=0.9994; A detection limit is estimated to be 1.0×10^{-7} mol·L^{-1}.

3.5 Interference Studies

In order to confirm the availability of Ag-PGly/GCE to the separated determination of CC in the presence of resorcin and hydroquinone, we scanned the solution of CC, resorcin and a mixture containing CC, resorcin and hydroquinone in PBS (pH 5.0) by CV under the selected conditions. The results showed that there was no peak of resorcin and the difference of oxidation potential between CC and hydroquinone was 113mV. So CC has been selectly determined at the Ag-PGly/GCE. No interference has been found when including up to 1000 μmol·L^{-1} of K^+, Na^+, Cu^{2+}, NO_3^-, $C1^-$, SO_4^{2-}, Ac^-, Ca^{2+} and Mg^{2+}.

4. APPLICATIONS

In order to assess the possible applications of the proposed method in direct determination of CC in prensence of hydroquinone and resorcin, synthetic sample consisting of CC, hydroquinone and resorcin in local tap water were tested. The determination of samples was carried out at the Ag-PGly/GCE in PBS (pH 5.0). The results are listed in Table1. Quantitative recoveries of 97.5% ~100.5% were obtained.

Table 1. Determination results of CC (n=6)

Samples	CC sample $\times10^{-5}$ mol·L^{-1}	Standard $\times10^{-5}$ mol·L^{-1}	Total $\times10^{-5}$ mol·L^{-1}	Recovery %
1	2.10	2.00	4.05	97.5
2	4.01	2.00	6.02	100.5
3	6.54	2.00	8.50	98.0

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