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Easy processing laser reduced graphene: A green and fast sensing platform for hydroquinone and catechol simultaneous determination

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ABSTRACT

A green, fast and facile approach for the preparation of graphene is proposed for constructing an electrochemical sensing platform. The fabricated platform is applied for the simultaneous determination of hydroquinone (HQ) and catechol (CC) based on laser reduced graphene (LRG) which is prepared by a consumer-grade laser pen (< $10). Scanning electron microscopy (SEM), atomic force microscope (AFM), X-ray photoelectron spectroscopy (XPS), Raman spectrum and X-ray diffraction (XRD) confirm that the synthesis of LRG could be achieved through a simple and efficient way without any chemical reducing agents and without time consuming process. The performance of LRG modified electrode shows the excellent electrocatalytic activity of LRG toward the redox reaction of HQ and CC. Under the optimized condition, the calibration curves for HQ and CC were obtained in the range of 1 to 300 μM, 2 to 300 μM, with detection limits (S/N = 3) of 0.5 μM and 0.8 μM, respectively. Therefore, our study may provide a promising sensing platform for a variety of electroanalysis applications.

1. Introduction

Hydroquinone (HQ, 1,4-benzenediol) and catechol (CC, 1,2-benzenediol) are two isomers of phenolic compounds, and due to their high toxicity and low degradability in the ecological environment [1], their determination is an interesting subject in electroanalysis. Moreover, the dihydroxybenzene isomers usually coexist in the environmental samples as pollutants and have similar structures and physicochemical properties, which make it difficult to simultaneously detect the isomers. Thus, it is crucial to develop highly sensitive and simple methods for the determination of HQ and CC simultaneously. Up to now, a number of analytical methods such as spectrophotometry [2], chromatography [3], chemiluminescence [4,5] and electrochemical methods [6–13] have been used for the simultaneous determination of HQ and CC. Among them, electrochemical technique has attracted more and more attention because of its simplicity, high sensitivity and feasibility. Unfortunately, the electrochemical responses of the dihydroxybenzene isomers containing the same electroactive groups, especially for HQ and CC, severely overlapped on ordinary electrodes, such as gold electrode and glassy carbon electrode (GCE). To address the problem, recently various advanced materials, including nanoparticles [6,7], polymers [8,9], mesoporous silica [10], ferrocene-derivative mediators [14] and carbon nanotubes [15], have been employed in the modification of electrodes for the simultaneous detection of dihydroxybenzene isomers.

Graphene, a two-dimensional (2D) network of sp^2-hybridized carbon atoms packed into a honeycomb lattice, has led to an explosion of interest in the scientific community since its initial discovery in 2004 [16]. One of the promising applications of graphene is the construction of chemical modified electrode in the area of sensors, owing to its merits of large surface area, excellent conductivity, strong mechanical strength and unique electronic properties [17–19]. It has been reported that graphene based sensors were successfully applied to determine a range of significant analytes such as dopamine [20], hydrogen peroxide [21], glucose [22] and other important electroactive species [23–27]. Among these electrochemical sensors and biosensors, the popular methods for the preparation of graphene are the chemical [20], electrochemical [27] or thermal annealing [24,26] reduction of graphene oxide (GO). However, the processes for fabrication of chemically reduced graphene oxide usually involve toxic chemical agents such as hydrazine for an extended period of 24 h or more [28,29]. Also, the hydrazine treatment of GO may create a nitrogen atoms doping effect that considerably affects their electronic structure [30], which is hardly conducive to electrochemical mechanism study. In the case of electrochemically reduced graphene oxide, though the reduction of GO could be achieved, it is still difficult to obtain highly reduced graphene, which may be affecting the electrochemical catalytic properties towards the molecules.

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Furthermore, the GO can be reduced by thermal treatment at high temperatures (> 1000°C), involving highly energy consuming or expensive equipment [31,32].

Most recently, laser reduction of GO was achieved as an attractive technique to fabricate graphene features by using a 633 nm optical microscope-focused laser beam [33], as well as femtosecond (FS) laser [34]. Compared to the chemical and high temperature thermal methods, the laser irradiation processes do not rely on the use of chemicals or high temperature treatment; especially shorten the reaction time from several hours to a few minutes. Gao et al. reported an effective route to produce laser reduced GO films for micro-supercapacitors [35]. A light scribe DVD driver was used to reduce GO film for flexible all carbon device [36,37]. However, to the best of our knowledge, laser reduced graphene (LRG) based sensor has not been reported for the detection of dihydroxybenzene isomers compounds. Herein, we demonstrate a green, fast and low-cost approach for the determination of HQ and CC based on laser reduced graphene by a consumer-grade laser pen for the first time. After the surface morphology and structure of LRG were characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), Raman spectrum and X-ray diffraction (XRD), the electrochemical activities of HQ and CC on the LRG/GCE were further studied. The performance of the modified electrode, such as linear range and detection of limit, was also evaluated and discussed.

