Int. J. Electrochem. Sci., 2 (**2007**) 216 - 225

International Journal of ELECTROCHEMICAL SCIENCE
www.electrochemsci.org

Electrocatalytic Response of Hydroquinone and Catechol at Polyglycine Modified Glassy Carbon Electrode

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Received: 4 January 2007 / *Accepted:* 29 January 2007 / *Published:* 1 March 2007

Glassy carbon electrode (GCE) was modified with electropolymerized films of polyglycine. This polyglycine modified electrode was used to simultaneous electrochemical detection of hydroquinone (HQ) and catechol (CC) and showed an excellent electrocatalytical effect on the oxidation of HQ and CC by cyclic voltammetry (CV) in 0.1 M acetate buffer solution (pH 5.0). In differential pulse voltammetric (DPV) measurements, the polyglycine modified electrode could separate the oxidation peak potentials of HQ and CC present in binary mixtures by about 103 mV though the bare electrode gave a single broad response. A successful elimination of the fouling effect by the oxidized product of HQ on the response of CC has been achieved at the polyglycine modified electrode. The detection limit of HQ in the presence of 0.1 mM CC was 1.0×10^{-6} M and the detection limit of CC in the presence of 0.1 mM HQ was 5.0×10^{-7} M. The proposed method has been applied to simultaneous detection of HQ and CC in a water sample with simplicity and high selectivity.

Keywords: Polymer film modified electrodes; Electrochemistry; Glycine; Hydroquinone; Catechol

1. INTRODUCTION

The simultaneous detection of isomers is an interesting subject in electroanalysis [1-5]. The increasing demand for it has led to the development of a rapid, simple and non-separation method for the simultaneous detection of isomers where the chemically modified electrodes (CMEs) have emerged as an efficient and versatile approach, and have attracted considerable attention over the past decades due to its advantages in terms of reduced costs, automatic and fast analysis, high sensitivity and selectivity [6-8].

Hydroquinone (HQ) and catechol (CC) are phenolic compounds and often coexist as isomers in environmental samples. The simultaneous detection of HQ and CC is highly desirable due to their

coexistence as isomers and highly toxic environmental pollutants in environmental samples [9]. The established methods for the detection of HQ and CC are commonly performed after pretreatment and separation. This sample pretreatment and separation, as well as the significant operating complexity, the long times required and the large volumes of reagents consumed by established techniques, make it important to develop a new method capable of simultaneous detection without the need for prior separation of these compounds.

HQ and CC have a basic quinone structures that might be electrochemically oxidized at a platinum or carbon electrodes [8]. The oxidation process to quinone has been widely studied from electrochemical point of view [10-11]. But so many difficulties are existed to simultaneously determine HQ and CC. The major difficulty is that the voltammetric peaks corresponding to oxidation/reduction of two phenol isomers are, in many cases, highly overlapped. Moreover, the competition of the phenolic isomers by electrode surface makes the relationship between the voltammetric response and the isomers concentrations, in the mixtures, non-linear [12]. Recently, an enormous amount of research has been devoted to the development of new chemically modified electrodes for monitoring HQ or CC [13-21]. Among various chemically modified electrodes, polymer-modified electrodes (PMEs) are promising approach to detection of isomers.

Polymer-modified electrodes prepared by electropolymerization have received extensive interest in the detection of analytes because of their selectivity, sensitivity and homogeneity in electrochemical deposition, strong adherence to electrode surface and chemical stability of the films [22-24]. Selectivity of PMEs as a sensor can be attained by different mechanisms such as size exclusion [25], ion exchange [26], hydrophobicity interaction [27] and electrostatic interaction [28-32]. Up to the present, few literatures for the simultaneous detection of HQ and CC using PMEs have been reported. To our best knowledge, the simultaneous detection of HQ and CC at polyglycine modified electrode has not been reported.

