

Simultaneous Determination of Hydroquinone and Catechol by Poly (L-methionine) Coated Hydroxyl Multiwalled Carbon Nanotube Film

¹ Ying Zhang, Jingzhan Huang, Guifang Jiang,
Zhong-Rong Song, ^{2*} Zhigang Xie

¹ Chemistry and Chemical Engineering College, Chongqing University, Chongqing 400030, China

^{2*} Chongqing Key Laboratory of Environmental Materials & Remediation Technologies,
Chongqing University of Arts and Sciences, Yongchuan 402160, China

Tel.: 18883882801

E-mail: zy19900628zy@163.com

Received: 17 April 2014 / Accepted: 30 June 2014 / Published: 31 July 2014

Abstract: A simply and high selectively electrochemical method has been developed for the simultaneous determination of hydroquinone and catechol at a glassy carbon electrode modified with the poly L-methionine/multiwall carbon nanotubes, which significantly increased the reversible electrochemical reaction. The electrochemical behavior of catechol and hydroquinone at the modified electrode was studied by cyclic voltammetry and differential pulse voltammetry. The presence of hydroxyl MWCNTs in the composite film enhances the surface coverage concentration of poly L-methionine/multiwall carbon nanotubes. The results suggest that pH=6 is the optimum acidity condition for the selective and simultaneous determination of catechol and hydroquinone. Under the optimized condition, the response peak currents of the modified electrodes were linear over ranges of $8.0 \times 10^{-7} \sim 2.0 \times 10^{-4}$ mol/L ($R^2=0.997$) for hydroquinone and $8.0 \times 10^{-7} \sim 2.0 \times 10^{-4}$, $R^2=0.997$ for catechol. The sensor also exhibited good sensitivity with the detection limit of 8.0×10^{-8} mol/L and 1.0×10^{-7} mol/L for hydroquinone and catechol, respectively. This study provides a new kind of composite modified electrode for electrochemical sensors with good selectivity and strong anti-interference. It has been applied to simultaneous determination of hydroquinone and catechol in water sample with simplicity and high selectivity. Copyright © 2014 IFSA Publishing, S. L.

Keywords: Poly (L-methionine), MWCNTs, Hydroquinone, Catechol.

1. Introduction

Hydroquinone (HQ) and catechol (CT) are two important phenolic compounds, often coexist as isomers in environmental samples. Simultaneous determination of HQ and CT levels are of great necessary due to their high toxicity and low degradability [1]. However, it is a challenge to directly simultaneously measure the concentrations of the two isomers because the separation of oxidation peak potential between the two dihydroxybenzene

isomers is too narrow, resulting in poor selectivity. Up to now, many reported detection methods such as capillary electrophoresis [2], enzymatic method [3], synchronous fluorescence [4, 5], spectrophotometry [6], high-performance liquid chromatography (HPLC) and chemiluminescence [7, 8] have been developed for the selective determination of HQ and CT. However, most of them are operating complicated, expensive and suffer from sensitivity as well as reproducibility. Thus, it is favorably necessary to develop a rapid, accurate and trace

analytical method without previous separations of these compounds. Compared with the methods mentioned above, electrochemical methods are considered as suitable complementary tools for the detection of HQ and CT due to its simple operation, highly sensitive and fast response [9-12].

The glassy carbon electrode coated with multiwall carbon nanotubes (MWCNTs) film was fabricated, but the back-ground current was relatively high and the redox peaks were not obvious in the cyclic voltammograms [13]. The selectivity and sensitivity of the modified electrodes depends on the stability of the phenoxy radicals produced in the enzyme reaction, the electrode materials as well as the immobilization methods. The performance of the modified electrodes is mainly dominated by the electrocatalytic activity of the modified electrode materials and composites [14, 15]. In recent years, polymer modified electrodes have attracted more attention since controlling the thickness of chemically stable and homogeneous film can be prepared by electropolymerization methods [16-18]. The incorporation of MWCNTs into a polymer matrix results in the formation of new composite materials that properties of the individual components have excellent synergistic effects. To our best knowledge, the simultaneous determination of HQ and CT at poly L-methionine/multiwall carbon nanotubes (PLM/ MWCNTs) modified electrode has not been reported.

In this paper, an electrochemical method for the simultaneous determination of HQ and CT was developed based on the corresponding oxidation peak currents of HQ and CT at a PLM/MWCNTs modified electrode. The proposed method has been applied to selective determination of HQ and CT in a water sample with satisfactory results.

