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A simple and fast microwave assisted approach for the reduction of graphene oxide

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Abstract

Herein, a simple and fast method for chemical reduction of graphene oxides (GO) was carried out, the most common monosaccharide (glucose) here served as a green, non-toxic and high-effective reduction reagent. After reacted in an alkaline microwave-assisted environment for several hours, the water-soluble glucose reduced graphene oxide (GRGO) was obtained. Meanwhile, the as-prepared GRGO powders can be easily dispersed in several common organic solvents. And the colloidal solutions show no signs of agglomeration even after a week. The Raman spectra XRD and the TG analysis as well as other tests show the GO sheets were reduced successfully. The electrochemical testing results reveal that GRGO3-based flexible electrode has specific capacitance as high as 179 F g^{-1} at the potential scanning rate of 2 mV s^{-1}. This environment friendly short-time microwave-assist solvothermal treatment is efficient and has a promising prospect of application.

Keywords: A. Microwave processing; Chemical preparation; Graphene oxide; Flexible electrode

1. Introduction

Graphene, a single hexagonally sheet of sp^2-hybridized carbon atoms tightly packed into a two-dimensional honeycomb lattice, has excellent electrical mechanical, optical properties and thermal properties as well as its high specific surface areas [1–4]. Over the past few years, due to the unique properties of this material, graphene based flexible thin-film transistors, hydrogen storage materials and supercapacitor electrode materials has attracted great research interests. Thus, large-scale production of graphene is needed. Many techniques have been reported to produce graphene, such as chemical vapor deposition (CVD) [5,6], micromechanical exfoliation of graphite [7], epitaxial growth on electrically insulating (SiC) surfaces [8], and chemical reduction of graphene oxide (GO) [9–11]. Among all these methods, the solution-processable chemical GO reduction approach is considered as the most promising route toward mass production of graphene based materials.

Graphene oxide is a water-dispersible material, with many hydroxyl and epoxide groups on its basal plane, and carbonyl and carboxyl groups on its edges [12,13]. Graphene oxide is usually synthesized by exfoliation of graphite oxide, which is obtained by oxidizing graphite using strong acid and oxidants [14].

Typically, strong reductants such as hydrazine monohydrate [15], sodium borohydride [16,17], and strong alkali [18] are used to reduce aqueous dispersions of GO. However, these hydrazine and sodium borohydride are corrosive, flammable and highly toxic which have hazard to personnel health and the environment. And research shows that trace amounts of hydrazine could be harmful to such applications such as organic solar cells [19]. Recently, some mild non-toxic and environment-friendly reductants have been researched widely. Urea [20], ascorbic acid [21,22], amino acid [23,24] and reducing sugar [25,26] are used as substitutes for hydrazine monohydrate. However, although those methods have advantages of low-cost, non-toxic and large-scale production, the reduced graphene oxide in those methods usually has a low solubility in water and most organic solvents. The reduced graphene oxide sheets can easily agglomerated, this means that for further use of those reduced GO, capping reagents

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(polymers or surfactants) should be used which may affect the properties of the graphene sheets.

Herein, we describe a new approach for the reduction of graphene oxide using glucose in an alkaline environment with the assist of microwave heating. The main advantage of microwave assist heating over other traditional heating methods is heating the reaction mixture uniformly and rapidly. Microwave assist heating can provide significant enhancement in the transfer of energy directly to the reactants which causes an instantaneous internal temperature rise [27,28]. Thus can shorten the reaction time greatly, and improve the reaction efficiency. The use of glucose as a new effective reductant for the reducing of GO can obviously remove a part of the oxygen-containing functional groups on its surfaces. And the GRGO powders can be dispersed in water as well as other polar solvents and holds stability for a long time (more than 7 d). Thus it is very important for further synthesis of graphene-based materials. The as-prepared GRGO also has a good electrochemical performance. The thin slice electrode made from the GRGO without adding any other active materials can reach a specific capacitance of 179 F g^{-1} at a scan rate of 2 mV s^{-1}.

