Journal of Electroanalytical Chemistry 742 (2015) 8–14

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

One-step and rapid synthesis of nitrogen and sulfur co-doped graphene for hydrogen peroxide and glucose sensing

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ARTICLE INFO

Article history:
Received 15 December 2014
Received in revised form 21 January 2015
Accepted 26 January 2015
Available online 3 February 2015

Keywords:
Graphene
Heteroatom doping
Electrocatalytic activity
Electrochemical sensor

ABSTRACT

Nitrogen (N) and sulfur (S) heteroatoms co-doping has been confirmed to be an effective strategy to significantly promote the electrocatalytic activity of graphene. However, developing N, S co-doped graphene (NS–G) with a high doping level at low cost remains a great challenge. Meanwhile, NS–G has rarely been investigated for electrochemical sensing. Here, a one-step and cost-effective microwave-assisted solvothermal method was developed to synthesize NS–G having a high N, S-doping level (N: 6.8 at.%, S: 2.1 at.%). When employed as an electrocatalyst for H_2O_2 reduction, NS–G exhibited a higher electrocatalytic activity than its undoped or mono-doped counterparts due to the synergistic effect of N, S co-doping. Consequently, the sensors based on NS–G displayed good sensing performances for sensitive detection of H_2O_2 (0.1–16.6 mM in linear range, 0.2 μM in detection limit) and glucose (0.1–12.6 mM, 0.5 μM), demonstrating the potential application of NS–G for electrochemical sensing.

1. Introduction

Graphene, a monolayer of sp^2-bonded carbon atoms arranged in a honeycomb two-dimensional lattice, have drawn immense attention due to its unique features such as high mobility of charge carriers, large specific surface area, and excellent mechanical, chemical and thermal properties [1]. These fascinating properties hold great promise of graphene for potential applications in transistors [2,3], composites [4–6], supercapacitors [7–9], batteries [10–12] and sensors [13–15]. Both theoretical and experimental studies have demonstrated that doping of heteroatoms, such as N, B, P, S, Cl, I, and Se, into graphene structure can effectively modulate its electronic and chemical properties [16]. Among the doped graphene materials, N-doped graphene (N–G) has been widely studied due to the large electronegativity between the doped N atom (3.04) and C atom (2.55), which can increase the charge densities on the adjacent C atoms to boost the electrocatalytic activity [17]. As such, N–G has drawn great attention for many electrocatalysis applications, including oxygen reduction reaction (ORR) [17–19], supercapacitors [20,21], lithium-ion batteries [22,23], and electrochemical biosensors [24–26].

To further improve the electrocatalysis performances of N–G, simultaneous co-doping of N with other heteroatoms has been investigated, which shows that the catalytic activity of co-doped graphene is better than its corresponding mono-doped counterparts owing to the synergistic co-doping effect [27–33]. Typically, co-doping of N and S into graphene (NS–G) has been confirmed to be an effective strategy to substantially promote the electrocatalytic activity due to the unique electronic structures of S and N atoms that can induce the redistribution of spin and charge densities [27]. For instance, NS–G provides a better electrocatalytic performance than graphene doped with N or S alone for ORR [27,31], dye-sensitized solar cells [34,35], and lithium-ion batteries [36].

Despite a growing interest in NS–G, to date, only limited methods have been developed for the successful synthesis of NS–G. Current approaches to prepare NS–G are mostly based on thermal annealing of graphene oxide (GO) with reactive N/S precursors (melamine/benzyl disulfide [27], 2-aminothiophenol [36], thiourea [33], poly(3-amino-5-mercapto-1,2,4-triazole) [37], etc.). However, these methods rely on the reactions between the N/S source and GO at high temperature in parallel with long time treatment, which not only exhibit clear drawbacks of high cost and complex procedure, but also result in relatively low doping level in the final products. Some alternative ways were proposed to prepare NS–G by hydrothermal or solvothermal treatment of GO and N/S-containing biological organisms, such as inulin [38], Chinese wolfberry [38], and sulfate-reducing bacteria [39]. Albeit these

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http://dx.doi.org/10.1016/j.jelechem.2015.01.029
1572-6657/

methods exhibit some advantages of low synthesis temperature and environmental friendliness, they still suffer from tedious multi-step procedures that are time or labor-consuming, which limit the practical application. Accordingly, development of a simple and cost-effective approach for the large-scale synthesis NS–G is highly desired.