2. Experimental

2.1. Apparatus and Reagents

Electrochemical experiments were performed with a LK2005A Electrochemical Workstation (Tianjin Lanlike Co., Ltd., China). A KQ 3200 Ultrasonic cleaner and a PHS-3C pH meter were used. Field emission scanning electron microscope (SEM) images was obtained with focused ion beam scanning electron microscopy (ZEISS AURIGA FIB/SEM). L-methionine was obtained from Tongda amino acids (Shanghai, China), HQ and CT were purchased from Sinopharm Chemical Reagent Co., Ltd., China. All other chemicals were analytical reagent grade and used without further purification and double-distilled water was used throughout. 0.10 mol/L phosphate buffered solution (PBS) was prepared from 0.10 mol/L KH_2PO_4 and 0.10 mol/L K_2HPO_4 and NaOH were used to control the pH. All the experiments were performed at room temperature (25 ± 0.5 °C).

2.2. Preparation of PLM/MWCNTs Modified Electrode

GCE ($\Phi=3$ mm) was polished on a wet metallographic sandpaper (size 1000), then, polished with 0.3 μm and 0.05 μm alumina/water slurry on a polishing cloth to a mirror-like finish, respectively. After that, the polished GCE was rinsed with water, acetone, absolute ethyl alcohol, and water for 5 min, respectively. Then, the electrode was placed in 1×10^{-3} mol/L L-methionine solution (pH=7.0, PBS), which was treated with cyclic scanning between -1.0 and 2.7 V at a scan rate of 100 mV/s, 12 times. Then PLM/GCE modified electrode was ready for using. 25 mg of MWCNTs was dispersed with the aid of ultrasonic agitation in 25 mL of N-N-dimethylformamide (DMF) to give 1 mg/mL black suspension. Different volumes of 1 mg/mL black suspension were cast on the surface of PLM/GCE modified electrode and then the solvent DMF was evaporated naturally to obtain MWCNTs/PLM/GCE electrodes.

2.3. General Procedure

The electrochemical properties were characterized by using a three-electrode electrochemical cell without stirring at room temperature. A bare GCE electrode ($d=3$ mm) or PLM/GCE or MWCNTs/PLM/GCE was used as the working electrode, a saturated calomel electrode (SCE) and Pt wire were used as the reference electrode and a counter electrode, respectively. All the potentials in this work were referred to the reference electrode and all electrochemical detection were carried out on an LK2005A instrument. Field emission scanning electron microscope (SEM) images was obtained with focused ion beam scanning electron microscopy (ZEISS AURIGA FIB/SEM), Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were employed for examining the electrochemical signal of bare GCE and the modified electrodes to a certain amount of HQ and CT in PBS (0.1 mol/L) buffer medium. The experimental parameters of CV is: a scan rate of 100 mV/s and a voltage range of -0.3 to 0.6 V. The DPV conditions were as follows: potential increase, 0.007 V; amplitude, 0.05 mV; pulse width, 0.5 s; pulse interval, 0.5 s. The concentrations of HQ and CT were quantified by the oxidation peak currents.

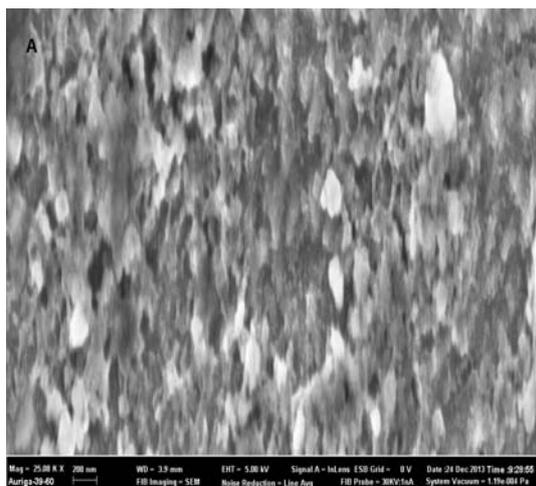
3. Results and Discussion

3.1. Fabrication and Characterization of Different Modified Films

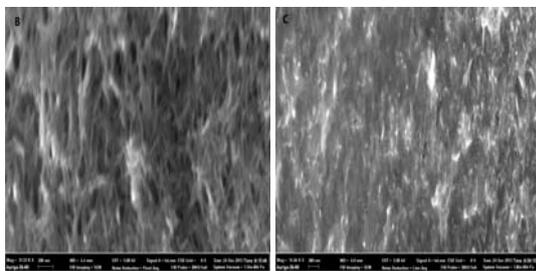
The morphologies and microstructures of the different modified films were investigated by SEM. Comparison of Fig. 1 (a) and Fig. 1 (b) SEM images

shows significant morphological difference between PLM and hydroxyl MWCNTs films.

