



An electrochemical sensor based on the three-dimensional functionalized graphene for simultaneous determination of hydroquinone and catechol



Jie Du¹, Linlin Ma¹, Duoliang Shan, Yanru Fan, Liping Zhang, Li Wang, Xiaoquan Lu^{*}

Key Laboratory of Bioelectrochemistry & Environmental Analysis of Gansu Province, College of Chemistry & Chemical Engineering, Northwest Normal University, Lanzhou 730070, PR China

ARTICLE INFO

Article history:

Received 4 January 2014

Received in revised form 27 February 2014

Accepted 28 February 2014

Available online 16 March 2014

Keywords:

Three-dimensional
Functionalized graphene
Hydroquinone
Catechol
Simultaneous detection

ABSTRACT

In this study, a simple and sensitive electrochemical analytical method is developed for simultaneous detection of hydroquinone (HQ) and catechol (CC) employing the three-dimensional functionalized graphene (3DFG) modified glass carbon electrode (GCE). The 3DFG modified electrode can distinguish between HQ and CC, with higher oxidation currents in comparison with bare GCE and two-dimensional graphene (Gr) modified electrode, showing the enhanced catalytic activity. The differential pulse voltammetry (DPV) shows that the isomers can be detected sensitively and selectively at 3DFG/GCE with peak-to-peak separation about 100 mV. Under the optimized conditions, the oxidation peak current increases linearly with concentration of HQ ranged from 3.10×10^{-7} to 1.31×10^{-5} M and concentration of CC ranged from 2.50×10^{-7} to 1.29×10^{-5} M, respectively. The detection limits are 1.0×10^{-7} M and 8.0×10^{-8} M for HQ and CC (S/N = 3), respectively. Moreover, the proposed method has been successfully applied to the simultaneous determination of HQ and CC in real water samples with satisfactory recoveries.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Hydroquinone (HQ) and catechol (CC), as the important industrial raw materials and synthetic intermediates, are widely used in the manufacturing of dyes, cosmetics, pesticides, antioxidants, and photography chemicals [1]. They are two isomers of dihydroxybenzene and are highly toxic to living beings [2]. The studies showed that HQ with high concentration could cause kidney damage [3] and lead to acute myeloid leukemia [4], and that CC could induce damage to DNA and cause cancer to human body [5]. What is more, due to their similar structures and properties, HQ and CC usually coexist in products and interfere with each other during their identification [6,7]. Therefore, it is crucial to develop a simple and reliable analytical method for the accurate and simultaneous determination of HQ and CC. For simultaneously determining these two compounds, various methods have been developed, such as liquid chromatography [8], synchronous fluorescence technique [9], chemiluminescence [10,11], spectrophotometry [12] and electrochemical methods [13–15]. Among them, electrochemical methods have attracted significant interests owing to their

excellent sensitivity and cheap equipment. To enhance the electrocatalytic activity of the electrode, modifications were introduced by using different types of nanomaterials, including Au nanoparticle/carbon nanofibers [16], Pt–MnO₂ composite particles [17], carbon nanoparticle–chitosan composite [18] and polydopamine-reduced graphene oxide nanocomposite [19]. Recently, our group has successfully used the porphyrin functionalized carbon nanotubes [20] and carbon nanotubes–ionic liquid composite [21] to detect dihydroxybenzene isomers simultaneously. These interesting results inspired us to investigate novel nanomaterials for the simultaneous determination of HQ and CC.

Graphene (Gr), a two-dimensional carbon material with single layer carbon atoms densely packed in a honeycomb structure, has shown its fascinating applications in nanoelectronics, sensors and energy storage because of its remarkable physical and mechanical properties [22–24]. Moreover, theoretical and experimental studies demonstrated that chemical doping of graphene with foreign atoms on graphene could tailor its electronic and surface chemical properties, which resulted in widely potential applications [25–28]. For instance, some electrochemical sensors based on the nitrogen doped graphene have been reported for study of direct electron transfer and detection of different targets such as glucose [29], nitro explosives [30] and dopamine [31,32]. Recently, increasing researchers have focused on the preparation of three-dimensional

* Corresponding author. Tel.: +86 931 7971276; fax: +86 931 7971323.

E-mail address: taaluxq@gmail.com (X. Lu).

¹ These authors contributed equally.

(3D) graphene. For example, Worsley et al. obtained a macroscopic 3D graphene assembly with high electrical conductivity and large surface area [33]. Xu et al. prepared three-dimensional networks of graphene hydrogel via a convenient one-step hydrothermal method [34]. Wu et al. reported controllable assembly of Fe₃O₄ nanoparticles supported on 3D graphene networks as oxygen reduction reaction catalysts [35]. In particular, Lin et al. reported functionalized graphene prepared by pyrolysis of graphene oxide with polypyrrole which possessed 3D porous structure and abundant graphitic N [36]. The 3D porous structure could enlarge surface area, which led to the enhancement of the detection sensitivity. The high percentage of graphitic N played a key role in enhancing catalytic ability of graphene [37–40]. The features of 3D functionalized graphene (3DFG) mentioned above strongly suggested that it was expected to be useful material for the detection of different target molecules in electroanalytical applications.

Herein, a facile strategy for simultaneous detection of HQ and CC was proposed by utilizing the 3D functionalized graphene as electrode modification material. Comparing with bare GCE and two-dimensional graphene (Gr) modified electrode, the 3DFG modified electrode showed superior electrocatalytic activity toward the oxidation of two isomers. HQ and CC exhibited two corresponding well-defined oxidation peaks with sufficiently differing peak potential and enhanced peak currents at the 3DFG modified electrode. In addition, the proposed method could be applied to the simultaneous determination of dihydroxybenzene isomers in real water samples with high selectivity.