In an effort to develop a voltammetric method for the simultaneously selective and sensitive detection HQ and CC, the present work employed a GCE which was modified with polyglycine. The polyglycine modified electrode could be used as a new sensor for selective and sensitive detection of HQ and CC in binary mixtures by successful elimination of the fouling effect by the oxidized product of HQ on the response of CC. The proposed method has been applied to simultaneous detection of HQ and CC in a water sample with simplicity and high selectivity.

2. EXPERIMENTS

2.1. Reagents

$_{DL}$-glycine was purchased from Shanghai Biochemical Institute (Shanghai, China) and it was used as received. Hydroquinone and catechol were obtained from Beijing Chemical Factory (Beijing, China). All other chemicals were of analytical grade and were used without further purification. A 0.1 M acetate buffer solution (ABS) was used to control the pH. All solutions were prepared with deionized water treated in a Millipore water purification system (Millipore Corp.). All experiments were carried out at room temperature.

2.2. Apparatus

Voltammetric measurements were performed with a CHI 440 electrochemical analyzer (CH Instruments, Chenhua Co. Shanghai, China). A conventional three-electrode cell was used, including a saturated calomel electrode (SCE) as reference electrode, a platinum wire counter electrode and a bare or modified glassy carbon disk working electrode (GCE). The pH values were measured with a PB-10 pH meter (Satorius). Unless otherwise stated, the electrolyte solutions were thoroughly degassed with N_2 and kept under a N_2 blanket.

2.3. Preparation of polyglycine modified glassy carbon electrode

Polyglycine modified glassy carbon electrode was prepared according to the literature [33]. Typically, prior to electrochemical modification, the bare GCE with a diameter of 3 mm was polished with diamond pastes and alumina slurry down to 0.05 μm on a polishing cloth (Buehler, Lake Bluff, IL). Then it was rinsed with water and sonicated in 1 +1 HNO_3, acetone and water for 3 min, respectively. After being cleaned, the electrode was then placed in 0.01 M glycine solution (pH 7.0 phosphate buffer solution) which was previously deaerated with high purity nitrogen for 10 min. The electrode was treated with cyclic scanning between -0.5 and 1.8 V at a scan rate of 100 mV s^{-1}, four times. A uniform adherent blue polymer was found on the GCE surface. After modification, the modified electrode was electroactivated by cyclic voltammetry from -0.2 to 0.8 V at 100 mV s^{-1} in pH 5.0 ABS. Then the electrode was ready for use after the final washing with water.

3. RESULTS AND DISCUSSION

3.1. Electrocatalytic response of HQ at the polyglycine modified electrode

Fig. 1A shows the cyclic voltammograms (CVs) at bare GCE (Fig. 1A curve a) and polyglycine modified electrode (Fig. 1A curve c) in presence of 0.10 mM HQ in ABS pH 5.0 at a scan rate of 100 mV s^{-1}. At the bare electrode, the oxidation and reduction of HQ result in broad waves with the corresponding peak potentials of 222 mV and 92 mV. So it shows irreversible behavior with ΔE_p, the difference between the anodic peak potential (E_{pa}) and the cathodic peak potential (E_{pc}), 130 mV. However, at the polyglycine modified electrode, the reversibility of HQ is significantly improved together with the current signal increasing. The oxidation peak potential negatively shifts to 207 mV and the reduction peak positively shifts to 152 mV with ΔE_p = 55 mV. The peak current is 5.58-fold larger than the corresponding one at the bare GCE. These suggest that the polyglycine can act as a promoter to enhance the electrochemical reaction. Polyglycine, itself, is electroinactive in the potential rage from -0.2 to 0.6 V (Fig. 1A curve b). Due to the high porosity of the polyglycine, the real surface area of the modified electrode is far greater than that of bare GCE. So the peak current increases evidently together with the background voltametric response at the polyglycine-coated GCE stronger than that at the bare surface.

