



Boron-doped graphene as high-performance electrocatalyst for the simultaneously electrochemical determination of hydroquinone and catechol



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ABSTRACT

Boron-doped graphene (BG) was prepared as a high-performance electrocatalyst for constructing an electrochemical sensing platform. Various characterizations revealed that the boron atoms had been successfully doped into graphene structures with the atomic percentage of 1.4%. The fabricated platform was applied for the simultaneous determination of hydroquinone (HQ) and catechol (CC). Because of its particular structure and unique electronic properties, originating from boron doping, BG showed more excellent electrocatalytic activity than that of pristine graphene (PG) toward the redox reaction of HQ and CC, respectively. Under the optimized condition, calibration curves for HQ and CC were obtained in the range of 5 to 100 μM , 1 to 75 μM , with detection limits ($S/N = 3$) of 0.3 μM and 0.2 μM , respectively. Due to its high sensitivity and selectivity, BG is expected to act as a promising candidate of advanced electrode material for detecting trace HQ and CC in wastewater.

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1. Introduction

Hydroquinone (HQ, 1,4-benzenediol) and catechol (CC, 1,2-benzenediol) are two isomers of phenolic compounds, which are widely used in industrial production of pharmaceuticals, dyes and food and so on. Unfortunately, they broadly distribute in soil and aquatic environment and are difficult to be degraded due to their high toxicity and high stability in the ecological environment [1]. Moreover they usually coexist in the environmental samples and have similar structures and properties, which make it difficult to simultaneously detect the isomers. Therefore, it is crucial to develop highly sensitive and simple methods for the simultaneous determination of HQ and CC. Recently, the high-performance liquid chromatography [2], spectrophotometry [3], chemiluminescence [4,5] and electrochemical methods [6–13] have been reported for the simultaneous determination of HQ and CC. However, these techniques have the disadvantages of sample separation, complicated pretreatment and relatively high cost. In contrast, electrochemical methods [14–18] have attracted more and more attention because of their simplicity, high sensitivity and feasibility. Since the redox peaks of HQ and CC are severely overlapped or too close to be simultaneously determined at ordinary electrodes, only one of

dihydroxybenzene isomers could be determined by the electrochemical methods. To address the problem, novel sensing materials with high stability, good catalytic activity and excellent conductivity, including nanoparticles [6,7], mesoporous silica [8], polymers [9,10], ferrocene-derivative mediators [19] and carbon nanotubes [20] have been developed 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 attracted widespread attention because of its merits of large surface area, excellent conductivity, strong mechanical strength and unique electronic property [21–23]. Graphene holds a great promise for many applications such as nano-electronics [24,25], sensors [26,27], nano-composites [28,29], batteries [30], supercapacitors and hydrogen storage [31] in recent years. It is important to prepare high catalytic graphene sheets while controlling the electrical property. One of the most effective strategies to tailor the electronic properties of graphene is by doping. It is well known that nitrogen and boron atoms are considered to be excellent candidates for the chemical doping of carbon materials. This is because of their comparable atomic size and the presence of five and three valence electrons available to form strong valence bonds with carbon atoms, which would provide p- and n-doping, respectively [32]. The doped atoms could be used to modify the electronic band structure of graphene and consequently to tune the mechanical properties and electrocatalytic activity as well [33–37], which can potentially enable

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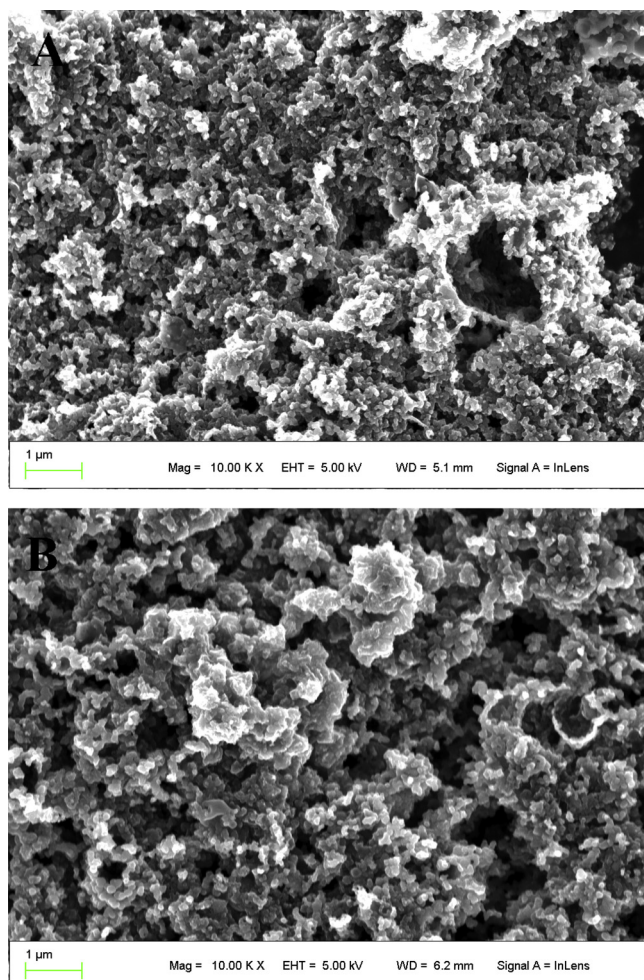


Fig. 1. SEM image of (A) PG and (B) BG.

its widespread applications. Therefore intensive theoretical researches focused on this topic, and many applications of doped graphene have been reported [38–42].

