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Multiwall carbon nanotubes-poly(diallyldimethylammonium chloride)-graphene hybrid composite film for simultaneous determination of catechol and hydroquinone

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ABSTRACT

A multiwall carbon nanotubes-poly(diallyldimethylammonium chloride)-graphene modified glassy carbon electrode (MWCNTs-PDDA-GR/GCE) has been fabricated and used for simultaneous determination of catechol (CC) and hydroquinone (HQ). Transmission electron microscopy (TEM) and electrochemical impedance spectroscopy (EIS) results revealed that MWCNTs-PDDA-GR was successfully prepared with enhanced electron transfer ability. Differential pulse voltammetry (DPV) results showed that MWCNTs-PDDA-GR/GCE exhibited an excellent electrochemical performance, two correspondingly well-defined oxidation peaks with significantly different peak potentials (120 mV) and enhanced peak currents appeared at the modified electrode. Under the optimized conditions, the sensing platform showed wide linear responses for HQ and CC from 5.0×10^{-7} to 4.0×10^{-4} mol L^{-1} with detection limits ($S/N = 3$) of 2.0×10^{-8} mol L^{-1} and 1.8×10^{-8} mol L^{-1}, respectively. The proposed MWCNTs-PDDA-GR/GCE proved successful toward the sensitive and simultaneous detection of HQ and CC in practical water samples.

1. Introduction

Hydroquinone (1,4-dihydroxy-benzene, HQ) and catechol (1,2-dihydroxy-benzene, CC) are two important dihydroxybenzene isomers with similar structures and properties, which widely coexist and are used as industrial raw and synthetic intermediates in cosmetic, pharmaceutical, tanning and pesticide industries, etc. [1]. During the manufacturing and application process of these industries, some of the isomers are inadvertently released into the environment. When these compounds entered subterranean aquifers, they do not dilute or degrade very quickly and would pose great threat to the environment and also to both fresh water and marine life even at very low concentrations with high toxicity levels [2]. Therefore, the simultaneous and accurate detection of the two substances is of much importance. However, because of their similar structures and properties, HQ and CC interfere with each other during their identification, resulting in a challenge to directly and simultaneously determinate these two isomers.

Up to now, several techniques have been employed for the simultaneous determination of HQ and CC [3–6]. However, these methods often suffer from some disadvantages. Alternatively, electrochemical method has become a powerful technique because of its advantages of fast response, high sensitivity and selectivity, simple equipment, and low cost [7,8]. However, the similar chemical structures of HQ and CC lead to the adjacent potentials of redox peaks at unmodified electrodes, resulting in poor detection selectivity. To solve these problems, a wide range of advanced materials have been used as enhanced electrode materials to simultaneously determine HQ and CC [9,10]. However, it is still a challenge to explore novel electrode materials for the simultaneous determination of HQ and CC with wider linear range and higher stability.

Graphene (GR), an atomic-layer thick two-dimensional (2D) carbon nanostructure, has attracted considerable interest due to its superior properties [11]. The unique crystal structure of GR makes it extremely attractive as a support material to promote the electrochemical reactivity of molecules on the modified electrode surface [12–14]. However, the hydrophobic property and irreversible aggregation of GR in aqueous solution limit its application in

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biological analysis. Noncovalent strategies have been successfully proved to be a simple and effective way to solubilize GR nanosheet.

Poly(diallyldimethylammonium chloride) (PDDA), a water-soluble quaternary ammonium and cationic polyelectrolyte, usually acts as a positively charged colloid when it is dissolved in aqueous solution [15]. This positively charged PDDA can be easily coated on the negatively charged surface by electrostatic interaction [16]. As for GR that is obtained by chemical reduction, a small quantity of functional groups, such as hydroxyl, carboxyl and epoxy, still remain on its edges and surface, which makes GR negatively charged. Thus, PDDA might be used to noncovalently functionalize GR sheet [17]. Moreover, PDDA is a stabilizer in preventing GR from aggregation [18], which could maintain the electronic structure of GR.

As for the carbon materials, morphological control by assembly of nano-materials is a creative approach to obtain multifunctional films [19]. Multiwall carbon nanotubes (MWCNTs), with quasi-one dimensional (1D) structures, have gained considerable research attentions due to their intrinsic chemical and physical properties [20]. Recently, immobilization of MWCNTs has become an attractive way to create a three dimensional (3D), porous, conductive and catalytic matrix on an electrode surface [21]. Therefore, the combination of 2D-structured GR with 1D-structured MWCNTs can form a conductive network to provide larger specific surface area and higher conductivity, which can further improve the analytical performance of electrochemical sensors [22]. Furthermore, by combining with MWCNTs, aggregation of GR can be efficiently reduced [23].