2. Experimental

2.1. Reagents and apparatus

Hydroquinone (HQ) and catechol (CC) were purchased from Aladdin (Shanghai, China). Commercial graphene (Gr) were purchased from Nanjing Pioneer Co., Ltd., (China). Phosphate buffer solution (PBS, 0.1 M) was prepared by mixing the stock solution of 0.1 M NaH₂PO₄ and 0.1 M Na₂HPO₄, and the pH was adjusted by NaOH or H₃PO₄. Other chemicals were all analytical grade and the solutions were prepared by doubly distilled water. All the reagents were used without further purification.

Scanning electron microscopy (SEM) pictures were collected on a Hitachi s-4800 field emission scanning electron microscope (Japan). Transmission electron microscope (TEM) image was taken with a JEM-3010 transmission electron microscope (JEOL Co., Ltd., Japan). X-ray diffraction (XRD) study was conducted by D/max2400 ($\lambda = 1.54 \text{ \AA}$). X-ray photoelectron spectroscopy (XPS) analysis was carried out on a PHI-5702 X-ray photoelectron spectrometer. The nitrogen adsorption/desorption isotherms were measured using a Micromeritics Tristar II (Micromeritics Instrument Corporation, USA). Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) experiments were performed on CHI-832 working station (CHI instrument, Co., Ltd., Austin, USA). Electrochemical impedance spectroscopy (EIS) experiments were performed on multi-potentiostat (VMP2, Princeton Applied Research, USA), controlled by EC-Lab (V9.24) software (Bio-Logic SA). A three-electrode system was used, where a GCE (2 mm diameter) or a modified GCE served as the working electrode, a Pt wire as the counter electrode and a saturated calomel electrode (SCE) electrode as the reference electrode. All the measurements were carried out at room temperature.

2.2. Synthesis of 3D functionalized graphene

Graphene oxide (GO) was prepared from natural graphite powder through a modified Hummers method [41]. 3D functionalized graphene was prepared according to the method reported

previously [36]. Briefly, the 200 mg synthesized GO was firstly dispersed in 40 ml 1.0 M aqueous HCl solution by sonication to form a homogeneous solution, and then 100 mg pyrrole was added into the GO solution. Subsequently, a suitable amount of 0.17 g (NH₄)₂S₂O₈ in 1 M HCl was added slowly into the system. The reaction was carried out at room temperature for 24 h. After that, the sample was collected by vacuum filtration, washed repeatedly with double distilled water, dried overnight, and followed by thermal treatment at 800 °C for 30 min under Ar ambient.

2.3. Preparation of modified electrodes

Prior to modification, the bare GCE was polished to a mirror-like shine with 0.03 μm alumina slurry, then washed successively with anhydrous alcohol and double distilled deionized water in an ultrasonic bath and dried in N₂ blowing. The 3DFG was dispersed in the mixture of water and isopropanol (V:V = 4:1) containing 0.05 wt% nafion. Then, 3.0 μL of 1 mg/ml above-prepared 3DFG solution was cast on the pretreated bare GCE surface and dried under infrared lamp. The obtained electrode was noted as 3DFG/GCE. For comparison, Gr/GCE was fabricated with the similar procedure by adding Gr to N,N-dimethylformamide (DMF).

3. Results and discussion

3.1. Characterization of 3D functionalized graphene

Fig. 1 shows the characterizations of the 3DFG. From the SEM image of 3DFG in Fig. 1A, it was confirmed that the functionalized graphene was a 3D porous structure. Further morphology observation has been preceded by TEM. Fig. 1B clearly illustrated that the 3DFG was of wrinkled laminar structure like a crumpled silk veil. Moreover, the XRD pattern of 3DFG was given in Fig. 1C. It displayed that the broad peak centered around 26.12° with an interlayer space of $\sim 0.34 \text{ nm}$ (for pristine graphene, the strong diffraction peak locates at 24.62°), which was partially restored the graphitic crystal structure [36,42]. To analyze the composition and chemical configuration of nitrogen atoms in 3DFG, XPS studies were carried out. As shown in Fig. 1D, the survey scan spectrum from XPS analysis showed the presence of the principal C1s, N1s and O1s core levels without any other impurities and an atomic concentration of doped nitrogen was 5.0%. The high resolution XPS spectrum of N1s (Fig. 1D, inset) displayed the presence of four nitrogen functional groups in 3DFG. The peaks at 398.2 eV, 400.3 eV, 401.2 eV and 402.8 eV corresponded to the pyridinic N, pyrrolic N, graphitic N and oxidized N, respectively [36,42]. These XPS analyses demonstrated that nitrogen atoms had been successfully incorporated into graphene frameworks and existed as four kinds of chemical status in graphene layers. The nitrogen adsorption/desorption isotherm of the 3DFG sample was shown in Fig. 1E. The Brunauer–Emmett–Teller (BET) analysis revealed that a specific surface area of $\sim 350 \text{ m}^2 \text{ g}^{-1}$ was obtained for 3DFG, and the size of pore distribution was mainly mesoporous (Fig. 1E, inset).

3.2. Characteristics of the modified electrode

The electrochemical performance of 3DFG/GCE was investigated by using 5.0 mM Fe[(CN)₆]^{3-/4-} redox probe. As Fig. 2A shown, compared with bare GCE and Gr/GCE, it could be seen that the redox peaks of 3DFG/GCE were significantly increased due to the larger surface area on the 3DFG modified electrode. As shown in inset of Fig. 2A, the oxidation peak currents of [Fe(CN)₆]^{3-/4-} increased linearly with the square root of scan rates.

Download English Version:

<https://daneshyari.com/en/article/218770>

Download Persian Version:

<https://daneshyari.com/article/218770>

[Daneshyari.com](https://daneshyari.com)