Fig. 1B shows the CVs of HQ at the polyglycine modified electrode at different scan rates. The oxidation peak potential was observed to shift positively with the increase in scan rate, and in addition,

exhibited a linear relation to the square root of the scan rate, $v^{1/2}$, with the linear regression equation i_{pa} / μA= -12.7992 + 3.5077 $v^{1/2}$ / (mV s^{-1}) $^{1/2}$ (correlation coefficient, r=0.9978). The result indicates that the oxidation of HQ at the polyglycine modified electrode is a diffusion-controlled process.

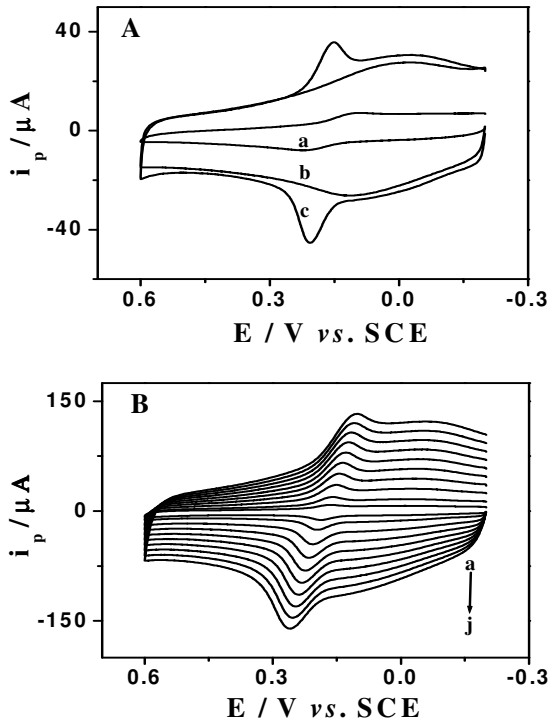

Figure 1. (A) Cyclic voltammograms at bare GCE (a) and polyglycine modified electrode (b, c) in presence of 0.1 mM HQ (a, c) and in the absence of HQ (b) in 0.1 M ABS (pH 5.0); scan rate,100 mV s^{-1}. (B) Cyclic voltammograms of 0.1 mM HQ at polyglycine modified electrode in 0.1 M ABS (pH 5.0) at different scan rates: (a) 20 mV s^{-1}; (b) 50 mV s^{-1}; (c) 100 mV s^{-1}; (d) 150 mV s^{-1}; (e) 200 mV s^{-1}; (f) 250 mV s^{-1}; (g) 300 mV s^{-1}; (h) 350 mV s^{-1}; (i) 400 mV s^{-1}; (j) 450 mV s^{-1}.

The effect of the pH value of ABS on the response of HQ was investigated by CV. The response of HQ is well-behaved in ABS, as the solution pH increases, the anodic peak potential shifts to the negative and the potential of E_{pa} *vs.* pH in ABS has a good linear relation in the range of pH 3.01 - 6.93. The linear regression equation E_{pa} / V = 0.4126 – 0.0514 pH (correlation coefficient, r = 0.9987) was obtained, which showed that the uptake of electrons is accompanied by an equal number of protons.

3.2. Electrocatalytic response of CC at the polyglycine modified electrode

The CVs of CC at polyglycine modified electrode is also compared with that at bare GCE. Fig. 2A shows the CVs at bare GCE (Fig. 2A curve a) and polyglycine modified electrode (Fig. 2A curve c) in presence of 0.10 mM CC in ABS pH 5.0 at a scan rate of 100 mV s^{-1}. At the bare electrode, the

oxidation and reduction of CC result in broad waves with the corresponding peak potentials of 326 mV and 208 mV. So it shows irreversible behavior with ΔE_p, 118 mV. However, at the polyglycine modified electrode, the reversibility of CC is significantly improved together with the current signal increasing. The oxidation peak potential negatively shifts to 308 mV and the reduction peak positively shifts to 264 mV with ΔE_p = 44 mV. The peak current is 4.40-fold larger than the corresponding one at the bare GCE. These results indicated that polyglycine can accelerate the rate of electron transfer of CC by a nonmediation mechanism in pH 5.0 ABS, and may be called a promoter.