In this study, we presented a simple and general method to prepare MWCNTs-PDDA-GR hybrid composite film through electrostatic adsorption between positively charged PDDA and negatively charged MWCNTs and GR. With the synergistic effect, the resulting composite was demonstrated to be an effective material for the fabrication of electrochemically modified electrode (MWCNTs-PDDA-GR/GCE). The performance of the fabricated electrode and the electrochemical behavior of the isomers of HQ and CC were investigated by cyclic voltammetry (CV). Two correspondingly well-defined oxidation peaks with significantly different peak potentials and enhanced peak currents were obtained. Moreover, the fabricated MWCNTs-PDDA-GR/GCE was successfully applied to the simultaneous detection of HQ and CC by differential pulse voltammetry (DPV) with highly sensitivity and selectivity.

2. Experimental

2.1. Reagents and apparatus

The hydroquinone (HQ) and catechol (CC) were obtained from Jinan Chemical Industry Research Institute (Jinan, China). Graphite powder was provided by Qingdao Fujin graphite Co., Ltd. Graphene (GR) was synthesized by the modified Hummers method [24]. Multiwall carbon nanotubes (MWCNTs) were provided by Tsinghua University. The carboxylation of MWCNTs was carried out according to our previous work [25]. Poly(diallyldimethylammonium chloride) (PDDA) was obtained from Sigma-Aldrich (St. Louis, MO, USA). All the other chemicals were of analytical grade and used without further purification. The 0.2 mol L^{-1} phosphate-buffered solution (PBS) with various pH was prepared by using the stock solutions of 0.2 mol L^{-1} NaH_2PO_4 and 0.2 mol L^{-1} Na_2HPO_4.

Cyclic voltammetry (CV), differential pulse voltammetry (DPV) and electrochemical impedance spectra (EIS) were performed on a CHI-660C electrochemical workstation (CHI Inc. Ltd., USA) coupled with a conventional three-electrode cell. A glassy carbon electrode (GCE, 3 mm in diameter) and the modified electrodes were used as the working electrodes. The auxiliary electrode was a platinum wire. A saturated calomel electrode (SCE) was the reference electrode. The morphologies of materials were recorded using transmission electron microscopy (TEM) (JEM-2100).

2.2. Synthesis of MWCNTs-PDDA-GR

A 1.0 mg the synthesized GR and 1.0 mg MWCNTs were mixed completely in 1.0 mL of double-distilled water with ultrasonic agitation to form a homogenous mixture of MWCNTs-GR. And then, 10 μL of PDDA (20% in water) was added to disperse the MWCNTs-GR hybrid, followed by successively ultrasonic agitation to obtain the mixture of MWCNTs-PDDA-GR.

2.3. Preparation of the modified GCE

Prior to the surface modification, the GCE was carefully polished with 0.3 μm and 0.05 μm alumina slurries to obtain a mirror-like surface. After sonication in water and ethanol successively for 20 s, the electrode was rinsed with water, and then dried under an infrared lamp. The MWCNTs-PDDA-GR/GCE was prepared by casting 4 μL of as-prepared MWCNTs-PDDA-GR suspension onto the surface of cleaned GCE. The solvent was then evaporated under an infrared heat lamp. As controls, GR/GCE and MWCNTs/GCE were also fabricated with the similar procedures for the preparation of MWCNTs-PDDA-GR/GCE by only replacing MWCNTs-PDDA-GR hybrid materials with GR or MWCNTs, respectively.

2.4. Electrochemical measurements

All electrochemical experiments were carried out at room temperature. The CV experiments were carried out by scanning a 0.2 mol L^{-1} PBS (pH 7.0) containing a single or mixed analytes at an applied potential range from −0.4 to 0.6 V with different scan rates between 20 and 310 mV s^{-1}. The DPV was performed at potentials from −0.2 to 0.4 V. The impedance measurements were performed in a 5.0×10^{-3} mol L^{-1} $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ redox probe solution with 0.1 mol L^{-1} KCl.

3. Result and discussion

3.1. Characterization of the hybrid composites

The morphologies of MWCNTs, GR and MWCNTs-PDDA-GR were investigated by TEM. Fig. 1A(a) shows the curved tubular structures of MWCNTs and Fig. 1A(b) shows the flake-like individual transparent GR sheets with wrinkles and rolled sheets. From Fig. 1A(c) of MWCNTs-PDDA-GR, we can clearly see that PDDA along with MWCNTs are well distributed on the GR nanosheets forming an interconnection network, which indicates the formation of the MWCNTs-PDDA-GR hybrid composite film.

EIS was employed to characterize the electron transfer properties of different modified electrodes. The value of the electron-transfer resistance (R_{ct}, the diameter of semicircles) depends on the dielectric and insulating features at the electrode/electrolyte interface. As shown in Fig. 1B, the bare GCE (curve a) exhibited an obvious semicircle over the high frequency range, which can be attributed to the poor electrical conductivity. It is clear that when GR (curve b) and MWCNTs (curve c) were immobilized on the GCE surface, respectively, the R_{ct} decreased which could be attributed to the modification of GR and MWCNTs that improved the conductivity of GCE and facilitated electron transfer. At the same time, in comparison with GR/GCE, MWCNTs/GCE exhibited a more decreased R_{ct} value, indicating a better conductivity of MWCNTs than GR. Moreover, after MWCNTs-PDDA-GR hybrid composite was coated on the GCE (curve d), the electron transfer resistance of the electrode further decreased, conforming that the