Preparation of Poly-(*p*-aminobenzoic acid)/Multiwall Carbon Nanotubes Composite Film Modified Glassy Carbon Electrode and Application to Detect Catechol and Hydroquinone Simultaneously

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ABSTRACT

The electrochemical reaction of catechol (CC) and hydroquinone (HQ) was investigated at poly-(*p*-aminobenzoic acid) (*p*-ABA)/multiwall carbon nanotubes (MWCNTs) composite film modified glassy carbon (GC) electrode via cyclic voltammetry (CV). Separation of the peak potentials for CC and HQ was about 105 mV in 0.1 mol/L H₂SO₄, which makes it suitable for simultaneous determination of these compounds. Under optimized conditions, the oxidation current of CC and HQ have been enhanced linearly with the concentration in the range of 1×10^{-5} – 1×10^{-3} mol/L ($r = 0.9979$) and 1×10^{-5} – 1×10^{-3} mol/L ($r = 0.9948$), with the detection limit of CC and HQ 4×10^{-6} and 2.7×10^{-6} mol/L, respectively. The proposed method has been applied to determine CC and HQ simultaneously with good results, which shows excellent stability and reproducibility.

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Keywords : Poly-(*p*-aminobenzoic acid), Multiwall Carbon Nanotubes, Catechol, Hydroquinone

1. Introduction

Phenolics are widely used chemical materials, and also a class of organic pollutants that are harmful to both humans and environment. Therefore, it is of great significance to study a fast, easy, accurate detection method. Catechol (CC) and hydroquinone (HQ) are each other's isomers, their physical and chemical properties are very similar, so they are difficult to separate and analyze quantitatively by chemical or physical methods. At present, the determination of dihydroxybenzene isomers have been performed with spectrophotometry,^{1,2} high performance liquid chromatography,³ fluorescence spectrometry⁴ and capillary electrophoresis⁵ and so on. However, these methods usually require pretreatment of samples, complicated operation, a large quantities of reagent, and are not suitable for field test.

CC and HQ have electrochemical activity, easily oxidized, so they are available for electrochemical detection methods.^{6,7} However, there is a great number of challenges for the simultaneous determination of CC and HQ. One major difficulty is that voltammetric peaks corresponding to the oxidation peaks of the two phenol isomers are seriously overlapped on most conventional solid electrode.^{8,9} In addition, their competitive adsorption at the electrode surface makes the relationship between the voltammetric response and concentration in the mixtures nonlinear.¹⁰ In order to solve these problems, many chemical modified electrodes were prepared for the simple, non-separate and simultaneous determination of isomers, such as carbon nanotubes modified electrode¹¹ and poly (glutamic acid) modified electrode.¹²

Polymer-modified electrodes (PMEs) have received attention in recent years,^{13,14} due to their good stability, reproducibility and homogeneity in electrochemical deposition and strong adherence to electrode surface. Electro-polymerization is a nice approach to immobilize polymers on electrodes by adjusting the electrochemical parameters to control the film thickness, permeation and charge transport characteristics.

In this article, we prepared firstly the poly-(*p*-aminobenzoic acid)/MWCNTs composite film via electrochemically polymeriza-

tion of *p*-aminobenzoic acid on the MWCNTs/GC modified electrode to explore the electrochemical behavior of CC and HQ. This kind of modified electrode can effectively catalyze the redox of CC and HQ in the 0.10 mol/L H₂SO₄, which provide a new method to detect CC and HQ simultaneously with satisfactory results.

2. Experimental

2.1 Apparatus and reagents

Electrochemical experiments were performed with a CHI650 electrochemical workstation (USA, CHI). A conventional three-electrode system was used where glassy carbon (GC) electrode (3 mm diameter) or chemically modified GC electrodes, rotating platinum wire electrode and a Ag/AgCl (saturated KCl) were used as working, counter and reference electrodes, respectively. All potentials in this work referred to this reference electrode.

Multi-walled carbon nanotubes (MWCNTs) (Diameter 10–15 nm, University of Marburg, Germany, Department of Chemistry, Materials Science Center), *p*-aminobenzoic acid (*p*-ABA) (fluka), N,N-dimethylformamide (DMF) (Kermel, Tianjin Chemical Reagent Co., Ltd.), Other reagents were of analytical grade and the water were redistilled water.

2.2 Preparation of *p*-p-ABA/MWCNTs modified electrode

GC electrode was polished with 1.0, 0.3, and 0.05 μ m alumina slurry sequentially and then washed ultra-sonically in water and ethanol for a few minutes, respectively, and dried for use.