2. Experimental section

2.1. Chemicals

Glucose ($C_6H_{12}O_6$, 99%) was purchased from Shanghai Chemical Reagents Company, ammonium hydroxide ($NH_3 \cdot H_2O$, 25%) and sodium sulfate anhydrous (Na_2SO_4, 99%) were supplied by Sinopharm Chemical Reagent Co. Ltd. Deionized water used during experiments was freshly prepared by an Ulupure system (18 MΩ). All of the chemicals used in this reduction were of analytical reagent grade. Cellulose membrane (50 mm, 0.22 μm) was bought from Shanghai Xinya Purification Device Factory.

2.2. Synthesis of GO and GRGO

GO was prepared from natural graphite powder using the modified Hummers. The GO suspension with a mass concentration of 0.2 mg mL^{-1} was prepared by dispersing the prepared GO powders into water with the help of ultrasonication (KQ-500E Ultrasonic Cleaner, KunShan Ultrasonic Instruments Co. Ltd).

Typically, to study the performance of glucose on the deoxygenation of graphene oxide, we first diluted the original graphene oxide solution to a concentration of 0.2 mg mL^{-1}. To avoid the agglomeration of the colloidal, the pH of the dispersions was adjusted to 9 by dropping diluent ammonia solution. After that, a certain amount of glucose was dissolved in the dispersion for about 30 min under stirring. In a typical reaction procedure, 50 mL solution was transferred into a double-walled 100 mL vessel, which has an inner liner and a cover made of Teflon PFA and an outer high strength sleeve. The vessel was sealed and maintained in a Microwave Accelerated Reaction System (MARS-5, CEM Corporation, USA) at 95 °C for 0.5 h, 1 h, 2 h and 3 h. To facilitate the distinction, we named the reduced graphene oxide as GRGO0.5, GRGO1, GRGO2, and GRGO3.

To remove the residual reductant, the reduced dispersions were washed repeatedly by vacuum filtration through mixed cellulose membrane with 50 mm in diameter and 0.22 μm pore size using ultrapure water. Then the filter cake, which was the reduced graphene oxide, was dispersed in a certain amount water again to form a stable suspension or dried at 80 °C for 24 h in vacuum to get powder samples. Both the suspensions and the powder samples were for the further characterization analysis.

2.3. Preparation of GRGO-based electrode materials

A certain amount GRGO tightly adhered on the cellulose membrane through a vacuum filtration, after drying for 2 d. The membrane-GRGO hybrid material was cut into a 1×1 cm^2 as electrode slice.

2.4. Characterization

The crystalline structure of samples was characterized with a X-ray diffractometer (XRD, Bruker D8-Advance, Cu Kα target, $\lambda = 1.5406$ Å). A field emission scanning electron microscope (FE-SEM, FEI, QUANTA FEG 250, United States) was used to observe the morphology and size of as-prepared samples. Ultraviolet–visible (UV–vis) absorption spectra were recorded on a Hitachi U-4100 UV–vis spectrophotometer at room temperature. The aqueous suspensions of graphene oxide or reduced graphene oxide were used as the UV–vis samples, and the pure deionized water was used as reference. The Fourier transform infrared (FT-IR) spectra were obtained on a FTS-165 (Bio-Rad, United States) spectrometer. The samples for FT-IR measurement were prepared by grinding the dried powder of reduced graphene oxide or graphene oxide with KBr, and then compressed into thin pellets. Raman measurements were performed on a High Resolution Raman spectrometer (LabRam HR Evolution, HORIBA JOBIN YVON S.A.S.). The powders of reduced graphene oxide or graphene oxide were placed on a clean SiO_2/Si substrate for the Raman measurement.

The Cyclic Voltammetry electrochemical measurement was performed on a CHI604D (Shanghai) electrochemical workstation with 2.0 mol L^{-1} Na_2SO_4 solution as the aqueous electrolyte. A Pt foil and a saturated calomel electrode were applied as the counter and reference electrodes, respectively.

3. Results and discussion

The reduction of GO with the presence of glucose can be directly observed by the color change of the dispersions, from bright yellow brown to black, as shown in Fig. 1(a). No distinct color change could be observed in the GO without the participation of glucose under 95 °C microwave assisted condition. The dispersion stability of reduced GO is a key problem due to the unique properties of graphene are based on the individual sheet and most of the applications require reduced graphene oxide (RGO) firstly being dispersed in water or some organic solvents. As mentioned in many papers [12,13,29], the