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Microwave-assisted solvothermal synthesis of sulfur-doped graphene for electrochemical sensing

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ABSTRACT

Heteroatom doping is an effective way to modulate the electronic structure and properties of graphene. Despite a growing interest in sulfur (S)-doped graphene (SG), synthesis of high-quality SG at low cost remains a great challenge. In this study, we developed a rapid, efficient and cost-effective microwave-assisted solvothermal (MAS) method for the preparation of SG. It was found that a short MAS time of 6 min could generate few-layer SG (0.5 μm in lateral size) having effective oxygen reduction, high level of S-doping, sole thiophene-S bonding configuration, and high electrical conductivity. Furthermore, the resulting SG could serve as an effective electrocatalyst for H_2O_2 reduction, showing improved electrocatalytic activity over its undoped counterpart and good sensing performances for highly sensitive and selective detection of H_2O_2, indicating that SG may be a promising candidate for electrochemical sensor applications.

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1. Introduction

Graphene, a monolayer of carbon atoms arranged in a honeycomb lattice, has attracted considerable interest owing to its excellent chemical, mechanical and thermal properties [1–3]. These unique characteristics offer a wide range of possibilities to synthesize graphene-based functional materials for various applications [4–7]. Recent progress has demonstrated that doping of graphene with heteroatoms such as nitrogen (N), boron (B), phosphorus (P) and sulfur (S) can further improve the electrocatalytic performance of graphene by enriching free charge-carrier densities, affording numerous active sites, and enhancing the interactions between carbon structure and other molecules/nanoparticles [8]. In particular, N-doped graphene (NG) has been extensively investigated as an electrode material for diverse applications in fuel cells, supercapacitors, lithium-ion batteries, and electrochemical biosensors [8].

S-doped graphene (SG) has attracted growing interest in recent 3 years. Both theoretical and experimental studies have revealed that the doping of S atoms into the graphene lattice causes the changed spin density and enhances the electrocatalytic activity of graphene [9,10]. Importantly, the thiophene-S bond in the graphene matrix is demonstrated as the active site for promoting electrocatalytic activity, and a small amount of S-doping with sole thiophene-S is sufficient to generate competitive or even better electrocatalytic activity compared to NG [11]. Nevertheless, there have been a few studies on the synthesis and application of SG because the larger formation energy is required to incorporate S atoms into graphene than N, B or P atoms, making the preparation of high-quality SG very difficult [12]. Even so, several approaches have been demonstrated to successfully dope S into graphene, such as annealing graphene oxide (GO) and benzyl disulfide (BDS) in argon [9]; thermal reaction of GO-mesoporous silica sheets in H_2S gas [10]; thermal exfoliating of GO in SO_2, H_2S, or CS_2 gas [13]; thermal shock/quench annealing of GO and phenyl disulfide [14]; combined ion-exchange/activation approach [15]; and solvothermal methods [16,17]. Unfortunately, all these methods suffer from high temperature treatment, toxic gases, complicated synthesis procedure or long synthesis time, which limits the practical application. Therefore, development of a simple, efficient and cost-effective method for the synthesis of SG is highly desired.

Microwave irradiation is proven to be a highly efficient heating method for transferring energy into the reaction system, which offers marked advantages such as simple and fast process and more homogeneous heating compared to conventional solution-based methods [18,19]. The application of microwave irradiation has been reported to effectively prepare NG with high doping degree and desired bonding configurations [20–23]. It would be very interesting to employ microwave irradiation for the efficient preparation of SG. Furthermore, most studies used SG material as an electrode material for oxygen reduction reactions [9,24], lithium-ion batteries [25] and dye-sensitized solar cell [26].

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However, little has been explored to apply SG in electrochemical sensing. To the best of our knowledge, there is no report on the microwave-assisted synthesis of SG and on the evaluation of its potential application for H_2O_2 sensing.

In this study, we developed a simple, fast and cost-effective microwave-assisted solvothermal (MAS) method for the synthesis of SG, as illustrated in Scheme 1. The morphology, structure, chemistry and electrical conductivity of as-prepared SG were characterized. In particular, X-ray photoelectron spectroscopy (XPS) was used to investigate the changes in S-doping degree and bonding configurations during the MAS process. Furthermore, we demonstrated that the resulting SG could serve as an effective electrocatalyst for H_2O_2 reduction, showing improved electrocatalytic activity over its undoped counterpart and good sensing performances for highly sensitive and selective detection of H_2O_2.

