



Selective sensing of catechol and hydroquinone based on poly(3,4-ethylenedioxythiophene)/nitrogen-doped graphene composites



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ARTICLE INFO

Article history:

Received 2 January 2014

Received in revised form 17 March 2014

Accepted 24 March 2014

Available online 12 April 2014

Keywords:

Nitrogen-doped graphene

Poly(3,4-ethylenedioxythiophene)

Catechol

Hydroquinone

Electrochemical sensing

ABSTRACT

A highly sensitive and selective method was developed for the simultaneous detection of catechol and hydroquinone on a poly(3,4-ethylenedioxythiophene)/nitrogen-doped graphene composite layer. The composite modified electrode was prepared by the electro-polymerization of 3,4-ethylenedioxythiophene on the nitrogen-doped graphene coated glassy carbon electrode. The composite film, characterized by Raman spectra and SEM, was highly efficient to catalyze the redox of catechol and hydroquinone. Two couple of well-defined redox peaks of catechol and hydroquinone could be observed with good reversibility and the enhanced current responses were obtained. Differential pulse voltammetry was used in the simultaneous and quantitative determination of catechol and hydroquinone under the optimized experiment parameters. The proposed sensor based on poly(3,4-ethylenedioxythiophene)/nitrogen-doped graphene exhibited a linear response to the concentrations ranging from 1 to 10 μM with a low detection limit of 0.26 μM for catechol and 0.18 μM for hydroquinone, respectively.

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1. Introduction

Hydroquinone (HQ) and catechol (CT) are two vital isomers of phenolic compounds which are widely used in the fields of medical, food, dye and photography chemicals [1]. During the manufacturing and application processes, some of them could be released into the environment, which had a negative influence on the environment. Due to their high toxicity and low degradability [2], it is of great importance to develop a simple, rapid and reliable analytical method for dihydroxybenzene isomers determination. Recently, electrochemical methods for the determination of HQ and CT have attracted increasing attention for its high sensitivity, low detection limit and simple operation. For the overlap of their redox peaks at ordinary electrode, to prepare a decorating material with superior electrocatalysis toward HQ and CT is a key process. Up to now, many nanomaterials have been used to the determination of HQ and CT, such as carbon nanotube [3], graphene [2], noble metals [4,5], and so on.

In the past few years, graphene has aroused a lot of attentions for its excellent electrochemical and mechanism performance and has been applied widely in the fields of optoelectronics, sensors, energy applications, novel nanoelectronics and so on [6]. Many works aimed to tailor its electronic band structure and physicochemical property of graphene to widespread its potential applications. In these methods, the doping of graphene is a promising approach to obtain high electric conductivity, high surface area and large amount of edge site [7]. On the basis of previous work, Nitrogen-doped (NGE) embodied superior catalysis characters toward different substances such as bisphenol A [8], ascorbic acid/dopamine/uric acid [9] and hydrogen peroxide [10]. As revealed before, pyridinic nitrogen doped graphene has better catalytic-performance toward the redox of HQ and CT than pyrrolic nitrogen doped graphene [11]. And NGE is also a promising material for the catalysis of oxygen reduction [7,12,13]. Moreover, NGE sheets can provide excellent platforms for the loading of nanomaterials [14,15]. The incorporation of NGE with platinum nanoparticles is in favor to enhance catalytic activity of Pt toward the electrochemical oxidation of methanol [16]. On the other hand, the introduction of NGE sheets into composite modified sensors can enable a low detection limit and increased sensitivity due to the enhanced electron transfer and sorption ability of NGE. And NGE

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composite based sensors have been used for the detection of alpha fetoprotein [17], chloramphenicol [14], and so on.

But to the best of our knowledge, few methods were developed for the preparation of NGE/conducting polymer composite based sensors. Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most studied conducting polymers with high electric performance. Several PEDOT-based composite materials have been applied to the determination of HQ or CT, such as PEDOT/Graphene oxide [18], PEDOT/Nafion/SWNT/IL [19], and PEDOT/MWCNT [20]. As these reports revealed, PEDOT composites show excellent behavior toward the redox of HQ or CT. Therefore, we believe the combination of NGE with PEDOT would provide a better approach to the simultaneous determination of HQ and CT, compared to our previous work [18].

In this paper, a new approach was developed to modify GCEs with a PEDOT decorated NGE composite. The PEDOT/NGE/GCE sensor showed enhanced electrochemical response toward the redox of HQ and CT, and well peak to peak separation of HQ and CT could be observed on the modified electrode. This modified electrode was then used to the simultaneous determination of HQ and CT and a low detection limit was achieved.

2. Experimental

2.1. Reagents and apparatus

Graphene oxide was prepared as we described previously [21]. NGE was prepared with graphene oxide as papers reported before [22,23]. Briefly, 50 mL of exfoliated 0.5 mg mL^{-1} graphene oxide (GO) solution was adjusted to pH 8.0 using dilute ammonia solution. Then, urea (1.5 g) was added under vigorous stirring into the GO solution and then heated to 95°C and refluxed for 10 h. Subsequent filtration, followed by repeated rinsing with water and ethanol. Finally, the collected sample, denoted as NGE, was dried in a vacuum oven. As reported, the as-prepared nitrogen-doped graphene is pyrrolic nitrogen doped graphene [23].