The PLM/MWCNTs biocomposite film in Fig. 1(c) shows that the plateaus of PLM deposited over hydroxyl MWCNTs to form MWCNTs–PLM biocomposite modified GCE electrode. Absolutely, such an open structure of the film can promote the diffusion of the ions from the electrolyte to the electrode surface [19]. Moreover, the well-combination of hydroxyl MWCNTs with PLM may lead to a large surface area of PLM/MWCNTs modified electrode, which will be conducive to improve the sensitivity of electrochemical sensors.



(a)



(b)

(c)

Fig. 1. SEM image of the PLM (a), hydroxyl MWCNTs (b) and PLM/MWCNTs film (c).

3.2. Electrochemical Characteristics of Different Modified Electrodes

EIS was employed to characterize the electron transfer property of the modified electrode. Fig. 2 shows the Nyquist plot of the bare GCE and 3 kinds of modified electrodes in 1.0 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ solution containing 0.1 M KCl. At high frequencies, a partially formed semicircle attributed to the charge transfer process is observed. And after PLM/MWCNTs was coated on the GCE, the diameter of semicircles decreased distinctly. It is due to the conducting PLM/MWCNTs film with a higher

specific surface area promoting the electron transfer between electrode interface and the solution. So, the deposition of PLM onto MWCNTs can effectively improve the conductivity of the electrode and simultaneously accelerate the electron transfer rate at the solution and electrode interface.

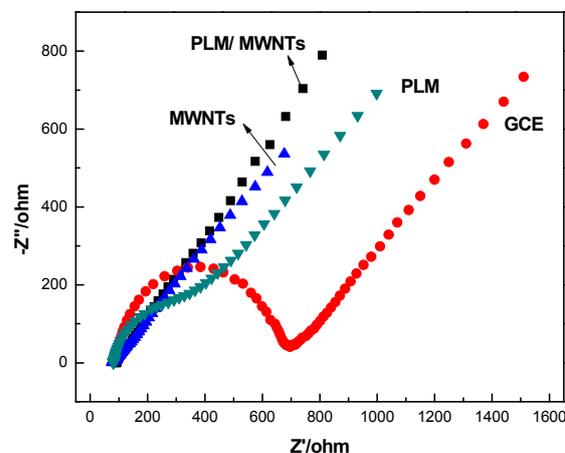


Fig. 2. Nyquist plots of the bare GCE, PLM, MWCNTs and PLM/ hydroxyl MWCNTs in 1.0 mM $[Fe(CN)_6]^{3-/4-}$ solution containing 0.1 M KCl. The frequency range is from 0.1 to 10^6 Hz.

3.3. The Electrochemical Distinction of HQ and CT by MWCNTs/PLM/GCE

To demonstrate the performance of the MWCNTs/PLM/GCE, we compared CVs on the different modified electrodes.

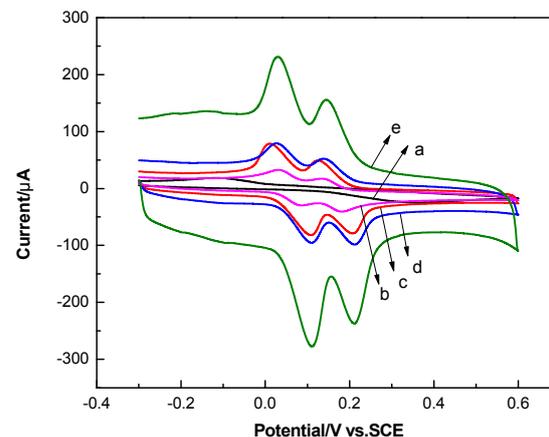


Fig. 3. CVs in PBS containing the mixture of 0.1 mM HQ + 0.1 mM CT at GCE (a), PLM (b), hydroxyl MWCNTs (c), the hydroxyl MWCNTs / PLM /GCE (d), the PLM/MWCNTs /GCE (e). Scan rate: 100 mV/s.

As shown in Fig. 3, a broad and overlapping anodic peak was observed at the bare GCE (curve a). Although the peaks of HQ and CT separated at the PLM/GCE (curve b) and hydroxyl MWCNTs/GCE (curve c), simultaneous determination of the two

substances could not be obtained due to the small response. In contrast, two well-defined voltammetric peaks with a remarkable increasing in peak current for HQ and CT, were observed in PLM/MWCNTs/GCE (curve e), and separations of the peaks were 110 mV between HQ and CC, respectively, which indicated the PLM/MWCNTs modified electrode has more sensitive catalytic effect on electrochemical oxidation of HQ and CT and can be used for both selective and simultaneous determination of HQ and CT. This could be due to several reasons: firstly, the effective electrode surface can be significantly increased following the addition of MWCNTs since the network-like electrodes formed. According to Compton's suggestion, discrimination can be greatly ameliorated between species which oxidize or reduce at similar potentials under planar diffusion condition [20].