2. Experimental

2.1. Synthesis of SG

All the chemicals were purchased from Tianjin Chemical Reagent Co., Ltd. (Tianjin, China) and used without further purification. GO was prepared from graphite (200 μm, 99.9% purity, Qingdao Dongkai Grapite Co., Ltd.) by a modified Hummer's method [27]. SG samples were synthesized by a controllable MAS process of GO suspension containing BDS under the microwave irradiation treatment. In brief, 0.1 g of BDS was firstly added to 0.2 g of GO dispersed in 100 mL of 10:1 ethanol/water mixed solvent. Then the mixture was ultrasonicated for 1 h to obtain a homogeneous suspension. Afterwards, the suspension was sealed in a quartz tube and transferred to a commercially available microwave oven (G80F23YSL-X1, 2450 MHz, 800 W) subjected to microwave irradiation for 2–8 min. After cooling to room temperature naturally, the products were collected by centrifugation, washed several times with deionized water and dried at 60 °C for 24 h under vacuum. The SG samples treated at different MAS times of 2 min, 4 min, 6 min, and 8 min were denoted as SG-2, SG-4, SG-6, and SG-8, respectively. For comparison, a series of rGO samples (rGO-2, rGO-4, rGO-6, and rGO-8) were prepared through the same procedure as SG samples without adding BDS.

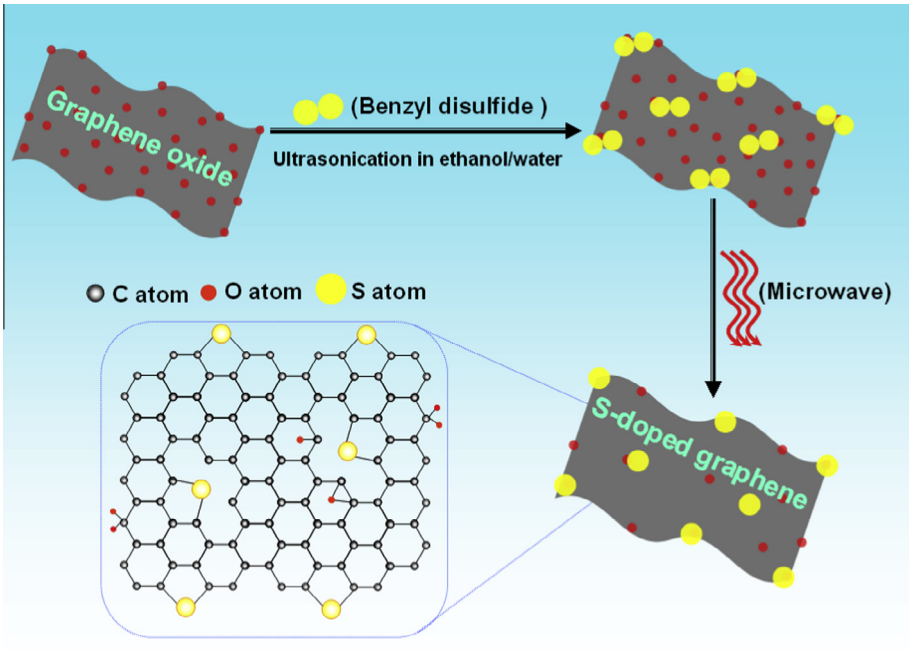
2.2. Characterizations

Scanning electron microscope (SEM, JSM-7401F), atom force microscope (AFM, Nanoscope III), transmission electron microscopy (TEM, JEM-2100), and high-resolution transmission electron microscopy (HRTEM, JEM-2100) were used for morphology observations. Nitrogen adsorption/desorption isotherms at 77 K were recorded on a ASAP 2020 instrument. Raman spectra were recorded on a Raman spectroscope (Alpha 300R, WITEC). XPS analysis was conducted on a PHI 5000C ESCA system. Electrical conductivity of the samples was measured by a four-point probe method. Cyclic voltammetric (CV), electrochemical impedance spectroscopy (EIS), and amperometric measurements were conducted on a PGSTAT-302N electrochemical workstation using a conventional three-electrode system in which a bared or modified glassy carbon electrode (GCE) was used as working electrode, and a Ag/AgCl electrode and a Pt wire was used as reference and counter electrodes, respectively. The modified GCE was prepared by a casting method. The as-received GCE (0.3 mm in diameter) was firstly polished to a mirror-like surface by alumina paste, followed by ultrasonically rinsing with distilled water and ethanol, respectively, and drying with high purity nitrogen. The electrocatalyst was dispersed in chitosan solution (0.5 wt.%, 2.0% acetic acid) and ultrasonicated for 1 h to form a uniform suspension (2.0 mg mL^{-1}). Then, 5 μL of the above suspension was cast onto the surface of the pretreated GCE and dried in air. All the as-prepared electrodes were stored at 4 °C in a refrigerator under dry conditions when not in use.

3. Results and discussion

3.1. Characterization of SG

Scheme 1 illustrates the MAS method for the preparation of SG. The MAS process is started by ultrasonically mixing GO with BDS in an ethanol/water mixed solvent, where abundant



Scheme 1. Schematic illustration of the synthesis process of SG.

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