



A facile approach to prepare graphene via solvothermal reduction of graphite oxide



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ABSTRACT

In this work, a facile reduction strategy is reported for the fabrication of graphene. Graphite oxide (GO) is reduced via a novel solvothermal reaction in a mixed solution of acetone and sodium hypochlorite (NaClO). The structure, surface chemistry, morphology and thermal stability of the as-prepared reduced graphene oxide (RGO) are characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, transmission electron microscopy (TEM), atomic force microscopy (AFM), thermogravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS). The results indicate that most of the oxygenated groups in GO are effectively removed in this solvothermal reaction. The novel reduction method provides a simple, cost-effective and efficient strategy for the fabrication of graphene.

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1. Introduction

Graphene, a one-atom-thick layer of sp^2 -hybridized carbon atoms arranged in a hexagonal lattice, has attracted considerable interest from fundamental and application research fields because of its impressive electronic, optical, magnetic, thermal and mechanical properties [1]. Moreover, graphene shows great potential for application in various fields, such as supercapacitors, solar cells, sensors and polymer nanocomposites [2,3]. The wide exploitation of graphene requires the large-scale production of the thin carbon nanosheets at low cost. Since graphene was first obtained using a micromechanical cleavage approach by Geim et al., various strategies have been developed for the synthesis of graphene, including chemical vapor deposition, arc discharge, epitaxial growth, ultrasonication exfoliation of graphite and reduction of graphite oxide (GO) [4]. Among these, solution-based chemical reduction of GO is regarded as the most promising and desirable method for the large-scale production of reduced graphene oxide (RGO) [5]. The common scheme for the chemical reduction of GO involves the following three steps, namely oxidation–exfoliation–reduction process. Firstly, the raw graphite

is oxidized by strong oxidants according to the Staudenmaier or Hummers method, which introduces the oxygen functional groups and increases the intra-gallery spacing (d -spacing) between the nanosheets. Secondly, GO is exfoliated in some specific solvents, such as water, under mild ultrasonication or stirring. Finally, the GO dispersions are reduced to restore the ordered crystal structure. The reduction of GO using hydrazine is the most widely employed method to prepare RGO because of its high reductive efficiency [5]. Apart from its potential hazard to humans and environment, hydrazine also suffers from some other drawbacks. For example, nitrogen moiety is introduced into the structure of RGO during the reaction [6]. Furthermore, hydrazine is an expensive reagent. To date, various reducing agents, such as sodium borohydride, urea, glucose and phytoextracts, have been used as the substitutes for hydrazine to prepare RGO [7]. However, some reducing agents are not satisfactory, due to their low reductive efficiency. Therefore, developments of simple, efficient and cost-effective GO reduction methods are highly desirable.

In addition, hydrothermal and solvothermal reactions are also simple routes to preparing RGO. The GO dispersion is sealed in an autoclave and the temperatures of the systems are raised well above the solvents' boiling point. The high temperature and the autogenous pressure in the autoclave promote the deoxygenation of GO [8]. Solvothermal reductions of GO have been conducted in several high boiling point solvents, most notably in N,N -dimethylformamide (DMF) [8] and N -methyl-2-pyrrolidone (NMP) [9]. However, reduction efficiency of these solvothermal reactions is inferior to

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that of hydrazine. The reduction of GO in DMF and NMP may also result in the formation of C–N bonds in the graphene nanosheets, similar to that of hydrazine [8,9].

In this work, we aim to develop a novel, simple and effective method to prepare RGO. Herein, a strategy for preparing RGO based on a novel solvothermal reaction is reported. The structure, morphology, surface chemistry and thermal stability of the RGO are studied.

2. Experimental

2.1. Materials

Graphite powder, concentrated sulfuric acid (H_2SO_4 , 98%), sodium nitrate (NaNO_3), potassium permanganate (KMnO_4), hydrogen peroxide (H_2O_2 , 30%), hydrochloric acid (HCl, 37%), barium chloride dihydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$), tetrahydrofuran (THF), acetone and sodium hypochlorite aqueous solution (NaClO, available chlorine $\geq 5.2\%$) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). All reagents were of analytical grade and were used as received without further purification. Ultrapure water was produced in our laboratory.

2.2. Preparation of GO

GO was synthesized from graphite powder by a modified Hummers method [10]. Graphite powder (10 g) and NaNO_3 (5 g) were slowly added into a 2 L beaker filled with 230 mL H_2SO_4 under stirring in an ice bath, before KMnO_4 (30 g) was added. The mixture was continuously stirred in the ice bath and a 35 °C oil bath for 30 min, each. 460 mL ultrapure water in a dropping funnel was slowly dripped into the reactor over 2 h. The reaction was heated to 98 °C and maintained at this temperature for 15 min. The mixture was diluted in 700 mL warm water, and 25 mL H_2O_2 was added to eliminate the unreacted KMnO_4 . The raw product was purified with 5% HCl solution and ultrapure water to remove metal ions and acid, until no SO_4^{2-} could be detected in the filtrate by BaCl_2 and the pH became neutral. After washing in THF, the powder obtained was dried at 50 °C for 24 h.