To date, to the best of our knowledge, the application of BG for electrochemical sensors has rarely been explored. In the present study, BG was synthesized via a hydrothermal method for constructing an electrochemical sensor to detect the dihydroxybenzene isomers. BG was easily prepared following a simple procedure by using CCl_4 , K and BBR_3 only for 20 hours at relatively low temperature (160°C). When compared with other methods which need several days preparation of graphene oxide and further doped with boron at high temperature, our approach was quite efficient and effective. The surface morphology and structure of BG were characterized by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and Raman spectrum. Besides, the BG modified electrodes were further characterized by electrochemical techniques. The electrochemical activities of HQ and CC were systematically studied and the mechanism of electrode reaction was also discussed. Finally, a selective and sensitive electroanalytical method was developed for the discrimination and determination of HQ and CC simultaneously.

2. Experimental

2.1. Reagents

All other chemicals were of analytical grade and used as received without further purification. Tetrachloromethane (CCl_4), potassium

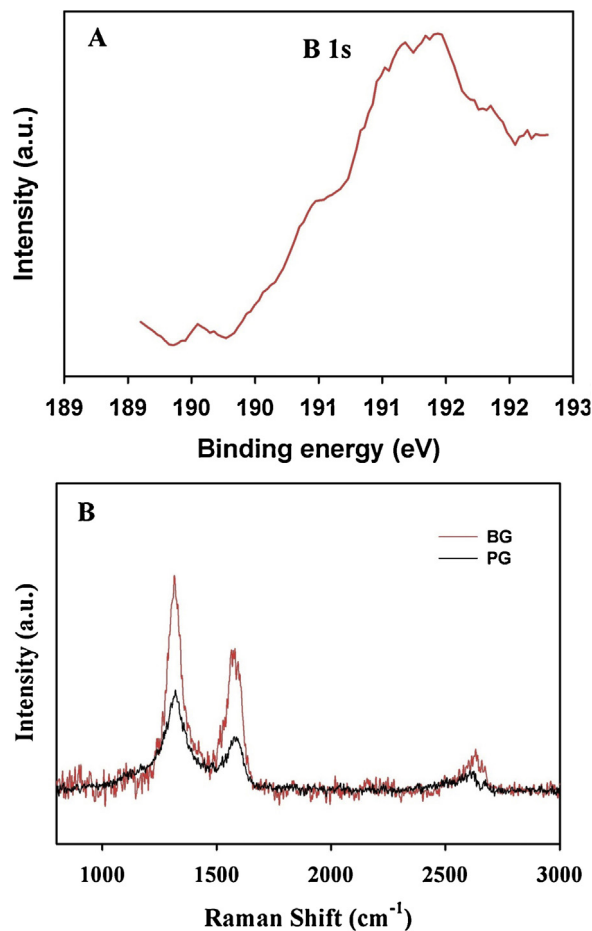


Fig. 2. (A) Raman spectra of PG and BG. (B) XPS spectra of BG.

metal (K) and boron tribromide (BBR_3) were purchased from Sigma–Aldrich. HQ and CC were obtained from the Sinopharm Group Chemical Reagent Co. Ltd. (China). HQ or CC was dissolved into water to prepare 0.1 M stock solution, which was diluted by water to desire concentrations before use. Other chemicals used were purchased from the local companies. Unless otherwise stated, a 0.1 M phosphate buffer solution (PBS) was used as the supporting electrolyte source for voltammetric analysis. Doubly-distilled water was used throughout the experiments.

2.2. Apparatus

SEM images were obtained on an S-4800 (Hitachi, Japan). Raman spectra were taken on LabRAM Aramis (HJY, France). XPS measurements were recorded with an ESCA Probe (Axis Ultra DLD, Kratos) using mono Chromatic Al $K\alpha$ radiation ($h\nu = 1486.6$ eV). Electrochemical measurements were performed using CHI660B electrochemical workstation (Chenhua, China). A three-electrode configuration was employed with a glassy carbon working electrode (GCE, 3.0 mm in 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. Synthesis of BG and PG

Pristine graphene (PG) and BG were synthesized as the previous report [43]. In a typical procedure, PG was fabricated by reacting potassium (K, 1.0 g) and tetrachloromethane (CCl_4 , 10.0 mL) in a sealed Teflon-lined stainless steel autoclave (50 mL). The autoclave

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