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Preparation and characterization of graphene derived from low-temperature and pressure promoted thermal reduction

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ABSTRACT

The reduction of graphene oxide was promoted remarkably under pressure via low temperature thermal treatment. Traditionally, graphene oxide is usually reduced in a preheated high temperature environment as a precondition of the thermal reduction. We report a pressure promoted method for low temperature thermal reduction and exfoliation of graphene oxide in large quantity at 260 °C. The physicochemical properties of parent graphite, as well as the microstructure and physicochemical properties of graphene oxide and resultant graphene were investigated by Raman spectrometer, thermograviment analyzer (TGA), transmission electron microscope (TEM), X-ray diffractometer (XRD) and Fourier transform infrared spectroscopy (FT-IR). Results show that graphene oxide was reduced to graphene with less stack via low-temperature pressure promoted thermal treatment, meanwhile, the degree of disorder reduced: the ratio of I_D/I_G in Raman spectrum decreases from 0.64 to 0.56. Moreover, graphene derived from low-temperature pressure promoted treatment exhibit better thermal stability than graphene oxide, and oxygen functional groups were removed with a high level. All of results exhibit improved comprehensive properties than graphene synthesized via traditional thermal reduction at 1000 °C.

1. Introduction

Graphene has been extensively studied in the last few years even though it was separated for the first time in 2004 [1–7]. As a burgeoning two-dimensional planar material, graphene has attracted much attention because of unique electronic transportation, superior thermal conductivity, and excellent mechanical properties [8–14]. Meanwhile, the great potential applications of graphene have also been investigated, such as transparent electronic conduction, and structure materials [11,15–18].

Nowadays, various methods are used to prepare of graphene, such as chemical vapor deposition, carbon nanotubes unzipping, graphite mechanical exfoliation, epitaxial growth, microwave plasma induced gas-phase synthesis and graphene oxide reduction methods [8,19–25]. Nevertheless, graphene oxide reduction method still is the main preparation method due to its low cost and

high yields features, and the most widely used methods are chemical and thermal reduction methods. In chemical reduction method, strong reductants were often used to reduce the oxygen functional groups such as hydrazine hydrate [26–33]. In the past reports, vitamin C and sodium borohydride were also used to reduce graphene oxide as reductant [26–33]. And graphene of thermal reduction is reduced via pyrolysis of the oxygen groups in high temperature under the protective gas. Among these methods, thermal reduction is the most promising treatment method for large yield production [19,34–36]. McAllister et al. [34] rapid heated graphene oxide to ca. 1000 °C to ensure the reduction process is completed. In his view, the process of exfoliation and reduction occurred at 550 °C which is the critical temperature. But the experimental temperature of exfoliation and reduction was around 1000 °C for completely reduction [34,35,37]. The high temperature treatment is hard to be controlled in thermal reduction process, which is a great obstacle for mass production and lowering the cost. Under this precondition, more and more researchers tried to lower the thermal treatment temperature of graphene oxide reduction via various methods. Boehm et al. reduced thermally expanded graphite oxide (TEGO) at low

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temperature (less than 400 °C) to form graphene, and this temperature is less than the critical graphene production temperature of McAllister [38]. Zangmeister reduced graphite oxide (GO) thin films to form graphene at 220 °C with various analyses [26]. W Lv et al. produced few-layered graphene by thermal reduction method at low temperature (200 °C) under vacuum [8]. The key point of this is the effect of vacuum assisted, which was applied on the surface of expanding graphene layers to pull open two layered graphene as to separate two sheets of paper from stick together. Afterwards, HB Zhang prepared graphene sheets with a high surface area at 135 °C under vacuum in the similar thermal reduction method. Moreover, their resultants have more superior surface area than others' under the vacuum assisted [19]. Surely, these approaches can reduce graphene oxide at low temperature, but the cost and energy consumption still is a problem to form graphene. In addition, vacuum condition of reduction process is an obstacle for filling composite as nanofillers.

In our works, we treated dry graphene oxide via thermal reduction at low temperature (260 °C) and the treatment process must be accompanied with the nitrogen pressure promoted, which is different with the traditional and vacuum assisted methods. By the pressure promoted, CO_2 propped the graphene layers open under pressure promoted which was from the pyrolysis of the oxygen functional groups. Various characteristics and morphologies of graphene were investigated respectively. During the comparing with the graphene which treated at 1000 °C, the resultant shows the graphene treated at 260 °C has high degree of exfoliation, low degree of disorder and less stacked.