3.4. Effect of Cycle Number during PLM/MWCNTs Deposition on the Electrochemical behavior of CT and HQ

To the best of knowledge, the growth of the conducting polymer films on the electrode is successive with the increasing of cycle number of CV. That is to say, the thickness of film depends on the cycling number of CV during electropolymerization [21]. The PLM/MWCNTs films were prepared on the polished GCE over the scan cycle range of 3–15. The effect of PLM film thickness was studied on the electrochemical behavior of HQ and CT by CV. Fig. 4 (a) and Fig. 4 (b) show the variations in the electrocatalytic characteristic of PLM/MWCNTs modified GCE obtained after different cycle numbers toward to HQ and CT.

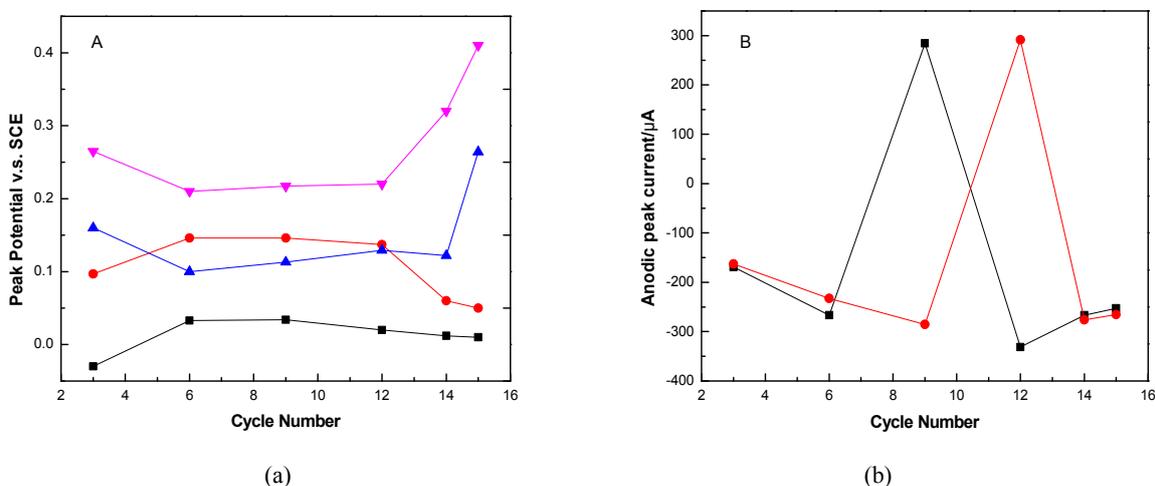


Fig. 4. Dependence of the peak potentials (a) and anodic peak currents (b) of 50 mM HQ and 50 mM CT on the cycle number during the electropolymerization of PLM/MWCNTs.

The anodic peak currents of HQ and CT increase clearly with an increase of film thickness under the cycle number from 3 to 15. Moreover, at the 12th cycle, the ΔE_p of both HQ and CT becomes the lowest value and the peak currents of HQ and CT reaches the maximum. As the cycle number increases further, the electrochemical activity of PLM/MWCNTs film becomes decreasing. It means the charges or electrons of HQ and CT would take longer time to transfer through a thicker PLM/MWCNTs film to the electrode surface. Therefore, the cycle number of 12 for polymerization was chosen for further experiments.

3.5. Effect of Amount of MWCNTs

The effect of amount of MWCNTs was investigated at the electrode surface on the peak currents of HQ and CT varying the volume of MWCNTs of 1.0 mg/mL from 1 μ L to 10 μ L. The results show that both peak current of hydroquinone

and peak current of CT increase greatly with the increasing of amount of hydroxyl MWCNTs, and reached a maximum at 7.0 μ L, and then decreased weakly.