For the preparation of MWCNTs/GC, 3 μ L of the MWCNTs suspension (1 mg/mL), which was prepared by dispersing the desired amount of purified MWCNTs in DMF with the aid of ultrasonic oscillation, was dropped on GC surface, followed by evaporating the solvent under an infrared lamp. Then the prepared MWCNTs/GC electrode was immersed in a 0.10 mol/L PBS containing 2×10^{-3} mol/L *p*-ABA solution (pH 7.0) and was polymerized by cyclic scanning between -1.5 to $+2.5$ V at 100 mV/s for 10 cycles to obtain the *p*-p-ABA/MWCNTs/GC electrode.

Figure 1. (Color online) Effect of MWCNTs content for catalytic current CC (a) and HQ (b) in 0.1 mol/L H_2SO_4 containing the mixture of 1 mmol/L CC and HQ, scan rate: 50 mV/s.

Before electrochemical measurement, the modified electrode was activated by cyclic voltammetry from -1.0 to $+1.0$ V in 0.10 mol/L PBS (pH 7.0).

3. Results and Discussion

3.1 Optimization of experimental conditions

3.1.1 Optimization of MWCNTs content

The same concentration (1 mg/mL) of MWCNTs with different volume of 3, 6, 9 μL was modified on the bare GC electrode. Then the same procedures were performed for electrochemical polymerization of *p*-ABA on the MWCNTs/GC modified electrode. The catalysis of CC and HQ were studied by the *p*-*p*-ABA/MWCNTs/GC modified electrode. Figure 1 shows that the catalytic current increased with the increase of MWCNTs but reduced when the content of MWCNTs is more than 3 μL . That means the film becomes certain thicker, which hinders the electron transfer and is not conducive enough to react with the substrate. So, 3 μL MWCNTs was chosen as the optimum content.

3.1.2 Optimization of electrochemical polymerization cycles

Cyclic voltammetry was used to form the polymer film. The prepared MWCNTs/GC electrode was electrochemically polymerized with different cycles. Figure 2 showed that the catalytic current increased with the increase of polymerization cycles. But when the polymerization scans was more than 10 cycles, the current almost did not increase. So, 10 cycles of electrochemical polymerization was regarded as the optimum condition.

3.1.3 Choice of base solution

Four kinds of solution were chosen as base solution, which are 0.1 mol/L $\text{K}_2\text{HPO}_4\text{-KH}_2\text{PO}_4$, 0.1 mol/L HAc-NaAc , 0.1 mol/L H_2SO_4 , and 0.1 mol/L HCl . As shown in Table 1, the peak current of the mixed solution of hydroquinone is maximal and the reversibility is the best in H_2SO_4 . So we choose the 0.1 mol/L H_2SO_4 as the optimum base solution.

3.2 Electrochemical performance of the sensor

The electro-catalytic activity of the *p*-*p*-ABA/MWCNTs composite film modified GC was demonstrated by the comparison of the CVs of 1 mmol/L the mixed solution of hydroquinone in 0.1 mol/L H_2SO_4 , experimental results were recorded in Fig. 3 for four different working electrodes. It is clearly that there was only a broad redox peak of curve a, indicating that the redox peaks of CC and HQ overlapped at bare GC. Except for the bare GC electrode, two pairs

Figure 2. (Color online) Effect of electrochemical polymerization scans for CC (a) and HQ (b) in 0.1 mol/L H_2SO_4 containing the mixture of 1 mmol/L CC and HQ, the inserted chart is the electrochemical polymerization of *p*-ABA figure, scan rate: 50 mV/s.

Table 1. Peak current and peak potential of CC (A) and HQ (B) in different base solution.

A	E _{pa} (mV)	I _{pa} (μA)	E _{pc} (mV)	I _{pc} (μA)	ΔE_p (mV)
H_2SO_4	573.9	175.7	537.2	88.8	36.7
HCl	555.6	168.8	516.4	75.0	39.2
HAc-NaAc	430.0	123.6	300.7	68.1	129.3
$\text{K}_2\text{HPO}_4\text{-KH}_2\text{PO}_4$	397.3	113.9	291.5	62.1	105.8