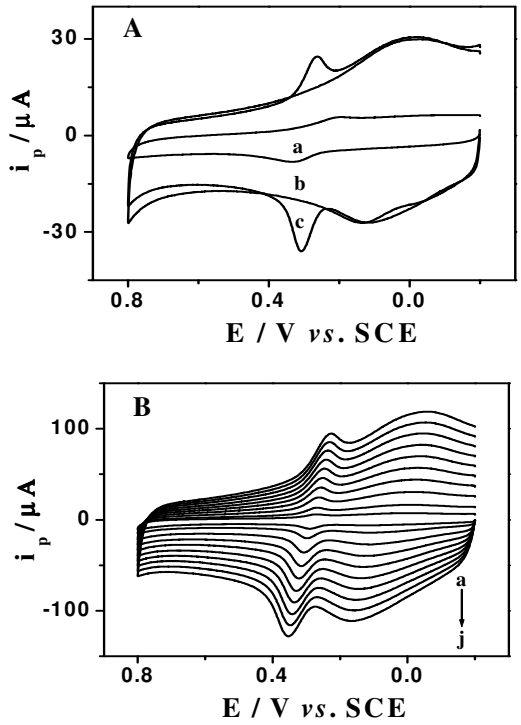

Figure 2. (A) Cyclic voltammograms at bare GCE (a) and polyglycine modified electrode (b, c) in presence of 0.1 mM CC (a, c) and in the absence of CC (b) in 0.1 M ABS (pH 5.0); scan rate,100 mV s^{-1}. **(B)** Cyclic voltammograms of 0.1 mM CC at polyglycine modified electrode in 0.1 M ABS (pH 5.0) at different scan rates: (a) 20 mV s^{-1}; (b) 50 mV s^{-1}; (c) 100 mV s^{-1}; (d) 150 mV s^{-1}; (e) 200 mV s^{-1}; (f) 250 mV s^{-1}; (g) 300 mV s^{-1}; (h) 350 mV s^{-1}; (i) 400 mV s^{-1}; (j) 450 mV s^{-1}.

Fig. 2B shows the CVs of CC at the polyglycine modified electrode at different scan rates. The oxidation peak potential was observed to shift positively with the increase in scan rate, and in addition, exhibited a linear relation to the scan rate, v, with the linear regression equation i_{pa} / μA= 3.5536 + 0.0983 v / mV s^{-1} (correlation coefficient, r=0.9960). The result indicates that the oxidation of CC at the polyglycine modified electrode was controlled by the adsorption CC rather than CC diffusing to the electrode.

The effect of the pH value of ABS on the on the response of CC was investigated by CV. The response of CC is well-behaved in ABS, as the solution pH increases, the anodic peak potential shifts

to the negative and the potential of E_{pa} *vs.* pH in ABS has a good linear relation in the range of pH 3.01 - 6.93. The linear regression equation E_{pa} / V = 0.5086 – 0.0499 pH (correlation coefficient, r = 0.9973) was obtained, which showed that the uptake of electrons is accompanied by an equal number of protons.

3.3. Simultaneous detection HQ and CC

In order to evaluate the sensitivity and selectivity of the polyglycine modified electrode for the quantification of HQ and CC, the electrochemical behavior of binary mixtures of 0.1 mM HQ and 0.1 mM CC at the polyglycine modified electrode was investigated using CV. For the binary mixtures, 0.1 M ABS was used to control the pH and the pH 5.0 was chosen, at this pH the oxidations of the two compounds have high electrochemical response.