3.6. The Effect of Buffer Solution pH

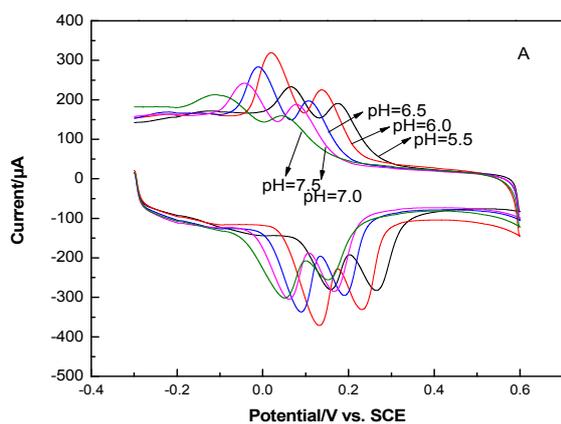
The effect of buffer solution pH on PLM/MWCNTs modified electrode for 5×10^{-4} M HQ and CT(1:1) were investigated in the 0.1 mol/L PBS solutions in a pH range of 5.5–7.5 by CV. It can be found that the E_{pa} values shifted negatively with the increase of solution pH for both HQ and CC (Fig. 5). The linear regression equations for HQ and CT are

$$E_{pa} = 0.5111 - 0.0622 \text{ pH} \quad (R^2 = 0.996) \quad \text{and}$$

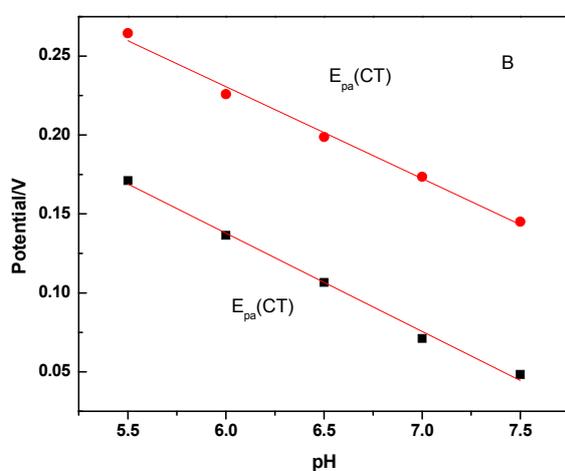
$$E_{pa} = 0.5802 - 0.0583 \text{ pH} \quad (R^2 = 0.993)$$

respectively. These two almost parallel lines indicate that the peak potential difference between HQ and CT is constant. On the other hand, it also means the number of protons and electrons involved in the

redox process of HQ or CT are equal. Furthermore, the slopes of the regression equations are nearly to the theory value of 58.5 mV/pH [22]. Due to the lack of protons, the electrochemical reaction becomes more difficult at high pH value. On the other hand, HQ and CT can easily turn into anions at a high pH and the generating electrostatic repulsion between the dihydroxybenzene isomers and PLM/MWCNTs may lead to the peak current decrease. Thus, the PBS buffer at pH 6.0 was chosen as supporting electrolyte and the optimized value for the electrochemical detection of HQ and CT.



(a)



(b)

Fig. 5. CVs at PLM/MWCNTs in CPS with different pH containing 50 mM HQ and 50 mM CT (a); effect of pH value on the anodic peak potentials and anodic peak currents of HQ and CT (b).

3.7. The Effect of Scan Rate

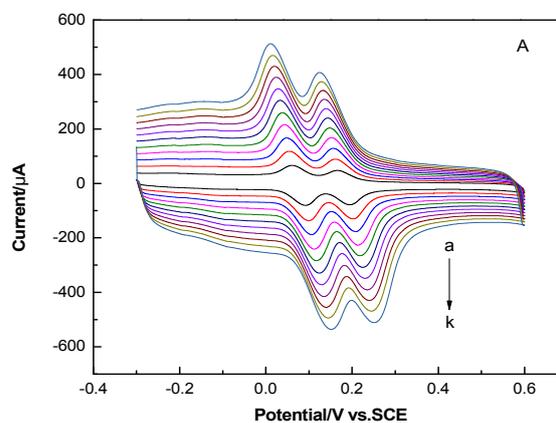
The effect of scan rate at the PLM/MWCNTs modified electrode was investigated by the CV in 0.1 M PBS (pH =6.0) containing of 1×10^{-4} M HQ and CT(1:1) (Fig. 6). The anodic and cathodic peak currents (I_{pa} and I_{pc}) increase with the increasing of the scan rate from 20 to 300 mV/s. In addition, the

oxidation and reduction peaks current of CT and HQ exhibited a good linear relation to the square root of the scan rate with the linear regression equation:

