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One-pot hydrothermal synthesis of a mesoporous SiO_2–graphene hybrid with tunable surface area and pore size

Xun Zhou, Tiejun Shi*

School of Chemical Engineering of Hefei University of Technology, Hefei, 230009, PR China

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ABSTRACT

A one-pot hydrothermal synthesis was used to obtain a mesoporous SiO_2–graphene hybrid from tetraethylortho silicate and graphene oxide without any surfactant. Graphene obtained from hydrothermal reduction, with a certain oxygen-containing groups, plays a key role in attaching SiO_2 nanoparticles, as examined by X-ray diffraction, Raman spectroscopy, transmission electron microscopy and scanning electron microscopy, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy and atomic force microscopy. The synthesis technique combines protection, reduction and functionalization in one step. Nitrogen adsorption/desorption isotherms showed that the hybrid was tunable in surface area (244.7–524.61 m^2/g), pore size (8.9–69.26 nm) and its distribution by simple adjustment of the mass ratio of tetraethylortho silicate and graphene oxide.

1. Introduction

Graphene, a single layer carbon material in a close arrangement of honeycomb two-dimensional lattice, has attracted tremendous interest and attention from scientific communities in recent years, due to the remarkable properties of its Young's modulus (~1100 GPa), fracture strength (125 GPa), thermal conductivity (~5000 $W\,m^{-1}\,K^{-1}$), mobility of charge carriers (200,000 $cm^2\,V^{-1}\,s^{-1}$), specific surface area (theoretical value of 2630 $m^2\,g^{-1}$), magnetism and plus fascinating transport phenomena such as quantum Hall effect [1]. With radiant bloom of research in theory, the applications of graphene and its various hybrids have been exploited in fields of mechanically reinforced composite materials [2], supercapacitors [3], catalysis [4], Li-ion batteries [5] and solar cell [6], nanoelectronic devices [7], gas sensors [8], drug carriers [9].

Before hybridizing graphene, preparing graphene as one of the greatest challenges must be firstly overcome. Up to now, graphene has been obtained in four different methods: (1) chemical vapor deposition, such as the decomposition of ethylene on single crystal nickel surfaces [10]; (2) epitaxial growth on electrically insulating surface of SiC [11]; (3) mechanical exfoliation of graphene from patterned graphite called "Scotch tape" or peel-off method [12]; (4) chemical and thermal reduction of graphene oxide (GO) [13,14]. Among those methods, the last one was most popular. Generally, the last method involved two steps that were preparation and reduction of GO. During preparation step, GO, bearing lots of hydrophilic oxygen-containing groups such as carboxyl, hydroxyl and epoxide, was obtained by graphite oxidation [13]. During reduction step, deoxygenation by either hydrazine [13] or heat treatment [14] occurred to restore the structure of graphene.

According to the previous reports, we have realized that fabricating graphene hybrid consists of three procedures: protection, reduction and functionalization. The protection is indicated by intercalating metal nanoparticles [15], inorganic nanoparticles [16], organic molecules [17,18] or surfactant [19], polymers [20] into the neighboring layers to inhibit the face-to-face aggregation. The reduction is interpreted as removing most of oxygen-containing groups connected on both-side surfaces or along the edge of GO sheet to recover the lattice structure and extraordinary properties [14,21–28]. The functionalization is described with covalently or uncovalently anchoring the intrinsic functional molecules or nanoparticles onto the graphene surface, which imparts new classes of two-dimensional functional composites [17,18,29]. In most cases, the three procedures were isolated respectively to different time domains, resulting in prolonging experimental duration and increasing experimental steps. Hence, it is highly desirable that the three processes can be combined into one. In this work, we attempt to attain SiO_2–graphene hybrid (SiO_2–G) in such way.

Hydrothermal reaction has been recognized as an effective way to fabricate mesoporous and high surface area SiO_2 nanoparticles from silica alkoxides [30]. In parallel, hydrothermal reaction was also suitable for reducing GO and modifying graphene. Recently, the work of Zhou was reported that hydrothermal dehydration was used for the "green" reduction of exfoliated GO to graphene

* Corresponding author. Tel.: +86 551 2905158; fax: +86 551 2905158.
E-mail address: stjhfut@163.com (T. Shi).

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[27]. The work of Yang was reported that hydrothermal method was used to assemble noble-metal-promoted three-dimensional single-layered GO [4]. The work of Xu was reported that one-step hydrothermal process was used to prepare self-assembled graphene hydrogel [31]. To our knowledge, although the sol–gel process has been reported to prepare SiO_2–GO hybrid [32], there is little information available about SiO_2–G in assistance of hydrothermal reaction without any surfactant.

Herein, we present one-step hydrothermal approach for producing SiO_2–G with tetraethyl ortho silicate (TEOS) and GO as the starting materials. GO was firstly prepared by Hummers method. Then, the single GO sheets were dispersed in water with the treatment of ultrasonication and centrifugation. The hybridization between graphene and SiO_2 and reduction of GO were synchronously completed under the hydrothermal condition at 150 °C for 10 h. The hybrid possessed the mesoporous structure and big surface area as high as 524.61 m^2/g. More attractively, the surface area, pore size and its distribution can be adjusted by changing the mass ratio of TEOS and GO.

2. Experimental

2.1. Materials

Graphite powder was bought from Qingdao Zhongtian Company with a mean particle size of 44 μm. Analytical grade Ethanol, $KMnO_4$, 98% H_2SO_4, 36% HCl, 30% H_2O_2 aqueous solution, TEOS were purchased from Shanghai Chemical Reagents Company and were used directly without further purification. Ultra-pure water was produced by lab.