Fig. 3 shows the CVs obtained for HQ and CC coexisting at bare GCE (Fig. 3a) and modified electrode (Fig. 3b). As shown in Fig. 3, the bare electrode cannot separate the voltammetric signals of HQ and CC. Only one broad voltammetric signal was observed for both analytes. The fouling of the electrode surface by the oxidation products results in a single voltammetric peak for HQ and CC. Therefore it is impossible to use the bare electrode for the voltammetric detection of HQ in the presence of CC.

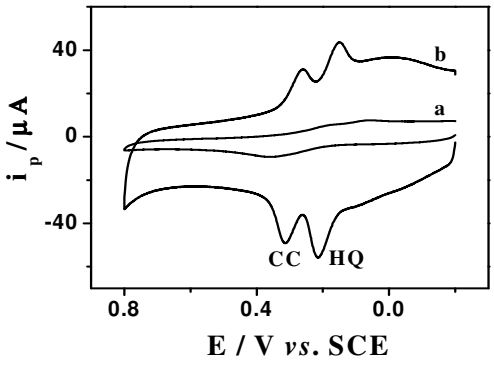

Figure 3. Cyclic voltammograms at bare GCE (a) and polyglycine modified electrode (b) in presence of 0.1 mM HQ and 0.1 mM CC in 0.1 M ABS (pH 5.0); scan rate,100 mV s^{-1}.

Moreover, the polyglycine modified electrode resolved the mixed voltammetric signals into two well-defined voltammetric peaks at 318 and 214 mV corresponding to the oxidation of CC and HQ, respectively. In theory, the density of the electron cloud is lower from HQ to CC, therefore their electroactivity is decreasing and the oxidation of HQ is easier than that of CC, which shows that the potentials of their oxidation peaks increase. The experimental results accord with this theory [2]. The polyglycine modified electrode shows good selectivity and excellent sensitivity in the simultaneous detection of HQ and CC. As the oxidation potential of HQ is shifted to the less positive side, the anodic current of CC has no contribution from HQ, because HQ is readily oxidized well before the

oxidation potential of CC reached. Thus elimination of the fouling of the electrode surface by the oxidation products could be achieved and the precise detection of CC in the presence of HQ is possible at the polyglycine modified electrode. The voltammetric signals of HQ and CC remained unchanged in the subsequent sweeps, indicating that the polyglycine modified electrode does not undergo surface fouling. Furthermore, the separation between the voltammetric peaks of HQ and CC is large (- 104 mV) and thus the simultaneous detection of HQ and CC or the selective detection of CC in presence of HQ is feasible at the polyglycine modified electrode.

