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Simultaneous determination of hydroquinone and catechol at PASA/MWNTs composite film modified glassy carbon electrode

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ABSTRACT

A poly-amidosulfonic acid and multi-wall carbon nanotubes composite (PASA/MWNTs) modified electrode has been constructed by electropolymerization on glassy carbon electrode (GCE). The electrochemical behaviors of hydroquinone (HQ) and catechol (CC) were investigated using cyclic and differential pulse voltammetries (DPVs) at the prepared electrode. Separation of the reductive peak potentials for HQ and CC was about 120 mV in pH 6.0 phosphate buffer solution (PBS), which makes it suitable for simultaneous determination of these compounds. In the presence of 1.0×10^{-4} mol L^{-1} isomer, the reductive peak currents of DPV are proportional to the concentration of HQ in the range of 6.0×10^{-6} to 4.0×10^{-4} mol L^{-1}, and to that of CC in the range of 6.0×10^{-6} to 7.0×10^{-4} mol L^{-1}. When simultaneously changing the concentration of both HQ and CC, the linear concentration range of HQ (or CC) is 6.0×10^{-6} to 1.0×10^{-4} mol L^{-1} (or 6.0×10^{-6} to 1.8×10^{-4} mol L^{-1}), and the corresponding detection limits are 1.0×10^{-6} mol L^{-1}. The proposed method has been applied to simultaneous determination of HQ and catechol in water sample, and the results are satisfactory.

1. Introduction

Hydroquinone (HQ) and catechol (CC) are two isomers of phenolic compounds, and they are important contaminants in medical, food and environmental matrices. Reliable analytical procedures are required for sensitive simultaneous determination in various matrices. So far, a great deal of methods have been established for their determination, including liquid chromatography [1,2], synchronous fluorescence [3], chemiluminescence [4,5], spectrophotometry [6], gas chromatography/mass spectrometry [7], pH based-flow injection analysis [8], electrochemical methods [9–13], etc. However, some of these mentioned methods have the disadvantages of time-consuming, high cost, low sensitivity and complicate pretreatment, electrochemical methods provide an easy and fast way in environmental analysis. Qi et al. [11] reported a MWNTs modified glassy carbon electrode for simultaneous determination of HQ and CC, the oxidation peak potentials of HQ and CC were observed at 162 and 264 mV, respectively. Zeng et al. [12] described a mesoporous carbon CMK-3 modified electrode, at which the cathodic and anodic peak potential differences between CC and HQ are up to 131 and 125 mV, respectively. However, those electrodes were constructed by casting carbon material at substrates, which may suffer from mechanical instability during detection.

Polymer-modified electrodes have attracted enormous interest in the past few years, due to their good stability, reproducibility, more active sites, homogeneity in electrochemical deposition and strong adherence to electrode surface [14]. Amidosulfonic acid molecules contain electro-rich N atoms and have high SO_3^- electron density. As far as we know, the negative charged poly-amidosulfonic acid (PASA) film modified electrode has been used for determination of DA in the presence of AA [15], and for the determination of isoniazid in pharmaceuticals [16]. Carbon nanotubes (CNTs) have received considerable attention since their discovery in 1991 [17] because of their exceptional mechanical and electrical properties. The subtle electronic properties suggest that CNTs, when used as an electrode material in electrochemical reactions, have the ability to promote electron-transfer reactions. Recently, polymer/CNTs composites have been extensively studied because incorporation of CNTs into conducting polymers can lead to new composite materials possessing the properties of each component with a synergistic effect that would be useful in particular applications [18]. Previous reports [14,19,20] have demonstrated that the polymer/CNTs modified electrodes possess excellent electrocatalytic ability for some biological molecules due to their adsorption onto the surfaces of the CNTs through strong π–π stocking force to form the composite film.

In this work, a PASA/MWNTs composite modified electrode has been fabricated by electropolymerization of amidosulfonic acid

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at MWNTs/GCE surface. The electrochemical behaviors of hydroquinone (HQ) and catechol (CC) were investigated using cyclic and differential pulse voltammetries (DPVs) at the prepared electrode. Separation of the reductive peak potentials for HQ and CC was about 120 mV in pH 6.0 phosphate buffer solution (PBS), which makes it suitable for simultaneous determination of these compounds. The proposed method has been applied to simultaneous determination of HQ and CC in water sample with high selectivity.

2. Experimental

2.1. Reagents

HQ and CC were obtained from Tianjin Chemical Factory (China). Amidosulfonic acid (>99.5%) was purchased from Tianjin Bodi Chemicals Co., Ltd. (China). MWNTs (obtained from Chengdu Organic Chemicals Co., Ltd., China) were treated with concentrated HNO_3 during purification process followed by filtering, rinsing with de-ionized water and drying in air. All other chemicals were of analytical reagent grade and used without further purification. Phosphate buffer solutions (PBSs) were prepared by 0.1 mol L^{-1} KH_2PO_4–Na_2HPO_4, and adjusted the pH with H_3PO_4 and NaOH. All aqueous solutions were prepared with de-ionized water. Water purified in a Milli-Q purification system (Millipore) was used for all dilutions and sample preparations.

