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Application of thermally reduced graphene oxide modified electrode in simultaneous determination of dihydroxybenzene isomers

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ABSTRACT

Thermally reduced graphene oxide (TRGO) was used as an excellent electrocatalyst for the construction of electrochemical sensor for simultaneous determination of dihydroxybenzene isomers including hydroquinone (HQ), catechol (CC) and resorcinol (RC). The surface morphology and structure of TRGO were investigated by utilizing transmission electron microscope, scanning electron microscopy, atomic force microscope, Raman spectroscopy and X-ray diffraction. The electrode modified with TRGO shows excellent electrocatalytic activity toward the oxidation of HQ, CC and RC. As a result, the oxidation peaks of three isomers in pH 6.0 PBS can be clearly discriminated due to large peak potential separation among them. In addition, HQ and CC can be simultaneously determined by using differential pulse voltammetry without any separation step. Under the optimized condition, the detection limits of HQ and CC are 0.75 and 0.8 μM (S/N = 3) with linear ranges of 1–500 μM in the presence of 50 μM isomer, respectively. The proposed method was successfully applied to the simultaneous determination of CC and HQ in synthetic water sample with reliable recovery. The proposed sensor has some important advantages such as low cost, ease of preparation, good stability and high reproducibility. Therefore, the present work promises for the application of graphene modified electrode in the simultaneous determination of multiple analytes.

1. Introduction

Dihydroxybenzene, as a fundamental chemical compound and synthetic intermediate, has been widely used in production of dyes, photostabilizer, developer, cosmetic, pesticides and some pharmaceuticals such as isoprenaline and berberine. However, this compound is toxic to many biological species and difficult to be degraded, thus threatening the environments and endangering the health of both humans and animals [1]. In the concern of health and environment issues, limiting the use of dihydroxybenzene in environmental and pharmaceutical products is critical and emergent. For instance, the level of phenolic compounds in discharged wastewater should be less than 0.3 mg/L according to the Chinese Standard [2]. Hydroquinone (1,4-dihydroxybenzene HQ), catechol (1,2-dihydroxybenzene CC) and resorcinol (1,3-dihydroxybenzene RC) are three isomers of dihydroxybenzene and often coexist in samples. Because of their different mechanism for generating toxicity and their distinct environmental effect, it is necessary to determine their respective content in addition to their total amount.

Up to now, several analytical methods have been proposed for the determination of these three compounds, including chromatography [3,4], capillary electrophoresis [5], spectrophotometry [6,7] and electrochemical methods [8,9]. Among all these techniques, spectrophotometry is expensive and easily interfered by related compounds, thus unsuitable for multi-component analysis. Though chromatography and capillary electrophoresis have potential for simultaneous detection of dihydroxybenzene isomers, they usually require complicated and time-consuming sample pretreatment processes, expensive instruments and long analysis time. The electrochemical method, especially voltammetric methods, has been developed as one of the most promising techniques in environmental and biological analysis because of its simplicity and convenience. Moreover, the redox couple quinol/quinone is usually used as a model in proteins in a variety of biological media. Therefore, measuring dihydroxybenzene isomers by electrochemical method is important and more practical. Unfortunately, due to the same electroactive groups, redox peaks of these isomers, especially HQ and CC, usually overlap together, rendering them

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be hardly resolved by conventional electrodes. In addition, the use of conventional electrodes for the detection of these isomers has a number of other limitations as well, such as low selectivity and sensitivity, slow electron transfer kinetics and high overpotentials. In order to overcome these inherent difficulties, the chemical modification of inert substrate electrodes with suitable electrocatalysts offers feasible means to improve the interfacial electron transfer. So far, a few modified electrodes comprising carbon nanotubes (CNTs) [10], mesoporous carbon [11] and gold nanostructures [12] have been proposed for simultaneous detection of dihydroxybenzene isomers. However, these electrocatalysts have some disadvantages, e.g. high cost, complicated fabrication process and difficult functionalities. Thus, it is urgent to develop novel functional materials with excellent catalytic activity, good conductivity, and/or absorbability as the new generation of electrode materials.

Graphene, a single atomic plane of graphite, has recently attracted tremendous interests since its discovery in 2004 [13]. In comparison with CNTs, graphene exhibits potential advantages of low cost, high surface area, excellent conductivity, ease of processing and safety. Various methods of producing graphene sheets have been developed. Among them, the most promising way to massively produce graphene sheets was the chemical, electrochemical or thermal reduction of graphene oxide (GO) exfoliated from oxidized graphite [14–19]. The as prepared graphene is also called functionalized graphene sheets because it usually has abundant structural defects and functional groups which are believed to play an important role in performing its electrocatalytic activities [19–21]. In this sense, graphene produced from GO reduction is especially advantageous for electrochemical applications. Chemically reduced graphene oxide modified electrodes have been reported to show excellent electrocatalytic activities toward a variety of biomolecules such as H_2O_2, DNA [22], NADH [23], dopamine [24], and other important electroactive species [21,25,26]. However, the process for fabrication of chemically reduced graphene oxide usually involves toxic hydrazine as reducing agent, and the excessive reducing agents employed in this approach could contaminate the resulting materials. In the case of electrochemically reduced graphene oxide, though the fabrication process is simple and green, it is difficult to obtain processable graphene sheets in large quantities. The thermally reduced graphene oxide (TRGO), produced from the thermal reduction of GO, can overcome the above limitations. In this approach, the oxygenated species on GO surface could be efficiently eliminated by annealing at high temperature, and the prepared graphene has relatively high surface-to-volume ratio. As expected, the electrochemical performances and applications of thermally reduced graphene oxide (TRGO) is worthy of further exploration.