All other chemicals were of analytical reagent grade and used as received. Millipore water from a Milli-Q water purifying system ($18 \text{ M}\Omega \text{ cm}^{-3}$) was used throughout all experiments. Phosphate buffer solution (PBS) was prepared by mixing the solution of $0.2 \text{ M NaH}_2\text{PO}_4$ and $0.2 \text{ M Na}_2\text{HPO}_4$. Citric acid/disodium hydrogen phosphate buffer solutions (CPS) with different pH value were prepared from 0.1 M citric acid and $0.2 \text{ M Na}_2\text{HPO}_4$. All experiments were performed at room temperature ($25 \pm 0.5^\circ\text{C}$).

All electrochemical experiments were carried out with a CHI 660D electrochemical workstation (CH Instruments, Shanghai, China). A conventional three-electrode system was used for all electrochemical experiments. A bare or modified GCE (3 mm diameter) as working electrode, a saturated calomel electrode (SCE) and a platinum wire electrode were used as reference and auxiliary electrodes, respectively. Raman spectra were recorded on a Renishaw Invia Raman Microprobe using a 514.5 nm argon ion laser. The morphologies of modified electrodes were studied by SEM (S-4800 Hitachi).

2.2. Construction of PEDOT/NGE modified electrode

GCE was firstly sequentially polished with $1 \mu\text{m}$, $0.3 \mu\text{m}$ and $0.05 \mu\text{m}$ alumina/water slurry (Shanghai Chenhua Co., Ltd. China) on a polishing cloth to a mirror-like finish. Then the polished GCE was ultrasonicated in water and acetone for 5 min, respectively.

NGE was dispersed in DMF by ultrasonication for 2 h, resulting in a homogeneous black suspension of 1 mg mL^{-1} . Ten microliter of this solution was dipped on the polished GCE and dried with N_2 to construct a NGE modified GCE (NGE/GCE).

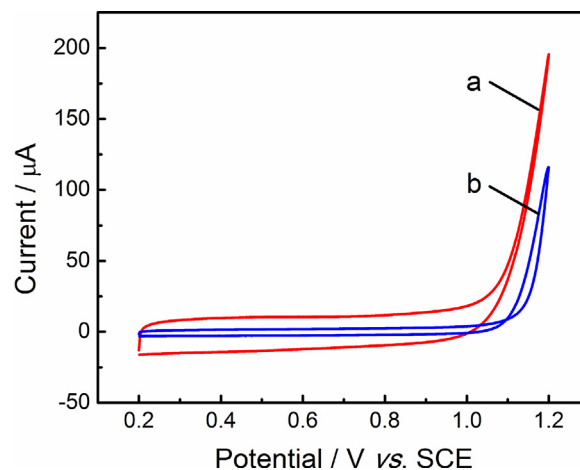


Fig. 1. The first cycle of CVs for the polymerization of EDOT at NGE/GCE (curve a) and at bare GCE (curve b). Scan rate = 0.1 V s^{-1} .

The fabrication of PEDOT/GCE and PEDOT/NGE/GCE were prepared by a one-step electrochemical deposition. The deposition of PEDOT was performed in the solution containing $0.1 \text{ M LiClO}_4 + 0.01 \text{ M EDOT}$ on GCE or NGE/GCE via cyclic voltammetry (CV).

2.3. Electrochemical measurements

CV and Differential pulse voltammetry (DPV) were employed for examining the electrochemical signal of the as-prepared electrodes to a certain amount of HQ and CT. The DPV conditions were as follows: Potential Increase, 0.004 V ; Amplitude, 0.05 V ; Pulse width, 0.05 s ; Pulse Interval, 0.2 s . Electrochemical impedance spectroscopy (EIS) was employed to characterize the electron transfer property of the electrodes in a 0.1 M KCl solution containing $5.0 \text{ mM [Fe(CN)}_6]^{3-/4-}$. Impedance spectra were recorded over a frequency range from 0.1 to 10^6 Hz with amplitude of 5 mV . The accumulation process of HQ and CT in this work was performed for 10 s in the solution directly.

2.4. Preparation of real samples

All water samples (lake water) were collected from Nanjing. Prior to experiments, samples were filtered through $0.44 \mu\text{m}$ pore-diameter cellulose acetate membranes, and then adjusted to pH 6.8 using solid $\text{Na}_2\text{HPO}_3/\text{NaH}_2\text{PO}_3$. Spiking of the sample was achieved by injecting an HQ or CT solution into the sample and then homogenizing.

3. Result and discussion

3.1. Electrodeposition of PEDOT

Fig. 1 shows the first cycle of cyclic voltammograms (CVs) for the electropolymerization of 10 mM EDOT at the GCE and NGE/GCE in 0.1 M LiClO_4 . As shown in Fig. 1, the background current of curve a for NGE/GCE is higher than that of curve b for GCE, moreover, the oxidation onset potential of EDOT at the NGE/GCE is lower than that at GCE, which means that NGE/GCE has better electrochemical performance, more electroactive sites and higher electrocatalytic activity to the oxidation of EDOT. It suggested that the introduction of NGE can be in favor of the nucleation and growth of PEDOT.

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