2.2. Voltammetry and electrochemical impedance spectroscopy

Electrochemical measurements were carried out with a model CHI660C electrochemical workstation (CH Instruments, Chenhua Co., Shanghai, China) controlled by a personal computer. A conventional three-electrode system was used in the measurements, with bare GCE or modified GCE as the working electrode, a Pt wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All potentials in this paper refer to the SCE. For differential pulse voltammetry (DPV) measurements, a pulse width of 25 mV, a frequency of 30 Hz, and a pulse increment of 4 mV were employed. The electrochemical impedance spectroscopy (EIS) measurements were performed in the presence 5 mmol L^{-1} $[Fe(CN)_6]^{3-/4-}$ solution containing 0.1 M KCl and plotted in the form of complex plane diagrams (Nyquist plots). They were recorded with a frequency range of 0.05–100 kHz. The amplitude of the applied sine wave potential was 5 mV, with a formal potential 0.2 V. A Randle's equivalent circuit was used to fit the obtained impedance spectra. The R_{et} was calculated for each fitting by the Zsimpwin™ Software (Princeton Applied Research, USA).

2.3. Preparation of PASA/MWNTs/GCE

The GCE (2 mm in diameter) was carefully polished on chamois leather containing 0.05 μm alumina slurry, and then washed ultrasonically in water and ethanol, respectively. For the preparation of MWNTs/GCE, 5 μL of the MWNTs suspension (0.1 mg mL^{-1}), which was prepared by dispersing the desired amount of purified MWNTs in N,N-dimethylformamide (DMF) with the aid of ultrasonic oscillation, was dropped on GCE surface, followed by evaporating the solvent under an infrared lamp. The proposed MWNTs/GCE was first activated by 20 cyclic sweepings from −1.2 to +1.2 V in PBS. The PASA/MWNTs/GCE was formed by cyclic sweeping from −1.5 to +2.5 V for 10 cycles in PBS containing 5.0×10^{-3} mol L^{-1} amidosulfonic acid solution. The electrodes were rinsed by water and stored in PBS before use.

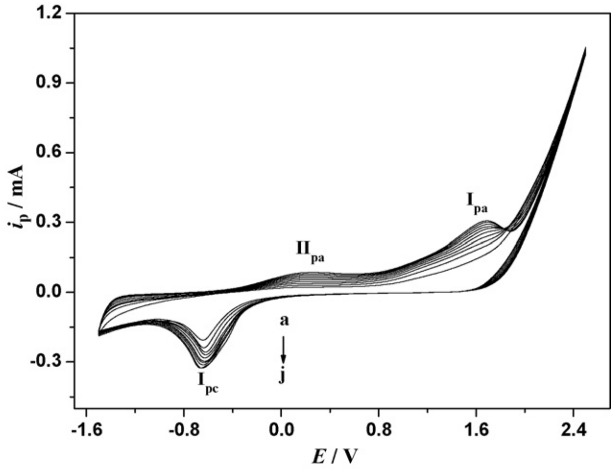

Fig. 1. Repetitive cyclic voltammograms (a–j) of 5.0×10^{-3} mol L^{-1} amidosulfonic acid in pH 7.0 PBS at the MWNTs/GCE surface. Scan rate: 100 mV s^{-1}.

3. Results and discussion

3.1. Electropolymerization of amidosulfonic acid at the MWNTs/GCE surface

Fig. 1 shows the successive cyclic voltammograms of 5.0×10^{-3} mol L^{-1} amidosulfonic acid at the MWNTs/GCE in pH 7.0 PBS by potential scanning between −1.5 and +2.5 V. As can be seen from Fig. 1, at the first cycle, an oxidative peak and a reductive peak were found, at the potential of +1.65 V (Fig. 1, I_{pa}) and −0.7 V (Fig. 1, I_{pc}), respectively. In the subsequent scanning, a new oxidative peak (Fig. 1, II_{pa}) appeared at the potential of +0.15 V, and then larger peak was observed with the continuous scanning, indicating the continuous growth of the film. A uniform blue-black film was produced at the surface of glassy carbon electrode, which indicated that the PASA was electropolymerized on the surface of glassy carbon electrode. After nine cycles, the peak currents almost kept constant, so ten cycles were chosen in the modification process.

3.2. Electrochemical impedance characterization of modified electrodes

Electrochemical impedance spectroscopy (EIS) can provide information on the impedance changes of the electrode surface during the modification process. The interface can be modeled by an equivalent circuit, also called a Randles circuit. This equivalent circuit includes the ohmic resistance of the electrolyte, R_s, the Warburg impedance, Z_w, the electron-transfer resistance, R_{et}, and the constant phase element, CPE. In fact, R_s and Z_w are not affected by chemical transformations occurring at the electrode interface, since they represent bulk properties of the electrolyte solution and diffusion of the applied redox probe. The C_{dl} changes are not sensitive to the electron-transfer resistance [21]. As a result, it can be expected that the R_{et} is the most directive and sensitive parameter that responds to changes on the electrode interface.

Fig. 2 displays the EIS results of the bare GCE and three modified electrodes in the presence of 5 mmol L^{-1} $[Fe(CN)_6]^{3-/4-}$ solution, which were fitted by digital simulation based on the equivalent circuit (Fig. 2, inset). The EIS includes a semicircular part and a linear part. The semicircular part at higher frequencies corresponds to the electron-transfer limited process, and the diameter is equivalent to the electron-transfer resistance (R_{et}). The linear part at lower frequencies corresponds to the diffusion process. For the bare GCE, the EIS is almost straight lines (Fig. 2a), which indicated no