2. Experimental

2.1. Raw materials

Commercial natural graphite flakes manufactured by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) with a main size of 30 μm and the purity is greater than 95%, was chosen as the raw material of graphene. Sodium nitrate (99%), sulfuric acid (98%), potassium permanganate (98%) and hydrogen peroxide (30%) were bought from Hongyan Chemical Reagent Co. (Tianjin, China) and used.

2.2. Preparation of graphene oxide

Graphite oxide was prepared via a Hummers method [39], with some modifications. While agitation was maintained, 1 g of graphite powder and 1 g of sodium nitrate was dispersed respectively in 50 mL of 98 wt% sulfuric acid in a round bottom three-neck flask, and kept at 0 °C or so. Next, 6 g of potassium permanganate was added slowly to avoid the risk of explosion, and the mixture was kept at 35 ± 5 °C for 2 h with continuous agitation. 80 mL deionized water was gradually added into the round bottom three-neck flask, and producing an odorous purple gas emission during this process. Then the mixture was transferred into the oil bath and kept at 90 ± 5 °C for 1 h with continuous agitation. Afterwards, 200 mL deionized water was added. The solution changed to a bright yellow color during the dropwise addition of 6 mL of 30% hydrogen peroxide, and continuous agitation for 2 h in order to increase the oxidation degree of graphene. Then, in order to clean out remnant salt, the reaction mixture filtered over a micro-filtration membrane (200 nm), and extensively washing and centrifugation process were repeated several times with deionized water and ethanol. At last, the wet graphene oxide was dried by vacuum drying at 50 °C for 1 week.

2.3. Low-temperature pressure-promoted thermal reduction graphene oxide

The low-temperature thermal reduction process was carried out in a stainless autoclave. Graphene oxide was heated up to 260 °C (heating rate 10 °C/min) for 3 h in a nitrogen atmosphere at 0—4 MPa pressure, the representation of the gradual forming of graphene via pressure-promoted process as shown in Fig. 1. Then, the bright yellow semitransparent composite was changed to the dark color composite. Here, 260 °C and 1000 °C were selected as the thermal reduction temperatures, so the resultant graphene were denoted as GP-260 and GT-1000 ("GP" means graphene via pressure promoted method, and "GT" means graphene via tradition thermal reduction method).

2.4. Characterization of materials

The morphologies of graphene oxide and graphene were investigated using a Tecnai G2 F30, FEI transmission electron microscope (TEM). The morphologies of cross sectional surfaces of the samples were observed using a JSM-6700, JEOL Field-emission scanning electron microscope (SEM). A TG-SDTA851e thermograviment analyzer (TGA) was used to measure the mass loss of graphene and graphene oxide as a function of temperature. The samples were heated in nitrogen atmosphere, and the heating rate was 10 °C/min. Raman spectroscopy was performed on a Renishaw inVia Laser-Raman Spectrometer using a 532 nm laser. X-ray diffractometer (X′ Pert PRO MPD, PANalytal) using CuKα radiation ($\lambda = 0.15406$ nm) was employed to analyze the structure of graphene and graphene oxide. FT-IR spectra of graphene oxide and graphene were obtained using a Prestige-21 FT-IR spectrometer with the range from 500 cm^{-1} to 4000 cm^{-1}.

3. Results and discussion

3.1. Structure of graphene derived from low-temperature pressure-promoted thermal reduction

During the oxidization process of preparing graphene oxide using commercial natural graphite flakes, the evolving carbon dioxide and water volatiles from the thermally decomposed fractions of graphene oxide serve as "jack" separate graphite layers to generate single or few layered graphene, meanwhile the volume of distance between graphene layers increased. However, the traditional thermal reduction graphene oxide adoptive methods are heating in inert gas or vacuum [5,8,26]. Therefore, temperature and atmospheric pressure in the process of reduction are two key factors that affect the graphene structure. In the present study, we tried to compare the graphene derived from traditional thermal reduction method with in-situ low-temperature reduction method, which is used as improved method that influences the graphene structure.

For increasing the distance of graphene layers and eliminating the defect of the graphene oxide, the reduction process via thermal treatment was performed. The graphene oxide is composed of vast graphite layers stacked as shown in Fig. 2a. The most area of the picture is dark and uneven color, indicating the most graphite has great thickness and the hackly unsmooth surface. The multi-stacked structure of graphite can be seen clearly in Fig. 2a, and the stack is vast and tight.

The front reduction, thermal exfoliation and reduction of graphene is resultant of the combined influence of the physical properties and chemical composition of graphene oxide, as well as process conditions. Initially, the unstable oxygen groups (like hydroxide radical and carbonyl functional groups) derived from