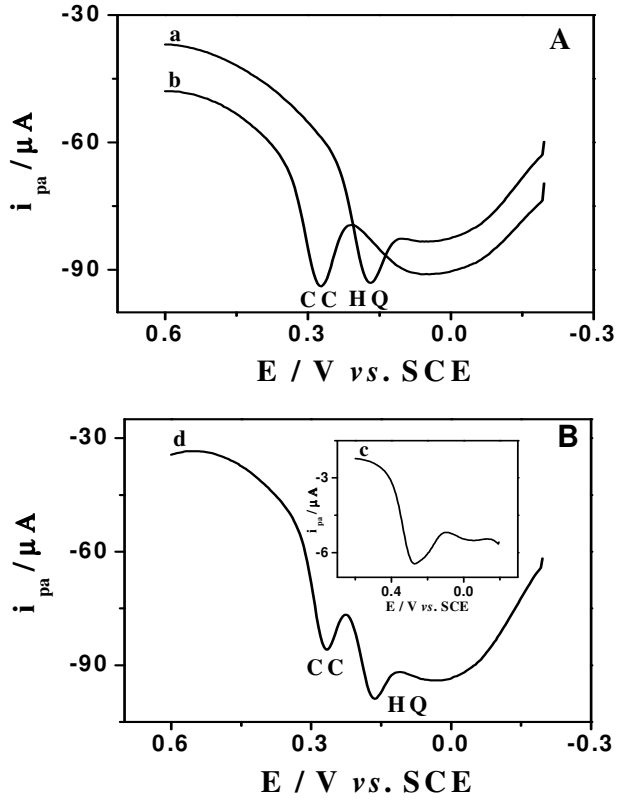

Figure 4. (A) DPVs for 0.1 mM HQ (a) and 0.1 mM CC (b) at polyglycine modified electrode in 0.1 M ABS (pH 5.0). **(B)** DPVs for the homogeneous solution of 0.1 mM HQ and 0.1 mM CC at bare (c) and polyglycine modified electrode (d)**.** Scan rate: 4 mV s^{-1}; pulse amplitude: 50 mV; pulse width: 50 ms; pulse time: 200 ms.

The next attempt was taken to detect HQ and CC simultaneously by using the polyglycine modified electrode with the more sensitive method, differential pulse voltammetry (DPV). Fig. 4B shows the DPVs of HQ and CC coexisting in a solution at bare and polyglycine modified electrode. The bare electrode can not separate the responses of HQ and CC and gave a large response due to the fouling effect (Fig. 4B, curve c). The polyglycine modified electrode gave two peaks (Fig. 4B, curve d). One peak was observed at 0.164 V and the current response at this potential is approximately the same as that given by HQ in the absence of CC (Fig. 4A, curve a). The another peak appeared with potential at 0.267 V and the current response at this potential is also approximately the same as that

given by CC in the absence of HQ (Fig. 4A, curve b). Thus, it is can be confirmed that these two peaks are for HQ and CC, respectively.