2. Experimental

2.1. Reagents

HQ and CC were obtained from Tianjin chemical factory (China). Graphite flakes was purchased from Sigma-Aldrich. All other chemicals were of analytical grade and doubly-distilled water was used throughout. HQ or CC was dissolved into water to prepare 0.1 M stock solution, which was diluted by water to desire concentrations before use. Unless otherwise stated, a 0.1 M phosphate buffer solution (PBS) was used as the supporting electrolyte source for voltammetric analysis. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) solution were used for the pH adjustment of PBS.

2.2. Apparatus

The surface morphology and microstructure of the as-prepared GO and LRG were investigated by SEM (Hitachi S-3700 N) and AFM (PARK, XE-100). XRD was recorded using a D8 Discover (Bruker) X-ray diffractometer with Cu Kα radiation. Raman spectra were taken on LabRAM Aramis (HJY, France). X-ray photoelectron spectroscopy (XPS) measurements were performed with an ESCA Probe (Axis Ultra DLD, Kratos) using mono Chromatic Al Kα radiation ($h\nu$ = 1486.6 eV). Electrochemical measurements were performed on CHI660E electrochemical workstation (Chenhua, China). A conventional three-electrode system was carried out with a glassy carbon working electrode (GCE, 3.0 mm diameter), an Ag|AgCl (3.0 M KCl) reference electrode and a platinum wire counter electrode. All experiments were performed at room temperature (25°C).

2.3. Reduction of solid-state GO and purification

GO was synthesized from graphite flakes as our previous report [38]. Solid-state GO (10 mg) was directly irradiated by a consumer-grade laser pen with a wavelength of ~780 nm and low power output of 200 mW. The obtained product (2 mg) was added into water (4 ml) to make a suspension by sonication for 5 minutes. And then the aqueous solution was centrifuged at 10000 rpm for 3 minutes. The precipitates were repeatedly purified by water for several times until the residual GO was removed from the product. Finally, the LRG was produced.

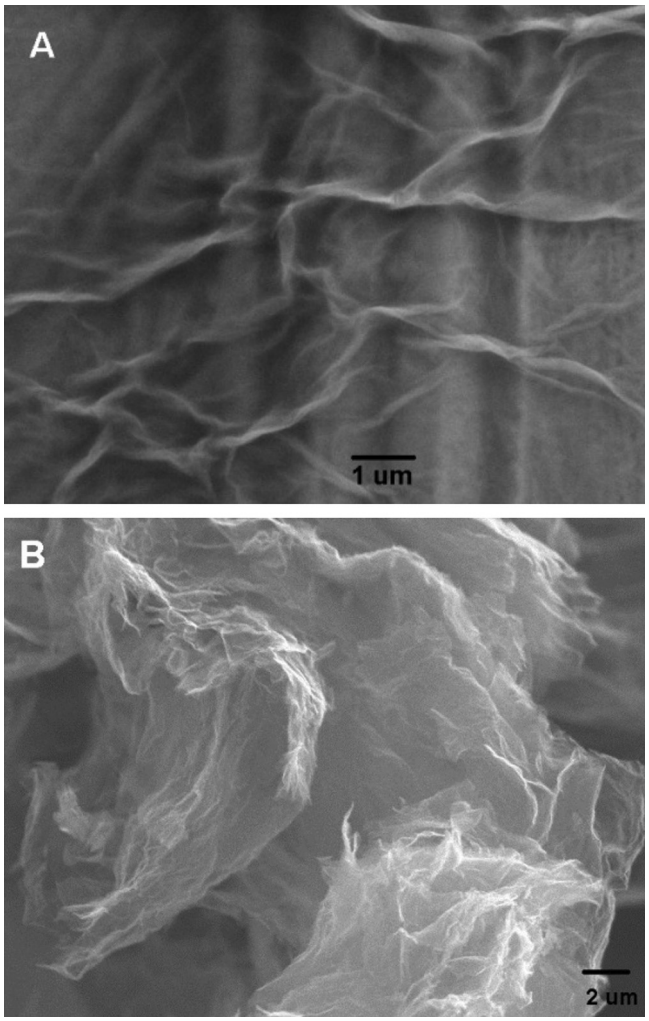

Fig. 1. SEM images of GO (A) and LRG (B).

2.4. Preparation of modified electrodes

GCE was carefully polished with 0.3 and 0.05 μm alumina slurries respectively. After 3 min of ultra-sonication in ethanol and water successively, the electrode was rinsed with water for several times and then dried. The LRG modified GCE (LRG/GCE) was prepared by dropping 5 μL aliquot of LRG aqueous solution (2 mg mL^{-1}) onto the GCE surface and drying at room temperature. A graphic illustration of the LRG based sensor fabrication and detection strategy is displayed in Scheme 1.

3. Results and Discussion

3.1. Characterization of LRG

Fig. 1 A and B shows the SEM images of GO and LRG, respectively. It can be observed that the structural properties of LRG are obviously different from the GO. The image clearly demonstrates the wrinkles and expanded structures of LRG caused by laser irradiation. The morphology of LRG was also characterized by AFM. Fig. 2 illustrates that the thickness of LRG was about 2.5 nm. Compared with the single layer graphene with thickness of 0.35 nm,