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Amperometric determination of hydroquinone and catechol on gold electrode modified by direct electrodeposition of poly(3,4-ethylenedioxythiophene)

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ABSTRACT

Poly(3,4-ethylenedioxythiophene) (PEDOT) was directly deposited onto a gold electrode through potentiostatic technology, and the PEDOT modified electrode was developed for the amperometric determination of hydroquinone and catechol in 0.1 M phosphate buffer solution (pH 7.0). Compared with the bare electrode, both hydroquinone and catechol exhibited well-defined redox peaks and much larger peak currents at PEDOT modified gold electrode, which suggested the higher specific surface area and conductivity of the PEDOT film. Under the optimized condition, the amperometric current response on PEDOT modified electrode were linear over ranges from 1.0×10^{-7} M to 4.9×10^{-5} M for hydroquinone, and from 9.1×10^{-8} M to 9.8×10^{-4} M for catechol, with the detection limits of 1.2×10^{-8} M and 0.9×10^{-8} M, respectively. The proposed method was applied on the determination of the mixture of hydroquinone and catechol with satisfactory results.

1. Introduction

As two important phenol compounds and synthetic intermediates, hydroquinone (1,4-dihydroxybenzene, HQ) and catechol (1,2-dihydroxybenzene, CC), are used in many fields, especially in the manufacture of dyes, cosmetics, pesticides and pharmaceuticals. These isomers of dihydroxybenzene widely exist in environment as a kind of important pollutant because they are toxic to humans and difficult to be degraded in the ecological circumstance [1,2]. Furthermore, they have been included in the lists of priority pollutants to be monitored in the aquatic environment by both of US Environmental Protection Agency (EPA) and European Union (EU) [3].

Based on the comprehensive consideration of industrial production and pollution prevention, it is necessary to develop a simple and rapid analytical method for simultaneous determination of HQ and CC [4,5]. In the past few years, many methods have been established, including synchronous fluorescence [6], chemiluminescence [7], spectrophotometry [8], pH based-flow injection analysis [9], solid-phase extraction [10], pulse radiolysis [11] and high performance liquid chromatography [12,13]. However, most of the methods mentioned above have some disadvantages, such as time consuming, high cost, low sensitivity and complicate pretreatment. Recently, research has turned to cost effective electrochemical techniques in a bid to reduce detection limit, so that reliable results can be acquired at relatively less cost [14]. The early investigation concerning the simultaneous electrochemical determination of the two isomers was conducted at a glassy carbon electrode modified with multi-walled carbon nanotubes (MWCNTs) [15,16], which yield promising results. Further research works on the simultaneous determination of dihydroxybenzenes were performed at the new complex modified electrodes [17]. Electrodes modified with poly(glutamic acid) [18], graphene/AuNPs/chitosan [19], penicillamine [20], grapheme nanosheets [21], boron-doped diamond [22], MWCNTs + nanogold [23], PASA/MWNTs [24], poly(p-aminobenzoic acid) [25] and polyglycine [26], are also developed.

In the last decades, the increasing interest for the conducting polymers (CP) [27], has led to deep research to their synthesis and applications [28,29]. These CP with electrical and optical properties have found promising applications in solar cells, batteries, electrochromic devices, sensors and molecular electronic devices [30,31]. CP offer myriad opportunities to couple analyte receptor interactions into observable (transducible) responses [32–38]. Among the numerous CP developed and studied over the past few decades, PEDOT has received a significant amount of attention as an electrode material for a variety of applications [39,40]. In addition, the PEDOT-modified electrodes have also been used for construction of sensing systems for the detection of morphine [41], nitrite [42], atrazine [43], dopamine [44] and ascorbic acid [45].

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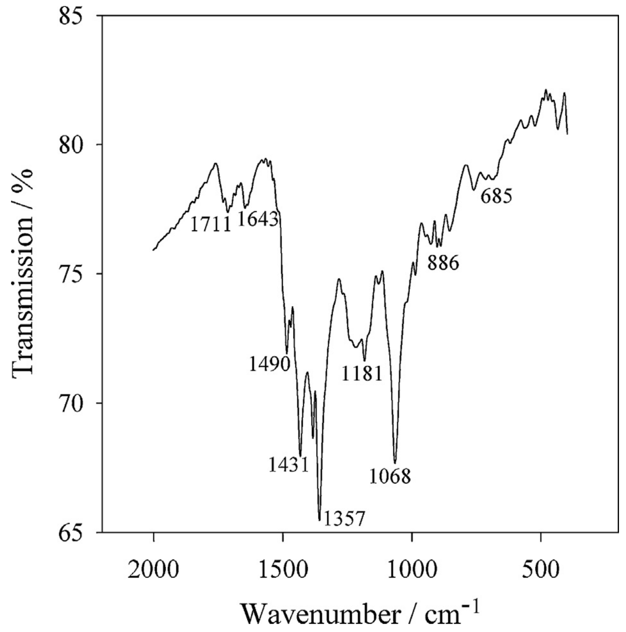

Fig. 1. FT-IR spectra of PEDOT.