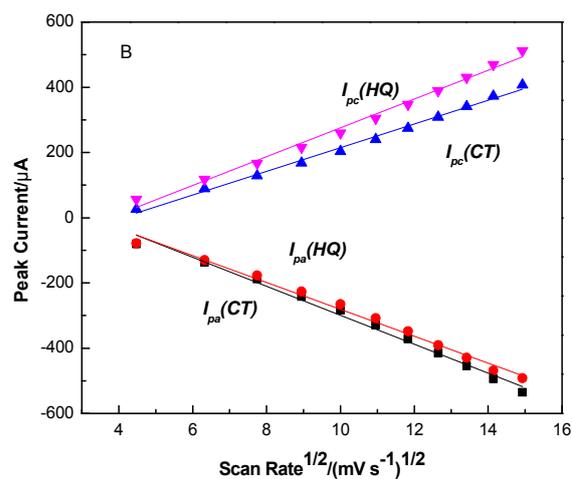
$$I_{pa} \text{ (mA)} = -165.45 + 44.11(\text{mV/s}) (R^2 = 0.991),$$

$$I_{pc} \text{ (mA)} = -148.77 + 36.36(\text{mV/s}) (R^2 = 0.995),$$

suggesting the redox reactions of HQ and CT are diffusion controlled.



(a)



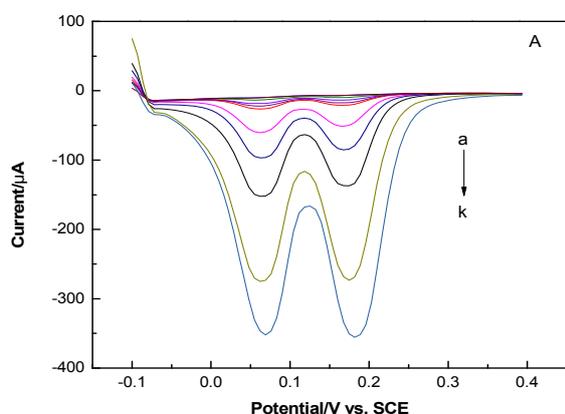
(b)

Fig. 6. CVs of 0.1 mM HQ and 0.1 mM CT at the PLM/MWCNTs /GCE in 0.1 M pH 6.0 PBS at different scan rates: (a–k) 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 220 mV/s.

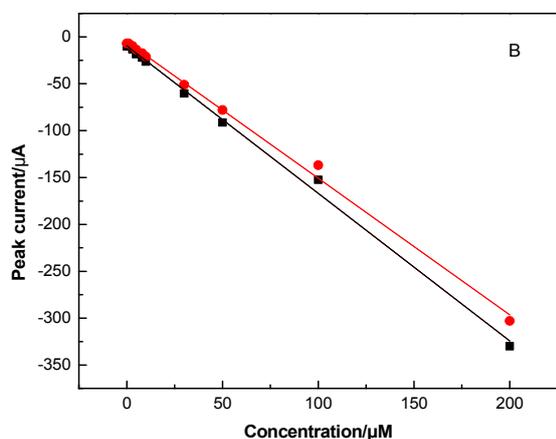
3.8. Simultaneous Determination of HQ and CT

The differential pulse voltammetry (DPV) was performed at PLM/MWCNTs/GCE, while changing the concentrations of HQ and CC simultaneously in pH 6.0 PBS solution. All of the DPV were recorded at a constant time interval of 3 min at room temperature with nitrogen purging before the start of each experiment. Fig. 7(a) and Fig. 7(b) shows the calibration plots constructed from the DPV responses

for HQ and CT in the optimized condition, respectively. The oxidation peak current of hydroquinone vs. hydroquinone concentration was linear in the range from $8.0 \times 10^{-7} \sim 2.0 \times 10^{-4}$ mol/L, and the regression equation is the following: $I_{pc}(\text{mA}) = -1.5747c - 2.423(\mu\text{mol/L})(R^2 = 0.997)$. The detection limit for HQ was 8.0×10^{-8} mol/L ($S/N=3$). The oxidation peak current of catechol vs. catechol concentration was linear in the range from $8.0 \times 10^{-7} \sim 2.0 \times 10^{-4}$ mol/L. The regression equation was $I_{pc}(\mu\text{A}) = -1.4571c - 5.096(\mu\text{mol/L})(R^2 = 0.997)$. The detection limit for CT was 1.0×10^{-7} mol/L ($S/N=3$). All the experimental results show that the work provides a novel method based on PLM/MWCNTs/GCE for the sensitive and simultaneous determination of HQ and CT without interference each other.



(a)



(b)

Fig. 7. DPVs of CT and HQ with different concentrations ((a–n) 0.8, 1, 3, 5, 8, 10, 30, 50, 100 and 200M) (a). Calibration plots constructed from the DPV responses for HQ and CT (b).