Microwave irradiation is a green, efficient and non-contacting heating method, which exhibits many advantages of simple operation, rapid and homogeneous heating as compared to aforementioned methods [40]. The use of microwave irradiation has been demonstrated for the successful synthesis of N–G with high doping level and desired bonding configurations [41–45]. Considering these merits, it would be very interesting to employ microwave irradiation for the efficient preparation of NS–G. From the other side, most studies used NS–G as an electrode material for ORR [27,31,33,37]. However, NS–G has rarely been investigated for electrochemical sensing [39]. Herein, a rapid, one-step and low cost microwave-assisted solvothermal (MAS) approach was employed to synthesize NS–G (Fig. 1). The morphologies and structures of as-prepared samples were systematically characterized. NS–G was then evaluated as an electrocatalyst for H_2O_2 reduction, which exhibited a higher electrocatalytic activity than its mono-doped or undoped counterparts, and good sensing performances for H_2O_2 detection. Furthermore, NS–G could serve as a glucose oxidase (GOD) platform for the construction of a glucose biosensor that could be used for sensitive detection of glucose in real serum samples.

2. Experimental

2.1. Materials and instruments

Graphite powders (200 μm, 99.9% purity) were purchased from Qingdao Dongkai Graphite Co., Ltd. D-(+)-glucose and chitosan (85% deacetylation) were purchased from Shanghai Chemical Reagent Co., Ltd. Glucose oxidase (GOD, Type X-S: from Aspergillus niger, 150,000 units/g) were purchased from Sigma–Aldrich. All other chemicals were purchased from Tianjin Chemical Reagent Co., Ltd. and used without further purification. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), energy disperse spectrum (EDS), and scanning transmission electron microscopy (STEM) elemental mapping were recorded on a JEM-2100 instrument. Raman spectra were recorded on a Raman spectroscope (Alpha 300R, WITEC). XPS analysis was conducted on a PHI 5000C ESCA system. Nitrogen adsorption/desorption isotherms at 77 K were conducted on a ASAP 2020 instrument.

2.2. Preparation of NS–G

GO was prepared from graphite powder by a modified Hummers' method [46]. NS–G was synthesized by the MAS route using thiourea (CH_4N_2S) as both N and S sources [47]. In a typical procedure, 1 g of GO was dispersed in 200 mL of deionized water under ultrasonication for 1 h, then 2 g of thiourea was added to GO suspension under ultrasonication for another 1 h. Subsequently, 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 10 min. After cooling to room temperature, the products were collected by centrifugation, washed several times with deionized water and dried at 60 °C for 24 h under vacuum. For comparison, undoped reduced graphene oxide (RGO, without addition of thiourea), mono-doped N–G (using urea as N source) and S-doped graphene (S–G, using NaS_2 as S source) were also prepared under similar conditions.

2.3. Electrochemical measurements

All electrochemical experiments (cyclic voltammetric (CV), electrochemical impedance spectroscopy (EIS), and amperometric response determination) were conducted on a PGSTAT-302N electrochemical workstation at room temperature using a conventional three-electrode system, including a modified glassy carbon electrode (GCE, 0.3 mm in diameter) as working electrode, a Ag/AgCl (saturated KCl) electrode as reference electrode and a platinum wire as counter-electrode. The modified GCE was prepared by a casting method. Prior to modification, the GCE (0.3 mm in diameter) was highly polished to a mirror-like surface with alumina paste, rinsed thoroughly with deionized water and dried

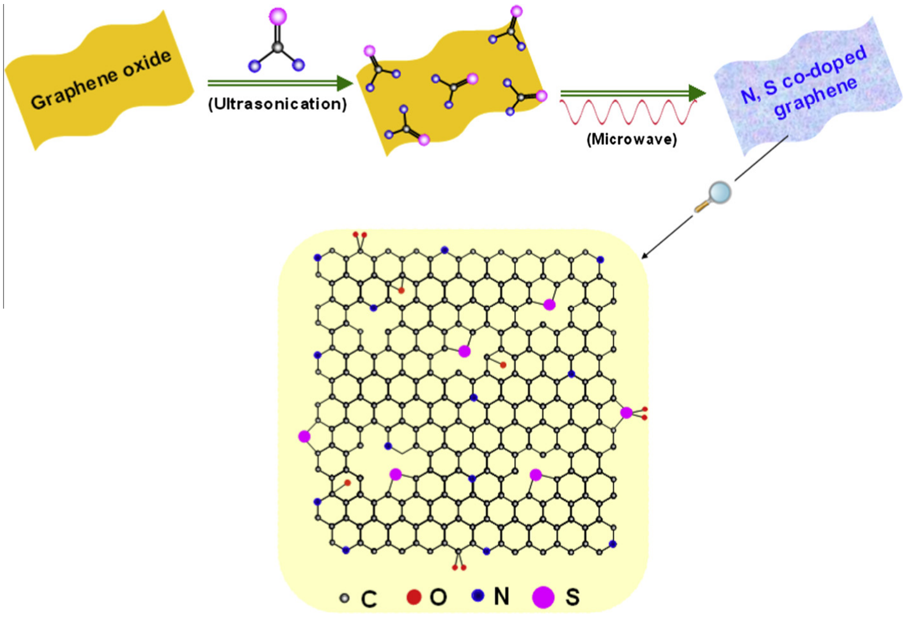

Fig. 1. Schematic illustration of the synthesis process of NS–G.