B	E _{pa} (mV)	I _{pa} (μA)	E _{pc} (mV)	I _{pc} (μA)	ΔE_p (mV)
H_2SO_4	470.5	164.9	432.7	125.7	37.8
HCl	453.6	170.6	414.4	118.5	39.2
HAc-NaAc	325.5	115.8	172.5	105.8	153.0
$\text{K}_2\text{HPO}_4\text{-KH}_2\text{PO}_4$	281.1	117.2	155.6	105.0	125.5

of peaks are exhibited, which indicate that the oxidation and reduction peaks of CC and HQ can be separated at other three modified electrodes. And, at the MWCNTs/GC electrode (curve b), two pairs of peaks are exhibited, which indicate that the oxidation and reduction peaks of CC and HQ can be separated, but the peaks current are rather small. Although both the oxidation and the reduction peaks of CC and HQ separate well at *p*-*p*-ABA/GC electrode (curve c), their peak currents are still smaller than those at *p*-*p*-ABA/MWCNTs/GC (curve d).

Obviously, it can be observed that the peak current at *p*-*p*-ABA/MWCNTs/GC electrode is nearly two times higher than the response currents at MWCNTs/GC electrode and increased by 10% for the *p*-*p*-ABA/GC electrode. The reversibility of CC and HQ were significantly improved together with the current signal increasing. For CC, the oxidation peak potential negatively shifts to 574 mV and the reduction peak positively shifts to 537 mV with $\Delta E_p = 37$ mV; For HQ, the oxidation peak potential negatively shifts to 471 mV and the reduction peak positively shifts to 433 mV with $\Delta E_p = 38$ mV. The peak-to-peak potential separation between CC and HQ was 105 mV.

Figure 3. (Color online) Cyclic voltammograms of the mixture of 1 mmol/L CC and HQ in the 0.1 mol/L H_2SO_4 at different electrodes, (a) GC, (b) MWCNTs/GC, (c) p-p-ABA/GC, and (d) p-p-ABA/MWCNTs/GC, scan rate: 50 mV/s.

Figure 4. (Color online) Cyclic voltammograms of p-p-ABA/MWCNTs/GC electrode at different scan rates (mV/s) of CC and HQ in the range at a–j: 10, 25, 50, 75, 100, 125, 150, 175, 200, 250.

The improvement of peak current together with sharpness of the peak clearly demonstrated that the p-p-ABA/MWCNTs composite film acts as an efficient promoter to enhance the electrochemical process, which is probably caused by the synergistic effect of the electro-catalytic property of p-p-ABA and MWCNTs. These results indicate that the p-p-ABA/MWCNTs composite film modified electrode can not only identify the CC and HQ simultaneously, but also improve the detection sensitivity.

3.3 Influence of scan rate

The scan rate dependence of peak current for the p-p-ABA/MWCNTs/GC electrode is presented in Fig. 4. It is clear that the anodic peak grew continuously with scan rate increasing. There is a good linear relationship between peak current and the square root of the scan rate ($v^{1/2}$) from 10 to 100 mV/s. The regression equations were $i_p = -0.45158 + 0.23896v^{1/2}$ ($r = 0.9963$) for CC and $i_p = -0.5608 + 0.26075v^{1/2}$ ($r = 0.9963$) for HQ, demonstrating the diffusion controlled process of CC and HQ at the p-p-ABA/MWCNTs/GC electrode at lower scan rates. However, there is a good linear relationship between peak current and the scan rate (v)

Figure 5. (Color online) CV of various concentrations of CC and HQ both from 1.0×10^{-5} to 1.0×10^{-3} mol/L in 0.1 mol/L H_2SO_4 : (a) 0 mol/L, (b) 1.0×10^{-5} mol/L, (c) 2.0×10^{-5} mol/L, (d) 4.0×10^{-5} mol/L, (e) 6.0×10^{-5} mol/L, (f) 8.0×10^{-5} mol/L, (g) 1.0×10^{-4} mol/L, (h) 2.0×10^{-4} mol/L, (i) 4.0×10^{-4} mol/L, (j) 6.0×10^{-4} mol/L, (k) 8.0×10^{-4} mol/L, (l) 1.0×10^{-3} mol/L, scan rate: 50 mV/s.

from 125 to 250 mV/s. The regression equations were $i_p = 0.99079 + 0.0111v$ ($r = 0.9991$) for CC and $i_p = 0.82118 + 0.01375v$ ($r = 0.9996$) for HQ, which strongly suggested that the redox reactions of CC and HQ were surface adsorption controlled at higher scan rates.