Many materials have been used to achieve sensitive and selective detection of HQ and CC, such as penicillamine [20], carbon nanotubes [15], grapheme nanosheets [21], using of conducting polymers, like poly(thionine) [28], polyaniline/polysulfone composite film [29] to improve their simultaneous determination have been reported. In contrast, only a few studies have been concerned with the role of the PEDOT modified gold electrode on the amperometric response of these diphenols (HQ and CC). In this work, a novel electrochemical sensor based on PEDOT modified gold electrode was developed, which exhibited excellent properties for the simultaneous and sensitive determination of HQ and CC, such as fast response, good selectivity and reversibility.

2. Experimental

2.1. Reagents

A 3,4-ethylenedioxythiophene (EDOT) was obtained from XZL Bio-Technology Co., Ltd. Hydroquinone, catechol and $LiClO_4$ were purchased from Guangfu Fine Chemical Research Institute. Acetonitrile was taken from Tianjin Kemiou Chemical Reagent Co., Ltd. All other chemicals were of analytical grade and were used without further purification.

2.2. Instrumentation

The electrochemical measurements were carried out with LK2006A electrochemical workstation (Tianjin Lanlike Chemical and Electron High Technology Co., Ltd.). A conventional three-electrode system was employed comprising a bare Au electrode (Aida Instruments Corp., Tianjin, China, 1.5 mm in diameter) or a modified Au electrode as the working electrode, a platinum wire as the counter electrode, and an Ag/AgCl electrode as the reference electrode. A FT-IR spectrometer (Bruker Vector 22, Germany) and a FE-SEM (H-7650, HITACHI) were used to characterize PEDOT films.

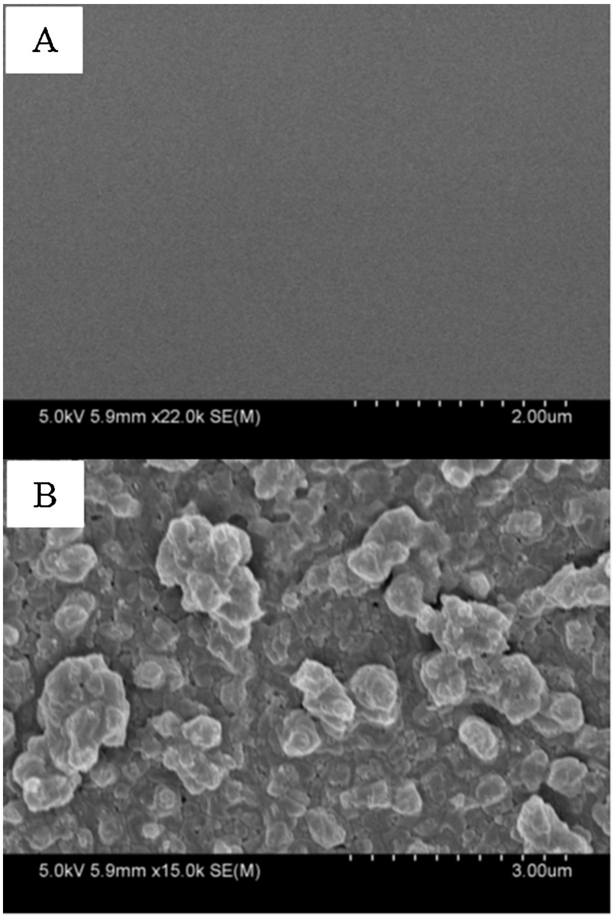

Fig. 2. FE-SEM images of bare (A) and PEDOT-modified (B) Au electrode.

2.3. Preparation of PEDOT modified electrode

Electrochemical polymerization was carried out with a three-electrode/one-compartment glass cell. The Au electrodes were finely polished by 1 μm and 0.05 μm aluminum slurry, and scanned over the potential range of +0.0 V to +1.7 V (vs. Ag/AgCl) in 0.5 M H_2SO_4 solution for about 30 min until the same voltammogram was obtained. A potentiostatic method (fixed potential technique) was used to deposit PEDOT films onto the Au electrode, which was performed by applying a positive potential at +1.2 V for an appropriate time at 0.01 M EDOT acetonitrile solution containing 0.1 M lithium perchlorate ($LiClO_4$). After electropolymerization, the PEDOT modified electrode was washed with ethanol and twice-distilled water and dried by N_2.

2.4. Electrochemical measurement

A three-electrode electrochemical cell was used in the cyclic voltammetric and amperometric experiments. A bare Au electrode (1.5 mm in diameter) or a modified Au electrode served as the working electrode, a platinum wire was used as counter electrode and the reference electrode was Ag/AgCl electrode. The electrochemical behaviors of the HQ and CC on different electrodes were investigated by cyclic voltammetry between −0.2 and +0.6 V at a scan rate of 100 mV s^{-1} in 0.1 M PBS buffer (pH 7.0). The applied potential was set at +0.13 V and +0.25 V for the amperometric determination of HQ and CC, respectively.