In the present paper, we demonstrate the ability of TRGO as a platform for simultaneous determination of dihydroxybenzene isomers based on their direct electrochemical oxidation at TRGO modified glassy carbon electrode. After the morphology and structure of TRGO were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), X-ray diffraction (XRD) spectroscopy and Raman scattering spectroscopy, the electrochemistry of three dihydroxybenzene isomers on the TRGO modified glassy carbon electrode was studied. It is found that the TRGO shows excellent catalytic activity toward the oxidation of the three isomers. Therefore, a TRGO based electrochemical sensor has been constructed and further used to identify and simultaneously determine the isomers without any pretreatment or separation steps. This work lays out prospects for the application of graphene modified electrode in simultaneous determination of multiple analytes.

2. Experimental

2.1. Reagents and apparatus

Hydroquinone (1,4-dihydroxybenzene), catechol (1,2-dihydroxybenzene) and resorcinol (1,3-dihydroxybenzene) (obtained from J&K Chemical Reagents Ltd., Beijing, China) were used without further purification. The stock solutions of the three isomers were prepared with twice distilled water and stored at 4 °C in the dark prior to use. Phosphate buffer solutions (PBS) were prepared by mixing the stock solutions of 0.05 M NaCl and different ratios of 20 mM KH_2PO_4 and 20 mM Na_2HPO_4 to adjust the pH value of detection solutions. Graphite powder (Sigma Aldrich) was used for synthesis of GO. Other chemicals were of analytical reagent grade.

SEM images were obtained on a Hitachi 4800 (Hitachi, Japan). TEM image was collected on a JEM 2100 (JEOL, Japan). AFM images were acquired by using an Agilent 5500 AFM/SPM system with Picoscan v5.3.3 software. X-ray diffraction was performed with a XRD-6000 X-ray diffractometer (Shimadzu, Japan) using Cu $K\alpha$ radiation. Raman scattering spectroscopic measurements were performed on a JY-HR800 Raman spectrometer using a 488-nm laser source. Electrochemical experiments were performed on a CHI 900 electrochemical station (CHI Instruments Inc., USA) with a conventional three-electrode system. The graphene modified glassy carbon electrode was used as the working electrode. A Pt wire and a saturated calomel electrode acted as the counter and reference electrodes, respectively. All electrochemical experiments were carried out in a supporting electrolyte of PBS (20 mM, pH 6.0) at room temperature (25 ± 1 °C).

2.2. Preparation of thermally reduced graphene oxide

The GO was synthesized from graphite powder by the modified Hummers method [27,28]. Typically, 2 g graphite, 1 g $K_2S_2O_8$ and 1 g P_2O_5 powder were added to a 3 mL concentrated H_2SO_4 solution. The resultant dark blue mixture was refluxed at 80 °C over a period of 6 h, followed by thoroughly washing with deionized water and drying. 2 g preoxidized graphite powder was added in 46 mL cold (0 °C) concentrated H_2SO_4. A 6 g $KMnO_4$ was added gradually under stirring and cooling conditions by keeping the reaction temperature below 20 °C. The mixture was then stirred at 35 °C for 2 h, and 92 mL H_2O was added. In 15 min, 280 mL water and 5 mL 30% (w/w) H_2O_2 solution were added to terminate the reaction. The color of the mixture changed to yellow-brown. The resulting product was then filtered, washed with 500 mL 1:10 HCl solution, and repeatedly washed with water until the pH value of filtrate reached neutral. It was further purified by dialysis for one week to remove residual salts, acids and metal species and was re-suspended by ultrasonication in water to obtain a homogeneous GO dispersion. Then, unexfoliated graphite oxide was removed by centrifugation at 3000 rpm and the precipitate was collected by centrifugation at 15,000 rpm for 10 min. Finally, the precipitate was dried in the vacuum.

The as-synthesized GO powder was placed in an alumina boat and heated to 800 °C at a temperature raising rate of 10 °C/min and then remained at this temperature for an additional 1 h under Ar flow. After cooling to room temperature, the graphene that is named as TRGO was obtained. The graphene was dispersed in DMF (1 mg/mL) with ultrasonication for 30 min.

2.3. Preparation of TRGO modified electrodes

The substrate GCE was successively polished with 0.3 μm and 0.05 μm Al_2O_3 powder, sonicated in acetone and twice distilled water each for 5 min, and dried under N_2 blowing before used in further experiments. The prepared graphene was dispersed in DMF (1 mg/mL) with ultrasonication for 30 min. A 7.5 μL of the graphene