2.2. Preparation of GO

GO was prepared from graphite powder by the well-known Hummers method [23,31,33]. Briefly, 98% H_2SO_4 (50 ml) was added into the 250 ml flask filled with graphite (2 g) at room temperature, followed by addition of solid $KMnO_4$ (7 g) slowly at 0 °C (ice bath). At 35 °C, the mixture was stirred by magnetic stirring bar for 2 h. Excess water was added into the mixture at 0 °C (ice bath) and then H_2O_2 (30%) was added until there was no gas producing. The solution was filtered and washed with 1:10 HCl aqueous solution (250 ml) to remove metal ions followed by repeated washing with water and centrifugation. The resulted solid was dispersed in water by ultrasonication for 1 h to make a GO aqueous dispersion. The obtained brown dispersion was then subjected to 30 min of centrifugation at 5000 rmp to remove any aggregates. Finally, the obtained GO was dried under vacuum at 60 °C for 3 days.

2.3. Preparation of SiO_2–G

In a typical procedure for preparing SiO_2–G, 15 ml homogeneous GO aqueous dispersion (2 mg/ml) was mixed with 15 ml ethanol, and then 0.25 g TEOS was dissolved in this solution under sonication for 1 h. Subsequently, the mixture was sealed in 50 ml autoclave and retained at 150 °C for 10 h. At last, the hydrothermal product was harvested under vacuum at 60 °C for 1 day. For varying the mass ratio of TEOS and GO, the same procedure was duplicated with different TEOS mass (0.50, 1.00 and 2.00 g). The samples were labeled as GO-0, SiO_2–G-1, SiO_2–G-2, SiO_2–G-3, SiO_2–G-4 corresponded to TEOS and GO mass ratio of 0:3, 25:3, 50:3, 100:3, 200:3, respectively. Note: SiO_2–G-2 as representation was characterized by X-ray diffraction (XRD), Raman spectroscopy, transmission electron microscopy (TEM), field emission scanning electron microscopy (FE-SEM), Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM).

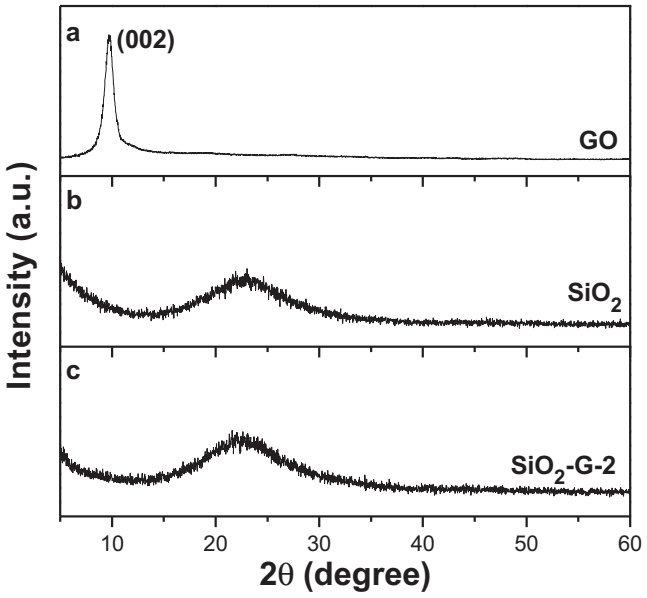

Fig. 1. XRD patterns of (a) GO, (b) SiO_2 prepared by same hydrothermal condition without GO, and (c) SiO_2–G-2.

2.4. Instruments

Water bath ultrasonication was performed with a KQ-100E sonicater (100 W). XRD was carried out by a powder diffractometer (Rigaku, D-MAX2500-PC) with Cu radiation between 5° and 90° under a scan rate of 0.5°/min and incident wavelength of 0.1549056 nm (Cu Kα). Raman spectra were recorded using a JY Labram-HR spectrometer with 514.5 nm wavelength incident laser light. TEM images were taken on a Hitachi H-800 TEM at an accelerating voltage of 200 kV by depositing GO and SiO_2–G-2 aqueous solution onto copper grids. FE-SEM observations were conducted on a FEI Sirion200 system with an accelerating voltage of 5 kV. FT-IR spectra were collected in transmission mode

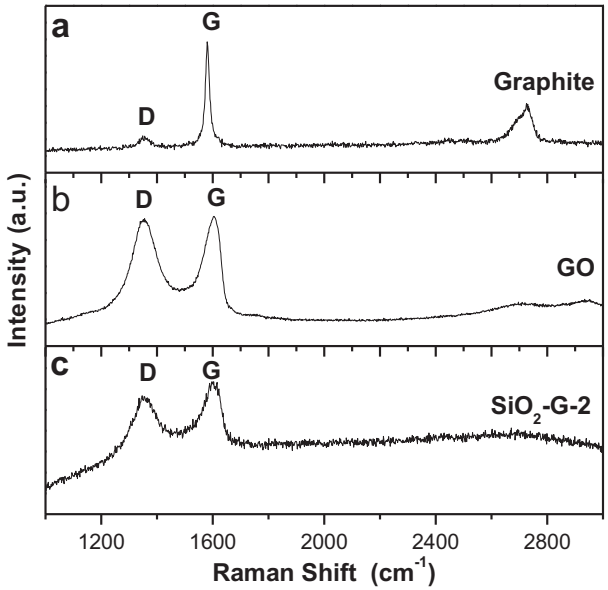

Fig. 2. Raman spectra of (a) graphite, (b) GO, and (c) SiO_2–G-2.