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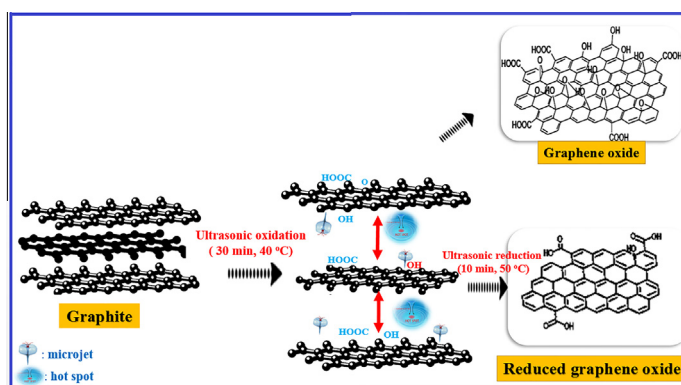
A benign ultrasonic route to reduced graphene oxide from pristine graphite



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GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 18 August 2016
 Revised 28 September 2016
 Accepted 28 September 2016
 Available online 4 October 2016

Keywords:

Ultrasound
 Cost-effective synthesis
 Graphene oxide
 Reduced graphene oxide
 Toxic
 Hydrazine

ABSTRACT

In this study, we report the synthesis of high purity reduced graphene oxide (rGO) from pristine graphite via a fast and cost-effective one-step ultrasonic reduction method. Ultrasonic treatment was employed to avoid the harsh reaction conditions, including high temperature and use of highly toxic hydrazine, required for the conventional rGO preparation method. The high temperature produced during the ultrasound irradiation at low temperature and short reaction time enabled the reduction of graphene oxide (GO) into rGO without the use of toxic chemicals. The oxygen functional groups on GO were successfully reduced by the sonochemical reduction. The rGO prepared using the ultrasonic method exhibited a curled morphology, a very thin wrinkled paper-like structure, sheet folding, minimal layers (~4 layers), and a layer spacing of ~1 nm. The sonochemical approach for the synthesis of rGO showed fast, high productivity, much improved safety, less energy, and time consuming characteristics as compared to other methods. More importantly, highly explosive and poisonous hydrazine is not required in this sonochemical technique, opposed to that required in conventional rGO synthesis, making it useful for many industrial applications of rGO.

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1. Introduction

The graphene sheet, a unique atom-thick two-dimensional structure, is often classified by the number of stacked layers

involved: single layer, few-layer (2–10 layers), and multi-layer. The unique properties of the graphene are limited to single or few-layer morphology, and it has a large theoretical specific surface area (2630 m²/g), high Young's modulus (~1.0 TPa), high intrinsic mobility (200,000 cm²/v s), great thermal conductivity (~5000 W/m K), and high optical transmittance (~97.7%) [1]. These properties attribute graphene a promising material for

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multifunctional composites, high-performance electronics, catalysis, sensors, energy conversion and storage, and easy modification of the surface of glassy carbon and graphite electrodes [2–5].

Graphene nanosheets have been prepared by several methods such as micromechanical cleavage, epitaxial, electrochemical, chemical, and thermal reduction of graphene oxide (GO) [6–11]. Compared to other methods, the chemical and thermal methods have become promising routes to produce graphene sheets. GO can be reduced into reduced graphene oxide (rGO) either chemically by using suitable chemical reducing agents, such as hydrazine hydrate and sodium borohydrate, or biological reducing agents including glucose, ascorbic acid, galactose [12,13]. GO can also be reduced into rGO by thermal methods involving rapid heating to high temperature [14]. Sometimes, the combination of chemical and thermal methods is used for the rGO preparation [15]. GO, an effective precursor of rGO, can be produced by the oxidation of graphite via many literature methods such as Brodie's method, Hummer's method, modified Hummer–Offeman method, and Staudenmaier method [16,17]. Unfortunately, most available methods require a lot of time/energy/oxidants/acid-consumption and have low productivity and evolution of toxic or pollutant gases such as NO_2 and N_2O_4 [18]. In addition, hydrazine used in this process is very toxic to humans and the environment, and high or extreme temperature requirements such as $\sim 1000^\circ\text{C}$ for the thermal route during the reduction of GO is the main drawbacks particularly for large-scale production of rGO for industrial applications [7]. Furthermore, extreme safety is required during the production, because hydrazine is highly explosive and poisonous, when used in large quantities [19]. Thus, the development of mild synthetic routes for the synthesis of rGO is of great significance and should be explored.