3.9. Reproducibility and Interference

Under the optimized conditions, the PLM/MWCNTs modified electrode was used to determine 1×10^{-4} mol/L benzodiazepines mixture for

10 times. The relative standard deviation (RSD) of HQ and CC peak current were 2.1 % and 3.1 %, respectively. The interfering species 100-fold such as Ag^+ , Na^+ , Ni^{2+} , K^+ , NH_4^+ , Pb^{2+} , Ba^{2+} , Co^{3+} , Cu^{2+} , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , I^- , CrO_4^{2-} , Br^- , NO_3^- , glycine, glucose, sulfanilic acid, 20-fold ascorbic acid, 20-fold sucrose had no significant interference to the response of HQ and CC (5×10^{-4} M). What's more, along-term storage stability of the PLM/MWCNTs/GCE was studied by keeping the modified electrode at room temperature. The peak current intensity only decreased 5.21 %, 3.36 % for HQ and CC after two weeks, respectively, which reveals the good stability and reproducibility of the proposed modified electrode.

3.10. Determination of Simulated Water Samples

The PLM/MWCNTs modified electrode was applied for the determination of CT and HQ in water samples. The recovery experiments were performed and the analytical results were listed in Table 1.

Table 1. The recovery of the immunosensor in real samples.

Sample No.	Added (μM)	Found (μM)	Recovery (%)
1	10	10.32	103.2
2	20	20.24	101.2
3	30	29.75	99.1
4	40	40.96	102.4
5	50	48.84	97.7

4. Conclusions

A PLM/MWCNTs modified electrode was prepared by electrochemical polymerization method, showed enhanced electron transfer properties and favorable electrocatalytic performance to the HQ and CT. The results suggest that the calibration curves obtained were linear in the concentration range of $8.0 \times 10^{-7} \sim 2.0 \times 10^{-4}$ mol/L with a detection limit of 8.0×10^{-8} mol/L for HQ ($R^2=0.997$) and $8.0 \times 10^{-7} \sim 2.0 \times 10^{-4}$ with the detection limit of 1.0×10^{-7} mol/L for CT ($R^2=0.997$). In addition, the modified electrode shows excellent electrochemical properties, such as strong anti-interference, wider linear range and favorable stability indicating the film could be used as a promising sensing platform for isomers determination. This work provides a new kind of composite modified electrode for electrochemical sensors and has been applied to simultaneous determination of CT and HQ in a water sample with satisfactory results.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (41101223), Municipal

Education Commission funded project of Chongqing, China (KJ 13122015) and Materials and chemical engineering college, Chongqing University of arts and sciences (y2013020).