3.4 Simultaneous determination of CC and HQ

The utilization of the p-p-ABA/MWCNTs/GC for the simultaneous determination of CC and HQ was demonstrated by changing their concentration. As shown in Fig. 5, a linear ranges for concentration of CC and HQ were 1.0×10^{-5} – 1.0×10^{-3} mol/L and 1.0×10^{-5} – 1.0×10^{-3} mol/L with the linear equations of $i_p = 4.87502 + 11.5799c$ ($r = 0.9979$) and $i_p = 7.06337 + 8.28607c$ ($r = 0.9948$), respectively. The relative standard deviations of CC and HQ were 2.11 and 0.26% ($n = 6$, $c = 0.6$ mmol/L), respectively. When the signal to noise ratio is 3, the detection limits of CC and HQ were 4.0×10^{-6} and 2.7×10^{-6} mol/L respectively.

The p-p-ABA/MWCNTs/GC modified electrode was studied by continuous cyclic voltammetry for 50 cycles in 0.6 mmol/L mixed solution of hydroquinone. The peak current is almost unchanged. And, the redox peak currents of CC and HQ did not change after keeping the electrode in air for a month. This demonstrated that the modified electrode has a good stability.

For oxidation peak current, in the mixed sample containing 0.6 mmol/L CC and HQ, the relative standard deviations (RSD) of 6 successive parallel determinations were 2.11% for CC and 0.26% for HQ, respectively. This showed that the electrode has good reproducibility. The excellent stability and reproducibility of the composite modified electrode make them attractive for the fabrication of electrochemical sensors.

3.5 Analytical application

Under the optimal conditions, the p-p-ABA/MWCNTs/GC modified electrode was used for the detection of CC and HQ in 0.1 mol/L H_2SO_4 . According to the blank standard addition method, we added different concentrations of the mixed solution of hydroquinone to the electrolytic cell, then determined their contents and calculated their recoveries. As shown in Table 2, the recovery of CC and HQ were 98.8–108.2% and 98.0–114.5%, and the average recovery of CC and HQ were 104.8 and 108.2%, respectively. It

Table 2. Recovery of the p-*p*-ABA/MWCNT/GC modified electrode (A) recovery of CC, (B) recovery of HQ.

A			
Added/ (10 ⁻⁴ mol/L)	Measured value/ (10 ⁻⁴ mol/L)	Recovery (%)	Average recovery (%)
2.00	2.13	106.5	104.8
4.00	4.23	105.8	
6.00	6.49	108.2	
8.00	7.9	98.8	

B			
Added/ (10 ⁻⁴ mol/L)	Measured value/ (10 ⁻⁴ mol/L)	Recovery (%)	Average recovery (%)
2.00	2.29	114.5	108.2
4.00	4.35	108.8	
6.00	6.69	111.5	
8.00	7.84	98.0	

shows that the proposed method can be efficiently used for the determination of CC and HQ simultaneously.

A comparison of the proposed method with the recent reports was listed in Table 3, which indicated that the proposed electrode is superior to the existing electrodes because of its reversibility, stability, reproducibility and ability to effectively determine CC and HQ simultaneously.

4. Conclusion

The present study demonstrates an excellent approach for the simultaneous determination of CC and HQ based on p-*p*-ABA/MWCNTs composite film modified GC electrode. The improvement

of peak current together with sharpness of the peak shape clearly demonstrated that the p-*p*-ABA/MWCNTs/GC composite film acts as an efficient promoter to enhance the electrochemical process, which is probably caused by the synergistic effect of the electrocatalytic property of p-*p*-ABA and MWCNTs. The excellent continuous stability and reproducibility of the composite modified electrode make them attractive for the fabrication of electrochemical sensors and potential applications.

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Table 3. The reversibility, reproducibility, and stability of the proposed electrode and the reported methods.

Reference	ΔE_p (mV)		ΔE_p between CC and HQ (mV)	RSD (%)		Stability	Method
	CC	HQ		CC	HQ		
15	33	32	104	—	—	a month	DPV
16	44	55	103	—	—	a week	DPV
17	84	80	—	1.47	1.82	—	SWV
18	47	49	—	0.73	0.61	i_p reduced 5% after 20 cycles	DPV
19	56	63	—	0.31	0.37	i_p reduced 2% after 40 cycles	DPV
20	31	33	108	—	—	—	DPV
21	60	55	105	2.8	2.2	a month	DPV
22	—	—	—	1.71	1.52	3 week	DPV
23	—	—	96	—	—	15 days	DPV
This work	37	38	105	2.11	0.26	i_p unchanged after 50 cycles or a month later	CV