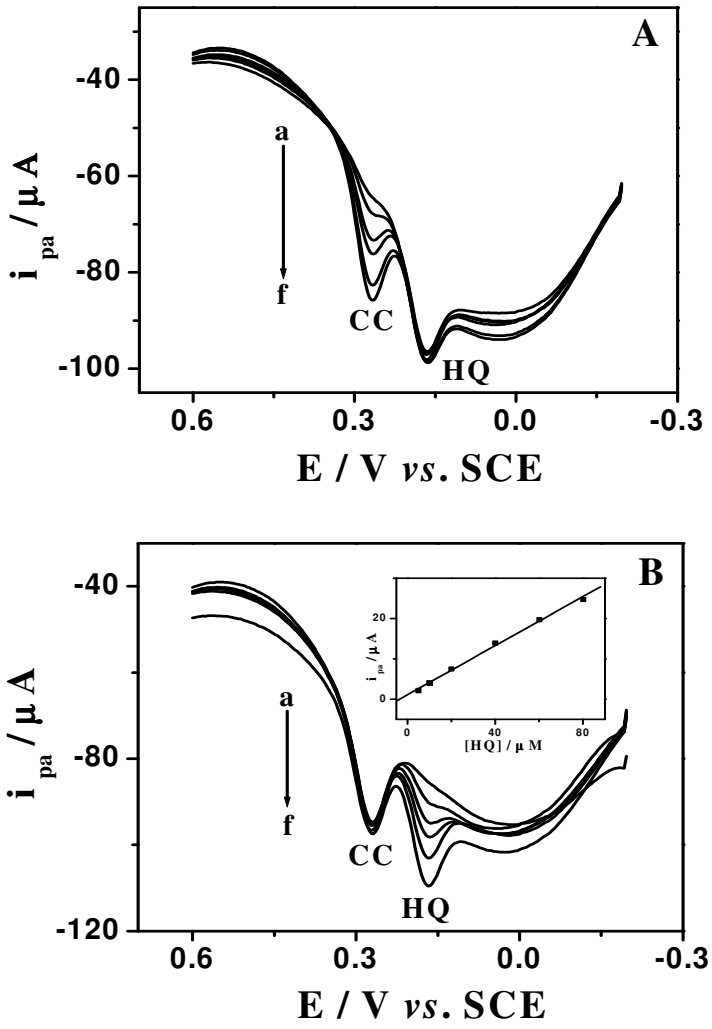

Figure 5. (A) DPVs of HQ and CC at Polyglycine modified electrode in 0.1 M ABS (pH 5.0), [HQ] was kept constant and [CC] was changed (i.e., [HQ] = 0.1 mM, [CC]: (a) 1, (b) 5, (c) 10, (d) 20, (e) 40, (f) 60 μM). The inset shows the relationship between the anodic peak current and the concentration of CC. **(B)** DPVs of HQ and CC at polyglycine modified electrode in 0.1 M ABS (pH 5.0), [CC] was kept constant and [HQ] was changed (i.e., [CC] = 0.1 mM, [HQ]: (a) 5, (b) 10, (c) 20, (d) 40, (e) 60, (f) 80 μM). The inset shows the relationship between the anodic peak current and the concentration of HQ. Scan rate: 4 mV s^{-1}; pulse amplitude: 50 mV; pulse width: 50 ms; pulse time: 200 ms.

Fig. 5A represents the DPV recordings at different concentrations of CC where the concentration of HQ was kept constant. The oxidative peak current for CC was increased linearly with the increase in CC concentration with the correlation coefficient of 0.9994 and the detection limit was 5.0×10^{-7} M based on the signal-to noise ratio of 3. Furthermore, while CC peak current increased with

the increase in CC concentration, the peak current of HQ kept almost constant. Fig. 5B represents the DPV recordings at different concentrations of HQ where the concentration of CC was kept constant. Here also the oxidative peak current for HQ was increased linearly with the increase in HQ concentration with the correlation coefficient of 0.9974 and the detection limit was 1.0×10^{-6} M based on the signal-to noise ratio of 3. Furthermore, while HQ peak current increased with the increase in HQ concentration, the peak current of CC kept almost constant. This suggests that the fouling effect by the oxidized product of HQ on the response of CC cannot occur at the polyglycine modified electrode. Thus, the simultaneously selective and sensitive detection of HQ and CC was achieved at the polyglycine modified electrode.

To ascertain further the reproducibility of the results, three different GCE was modified with polyglycine and their responses towards the oxidation of HQ and CC were tested. The separation between the voltammetric signals of HQ and CC and the sensitivities remained the same at all three modified electrode, confirming that the results are reproducible. The stability of the polyglycine modified electrode was also investigated. Its electrocatalytic effect did not change after storage in air for at least one week.

Analytical utility of the polyglycine modified electrode in simultaneous detection of HQ and CC has been examined using synthetic samples consisting of HQ and CC in local tap water without any pretreatment. The detection of HQ or CC in the samples was carried out using DPV at the modified electrode and 0.10 mM ABS (pH 5.0) was used to control the pH. When known amount of HQ were added to the water control samples containing CC, quantitative recoveries of 98.2% - 103.6% were obtained. When known amounts of CC were added to the water control samples containing HQ, quantitative recoveries of 96.7% - 104.5% were obtained. A feasibility of the polyglycine modified electrode in the simultaneous detection of HQ and CC is evident.

4. CONCLUSIONS

The present study demonstrates an excellent approach for the development of a novel voltammetric sensor of hydroquinone and catechol based on polyglycine coating. Fast electron transfer, high selectivity and excellent sensitivity for the oxidation of hydroquinone and catechol are achieved at the polyglycine modified electrode. The present modified electrode showed excellent sensitivity, selectivity and antifouling properties and can separated oxidation peaks towards hydroquinone and catechol, which are indistinguishable at the bare electrode. As the voltammetric signals of hydroquinone and catechol are well separated at the polyglycine modified electrode, the sensitive detection catechol in the presence of hydroquinone or the simultaneous detection of hydroquinone and catechol can be achieved. The modified electrode is stable and does not undergo surface fouling during the measurements. Chemically modified electrode modified with polyglycine is a promising approach to detection of isomers.

ACKNOWLEDGEMENTS
We gratefully acknowledge the financial support from the Doctor Foundation of Dalian Nationalities University(20056101).

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