In recent years, sonochemistry has become a more promising subject for the fabrication or modification of various nanomaterials such as nanochalcogenides and metal oxide nanoparticles [20,21], owing to its simplicity, high efficiency, and reaction time and energy saving characteristics for the reaction. The physical phenomenon required for the sonochemical process is acoustic cavitation where the formation, growth, and implosive collapse of the bubbles in liquid can occur [22]. The hot spot theory claims that very high temperatures $\sim 5000\text{ K}$ and high pressure $\sim 20\text{ MPa}$ are produced from the collapse of bubbles. Furthermore, since the collapse occurs in less than a nanosecond, very high cooling rates exceeding 10^{11} K/s are also obtained. Thus, it is easy to attain extreme reaction conditions, such as high temperature and pressure, and rapid cooling rates, which are not usually achievable in conventional synthesis methods, resulting in materials with unique properties [23,24]. The sonochemical techniques in the fabrication of nanomaterials offers good yields and high crystallinity of the products, reduces the reaction time from days to minutes, and produces a more homogeneous material as compared to the conventional chemical approaches.

rGO nanosheets can be formed from the reduction of GO by using a horn-type sonicator in the presence of hydrazine at 60°C [25]. Moreover, hydrazine has been used as a reductant for the synthesis of a stable rGO dispersion, using an ultrasound cleaning bath at 65°C [26].

In this study, we developed a facile and fast one-step ultrasonic method to synthesize either GO or rGO from graphite without releasing toxic or pollutant gases as in conventional Hummers methods and without using hydrazine for the chemical reduction of GO.

2. Experimental

2.1. Chemical and reagents

Pure grade graphite powder, potassium permanganate (KMnO_4), sulfuric acid (H_2SO_4) (98%), phosphoric acid (H_3PO_4) (85%), and hydrochloric acid (HCl) were purchased from Merck, and hydrogen peroxide (H_2O_2) (30%) was purchased from Sigma-Aldrich. They were used without further purification for experiment. Deionized water (DI) was used in the synthesis of GO and rGO.

2.2. Synthesis of GO and rGO

The improved Hummers method for ultrasonic synthesis of GO was modified by applying further sonication for the preparation of rGO from graphite powder.

In a typical procedure, 1 g of graphite and 6 g of KMnO_4 were mixed in 120 mL H_2SO_4 (98%) and 13.3 mL H_3PO_4 (85%). The resulting suspension mixture was put in an ultrasonic bath and irradiated for 25 min at 35°C to obtain a dark brown suspension. Next, 133 mL DI water with 1 mL H_2O_2 (30%) was added to the suspension to reduce residual permanganate to soluble manganese ions, and the color of the mixture changed from dark brown to dark yellow. Finally, the mixture was filtered and washed with aqueous HCl solution (1:12: HCl: H_2O , 260 mL) to remove metal ions. The filtered material was washed with distilled water to remove the remaining acid. The resulting solid was dried under air for 20 h to produce GO (Fig. 1(a)).

To obtain rGO, all the procedures prior to placing the sample under air atmosphere were repeated. However, instead of putting the synthesized sample under air, the obtained GO slurry status was mixed with 30 mL distilled water and irradiated for 15 min at 50°C using an ultrasonic technique. Then, the suspension mixture was filtered and dried at 80°C for 40 h to produce rGO (Fig. 1(b)).

2.3. Characterization techniques

The structural analysis of the nanocrystalline powders of GO and rGO was carried out by X-ray diffraction (XRD, BrukerD8Advance) equipped with monochromatic $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406\text{ \AA}$) in the 2θ range $10\text{--}60^\circ$ at room temperature. Raman spectra were measured using a labRam HR micro-Raman spectrophotometer (Bruker, model: Senteraa 2009, Germany) with a 532 nm laser excitation. The morphology of the GO and rGO samples was characterized by field-emission scanning electron microscope (FE-SEM), Model Quanta 250 FEG (Field Emission Gun). High-resolution transmission electron microscope (HR-TEM) spectra of the GO and rGO sheets were obtained using a JEOL TEM Model 2100 high-resolution transmission electron microscope. Fourier Transform Infrared (FTIR) transmittance spectra were recorded using a Perkin–Elmer Nicolet Nexus 470 FTIR spectrometer. UV–Vis diffuse reflectance spectrum (UV–Vis DRS) of the powders were measured using a perkin-Elmer Lambda UV–Vis spectrophotometer. X-ray photoelectron spectroscopy (XPS) data were recorded using a Thermo Scientific Sigma Probe spectrometer with a monochromatic $\text{AlK}\alpha$ source (photon energy 1486.6 eV), spot size 400 μm , pass energy of 200 eV, and energy step size of 1.0 eV to analyze the chemical states of elements in the samples. The reaction progress during the thermal reduction of the graphite, GO, and rGO was monitored by thermogravimetric analysis (TGA) in the range $20\text{--}800^\circ\text{C}$ under nitrogen atmosphere.

The sonication in this study was performed using an ultrasonic bath (Branson 5210, Branson Ultrasonic Cleaner, USA).

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