References

- [1]. Jun Wang, Jung Nam Park, Xian Yong Wei, et al, Room-temperature heterogeneous hydroxylation of phenol with hydrogen peroxide over Fe^{2+} , CO_2^{+} ion-exchanged Na β zeolite, *Chemical Communications*, Vol. 6, Issue 5, 2003, pp. 628–629.
- [2]. Shaolin Mu, Catechol sensor using poly(aniline-co-o-aminophenol) as an electron transfer mediator, *Biosensors and Bioelectronics*, Vol. 21, Issue 7, 2006, pp. 1237–1243.
- [3]. Oksana Nadzhafova, Matieu Etienneb, Alain Walcarius, Direct electrochemistry of hemoglobin and glucose oxidase in electrodeposited sol–gel silica thin films on glassy carbon, *Electrochemistry Communication*, Vol. 9, Issue 5, 2007, pp. 1189–1195.
- [4]. Weiyang Lin, Ling Liang Long, Wen Tan, A highly sensitive fluorescent probe for detection of benzenethiols in environmental samples and living cells, *Chemical Communication*, Vol. 46, Issue 9, 2010, pp. 1503–1505.
- [5]. Marcelo F. Pistonesi, María Susana Di Nezio, María Eugenia Centurión, et al, Determination of phenol, resorcinol and hydroquinone in air samples by synchronous fluorescence using partial least-squares (PLS), *Talanta*, Vol. 69, Issue 5, 2006, pp. 1265–1268.
- [6]. A. Afkhami, H. A. Khatami. Indirect Kinetic–spectrophotometric determination of resorcinol, catechol, and hydroquinone, *Journal of Analytical Chemistry*, Vol. 56, Issue 5, 2001, pp. 429–432.
- [7]. Lijun Zhao, Baoqiang Lv, Hongyan Yuan, et al, A sensitive chemiluminescence method for determination of hydroquinone and catechol, *Sensors*, Vol. 7, Issue 4, 2007, pp. 578–588.
- [8]. Hua Cui, Qunlin Zhang, Aung Myint, et al, Chemiluminescence of cerium(IV)–rhodamine 6G–phenolic compound system, *Journal of Photochemistry and Photobiology A: Chemistry*, Vol. 181, Issue 2-3, 2006, pp. 238–245.
- [9]. A. J. Saleh Ahammad, Subrata Sarker, Md Aminur Rahman, et al, Simultaneous determination of hydroquinone and catechol at an activated glassy carbon electrode, *Electroanalysis*, Vol. 22, Issue 6, 2010, pp. 694–700.
- [10]. He Zhang, Jinsheng Zhao, Houting Liu, et al, Electrochemical determination of diphenols and their mixtures at the multiwall carbon nanotubes/poly(3-methylthiophene) modified glassy carbon electrode, *Microchimica Acta*, Vol. 169, Issue 3-4, 2010, pp. 277–282.
- [11]. Qiaohui Guo, Jianshe Huang, Puqing Chen, et al, Simultaneous determination of catechol and hydroquinone using electrospun carbon nanofibers modified electrode, *Sensors and Actuators B: Chemical*, Vol. 163, Issue 1, 2012, pp. 179–185.
- [12]. Xuemei Ma, Zhaona Liu, Cuicui Qiu, et al, Simultaneous determination of hydroquinone and catechol based on glassy carbon electrode modified with gold-graphene nanocomposite, *Microchimica Acta*, Vol. 180, Issue 5-6, 2013, pp. 461–468.
- [13]. Honglan Qi, Chengxiao Zhang, Simultaneous determination of hydroquinone and catechol at a glassy carbon electrode modified with multiwall carbon nanotubes, *Electroanalysis*, Vol. 17, Issue 10, 2005, pp. 832–838.
- [14]. R. C. Santana, R. O. Cunha, M. G. Santos, et al, Growth, EPR and optical absorption spectra of L-threonine single crystals doped with Cu^{2+} ions, *Journal of Physics and Chemistry of Solids*, Vol. 68, Issue 4, 2007, pp. 586–593.
- [15]. B. L. Silva, P. T. C. Freire, F. E. A. Melo, et al, High-pressure Raman spectra of L-threonine crystal, *Journal of Raman Spectroscopy*, Vol. 31, Issue 6, 2000, pp. 519–522.
- [16]. Yogeswaran Umasankar, Arun Prakash Periasamy, Shen-Ming Chen, Electrocatalysis and simultaneous determination of catechol and quinol by poly(malachite green) coated multiwalled carbon nanotube film, *Analytical Biochemistry*, Vol. 411, Issue 1, 2011, pp. 71–79.
- [17]. Seyda Korkut, Bulent Keskinler, Elif Erhan, An amperometric biosensor based on multiwalled carbon nanotube-poly(pyrrole)-horseradish peroxidase nanobiocomposite film for determination of phenol derivatives, *Talanta*, Vol. 76, Issue 5, 2008, pp. 1147–1152.
- [18]. Haiying Du, Jing Wang, Pengjun Yao, et al, Preparation of modified MWCNTs-doped PANI nanorods by oxygen plasma and their ammonia-sensing properties, *Journal of Materials Science*, Vol. 48, Issue 9, 2013, pp. 3597–3604.
- [19]. Weimeng Si, Wu Lei, Yuehua Zhang, et al, Electrodeposition of graphene oxide doped poly(3,4-ethylenedioxythiophene) film and its electrochemical sensing of catechol and hydroquinone, *Electrochimica Acta*, Vol. 85, Issue 15, 2012, pp. 295–301.
- [20]. Fangxin Hu, Shihong Chen, Chengyan Wang, et al, ZnO nanoparticle and multiwalled carbon nanotubes for glucose oxidase direct electron transfer and electrocatalytic activity investigation, *Journal of Molecular Catalysis B: Enzymatic*, Vol. 72, Issue 3-4, 2011, pp. 298–304.
- [21]. Claudine Y. Lumibao, L. M. Viranga Tillekeratne, Jon R. Kirchhoff, Electrochemical and electrocatalytic properties of imidazole analogues of the redox cofactor pyrroloquinoline quinone, *Electroanalysis*, Vol. 20, Issue 20, 2008, pp. 2177–2184.
- [22]. Bankim J. Sanghavi, Ashwini K. Srivastava, Simultaneous voltammetric determination of acetaminophen, aspirin and caffeine using an in situ surfactant-modified multiwalled carbon nanotube paste electrode, *Electrochimica Acta*, Vol. 55, Issue 28, 2010, pp. 8638–8648.