2.3. Preparation of RGO

GO (80 mg) was dispersed in 30 mL acetone under mild ultrasonication for 1 h. NaClO aqueous solution (6 mL) was then dripped into the yellow brown dispersion. Next, the resulting mixture was transferred to a 50 mL Teflon lined stainless steel autoclave, sealed and heated at 120 °C for 2 h. Then, the autoclave was cooled to room temperature and the as-prepared product (RGO) was washed with water and THF, and dried in an oven at 80 °C for 24 h. In order to ascertain the role of acetone and water in

the reduction of GO, two control experiments were designed as comparisons. (I) Only 30 mL acetone, and (II) 30 mL acetone and 6 mL water were mixed with the GO powder. The control experiments were conducted under the same conditions described above. The products obtained were designated as GO1 and GO2.

2.4. Characterization

X-ray diffraction (XRD) patterns were obtained with a TTR-III X-ray diffractometer (Rigaku Co., Japan) using a $\text{Cu-K}\alpha$ tube and Ni filter ($\lambda = 0.1542 \text{ nm}$). Fourier transform infrared spectroscopy (FTIR) was recorded with a Nicolet 6700 spectrophotometer (Nicolet Instrument Co., U.S.). The samples were mixed with KBr and pressed into plates. Raman spectra were investigated from 1000 to 2000 cm^{-1} on a LABRAM-HR laser Confocal Raman spectroscopy (Jobin Yvon Co., Ltd., France) with a 514.5 nm argon laser line. The morphology of GO and RGO were observed by transmission electron microscopy (TEM), using a JEM-2100F microscope (JEOL Co., Ltd., Japan) with an acceleration voltage of 200 kV. The dispersions of GO and RGO after ultrasonication were dripped onto copper grids for observation. Atomic force microscopy (AFM) images were obtained in tapping mode on a DI Multimode V scanning probe microscope (Veeco Co., Ltd., U.S.). The aqueous dispersions of GO and RGO were drop-cast onto a freshly cleaved mica substrate. Thermogravimetric analysis (TGA) of the samples, ranging from room temperature to 800 °C, were performed with a TA Q5000IR thermo-analyzer (TA Instruments Inc., U.S.) at a linear heating rate of 20 °C/min, under nitrogen atmosphere. The surface functionalities of the nanomaterials were determined by X-ray photoelectron spectroscopy (XPS) on a VG ESCALB MK-II electron spectrometer (V.G. scientific. Ltd., UK) using $\text{Al K}\alpha$ line (1486.6 eV) as an excitation source.

3. Results and discussion

Generally, GO can be well dispersed and exfoliated in water and some specific solvents, due to the large amounts of the oxygen-containing functional groups decorating the surface of GO nanosheets. However, the oxygen functional groups are removed and the conjugated structures of the graphitic domain are restored after reduction. Thus, the color change of the GO dispersion before and after reduction directly reflects the reduction effect. Fig. 1(a) presents the photographs of the GO dispersions after solvothermal reaction (without purification). For the GO1 dispersion, the color is still yellow brown: that is to say, the reduction effect of single acetone on GO is not marked. However, the photograph of the RGO dispersion differs from that of GO1. Phase separation of the solvents is observed in the RGO dispersion. The black product is largely dispersed in the bottom oil phase, while the upper acetone remains pellucid. As shown in Fig. 1(b), the color of the GO aqueous

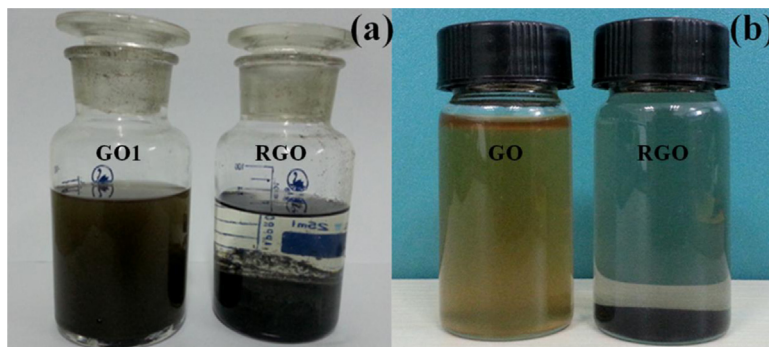


Fig. 1. (a) Photographs of GO1 and RGO dispersion after solvothermal reaction (without purification); (b) photographs of GO and RGO aqueous dispersion.

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