Journal of Industrial and Engineering Chemistry 20 (2014) 2883–2887

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Facile and safe graphene preparation on solution based platform

Fatima Tuz Johra, Jee-Wook Lee, Woo-Gwang Jung [*]

School of Advanced Materials Engineering, Kookmin University, Seoul 136-702, Republic of Korea

ARTICLE INFO

Article history:
Received 3 August 2013
Received in revised form 30 October 2013
Accepted 4 November 2013
Available online 12 November 2013

Keywords:
Graphene
Improved Hummers' method
Hydrothermal
Raman spectroscopy
ð-conjugation

ABSTRACT

Graphene has attracted increasing attention because of its interesting properties. In this study, graphene was prepared from graphite by a very simple and easy process. The two-step protocol involves conversion of graphite to graphene oxide (GO) by oxidation, and subsequent reduction of GO to graphene. The structures and properties of the obtained GO and graphene were characterized via X-ray diffraction, and Raman, NMR, UV–vis absorption, and X-ray photoelectron spectroscopic techniques. The morphologies of these products were observed via field emission scanning electron microscopy. The preparation protocol is simple, easy, environmental friendly, i.e., nontoxic, and the yield of graphene is high.

1. Introduction

Graphene, a two-dimensional honeycomb sheet of sp^2-hybridized carbon atoms, exhibits a number of extraordinary characteristics, such as a large theoretical specific surface area (2630 $m^2\,g^{-1}$), high intrinsic mobility (200,000 $cm^2\,v^{-1}\,s^{-1}$) [1,2], high Young's modulus (~1.0 TPa) [3] and thermal conductivity (~5000 $Wm^{-1}\,K^{-1}$) [4], optical transmittance (~97.7%) [5], and good electrical conductivity [6]. These characteristics render graphene popular and useful for applications such as transparent conductive electrodes [7,8] and super-capacitors, among many other potential applications. The thermal, mechanical, and electrical properties of graphene are derived from long range ð-conjugation.

Graphene can be obtained by various processes, including chemical vapor deposition [9], micromechanical cleavage of graphite [10], and exfoliation of graphite [11]. In this study, a solution-based chemical process is utilized as a simple approach for graphene generation. To address the poor carrier mobility of solution-processed graphene, which is due to the presence of a large number of defects [12], graphite flakes are utilized as the starting material. Graphite consists of a stack of flat graphene sheets and is inexpensive and readily available. The graphene preparation protocol involves two steps, i.e., oxidation of graphite to graphene oxide (GO) and subsequent reduction of graphene oxide to graphene. In the initial step, graphite flakes are exfoliated into single layers to facilitate graphene production. Graphene oxide was first prepared almost 150 years ago [13], and has found application in the cost-effective, large-scale production of graphene-based materials. Here, an improved Hummers' method is utilized to prepare graphene oxide, which offers the advantage of simplicity, notwithstanding the longer time needed relative to the Hummers' and modified Hummers' methods [14–16]. This method utilizes two powerful acid mixtures as the oxidizing agent and offers the advantages of high yield and environmental friendliness. Treatment of graphite by this method retains the layered structure of graphene oxide, whereas the interlayer spacing is larger than that in graphite. The resulting graphene oxide contains epoxy and hydroxyl groups and also a few carbonyl and carboxyl groups.

2. Experimental

High-purity graphite flakes (40 μm) were obtained from Taewon Scientific Co., and potassium permanganate ($KMnO_4$), 95% sulfuric acid (H_2SO_4), 85% phosphoric acid (H_3PO_4), 35–37% hydrochloric acid (HCl), 30% hydrogen peroxide (H_2O_2), 25–30% ammonia water (NH_4OH), 99.9% ethanol (C_2H_5OH), and 99% ethyl ether [$(C_2H_5)_2O$] were obtained from Duksan reagents and chemicals. A poly(tetrafluoroethylene) (PTFE) membrane filter was purchased from the Pall Corporation.

Graphene oxide was prepared from graphite flakes via an improved Hummers' method [17]. A mixture of H_2SO_4 and H_3PO_4 (9:1 vol. equiv.) was added to a mixture of $KMnO_4$ and graphite flakes (3:1 wt. equiv.). Because of heat evolution from the exothermic process, a delay (15–20 min) was introduced to bring the temperature down to room temperature. The mixture was then placed on a heating mantle at 50 °C, with constant stirring for 12 h. After completion of the reaction, the mixture was cooled to room

---

[*] Corresponding author. Tel.: +82 2 910 4643; fax: +82 2 910 4320.
E-mail addresses: wgjung@kookmin.ac.kr, drwgjung@gmail.com (W.-G. Jung).

http://dx.doi.org/10.1016/j.jiec.2013.11.022

temperature and poured onto ice [400 mL of deionized (DI) water were used to make the ice] with 30% H_2O_2 (~3 mL). The solution was then sieved using a testing sieve and the filtrate was centrifuged (4000 rpm, 4 h). The supernatant was then discarded, and the remaining solid was sequentially washed with water, 30% HCl, and ethanol (twice in each case); for each wash, the mixture was sifted through the sieve and the filtrate was then centrifuged (4000 rpm, 4 h) using a Mega 17R small, high-speed, refrigerated centrifuge machine, and the supernatant was decanted. After the multiple washing treatments, the remaining materials were coagulated using ethyl ether and then filtered through a PTFE membrane with a micropore size of 0.2 μm, followed by drying in vacuum.

Graphene oxide was placed in a beaker and sonicated with DI water (0.1 mg mL^{-1}) for 5 min, using an ultrasonicator. NH_4OH (2–4 mL) were added to adjust the pH to ~11. The mixture was transferred to a Teflon-lined stainless-steel autoclave and placed in an oven at 180 °C for 6 h. After completion of the reaction, this solution was centrifuged (4000 rpm, 4 h), and the obtained materials were washed with DI water and ethanol (twice in each case) to remove impurities. Finally, the obtained material was collected by vacuum filtration and dried in vacuum.

The obtained products were dispersed in water by sonication and spin coated onto a SiO_2/Si wafer (Piranha cleaned) for field emission scanning electron microscopy (FE-SEM) analysis. The FE-SEM images were obtained by analysis of the sample using a JEOL JSM5410 instrument. The obtained graphene was examined via transmission electron microscopy (TEM, JEOL JEM1210). Atomic force microscopy (AFM, XE-100, Park system) was used to determine the graphene thickness. X-ray diffraction (XRD) analyses were performed on a Rigaku D-max 2500 instrument (Japan), using Cu Kα radiation, under a voltage of 40 kV and a current of 200 mA. The refraction data of the finely powdered samples were recorded for 2θ angles between 3 and 55°. Raman spectra were recorded between 500 and 3000 cm^{-1} on a Horiba Jobin Yvon LabRam Aramis Raman spectrometer, using a 514.5 nm Ar laser at 0.5 mW power. The laser spot size was around 1 μm. NMR analysis was performed on a Bruker AVANCE III 500 MHz spectrophotometer. UV–vis spectral measurements were acquired using a Perkin Elmer Precisely Lambda 35 UV/VIS Spectrometer. An ultrasonicated suspension of the product in water was used for this analysis. The ultrasonication was performed using an Ulsso Hitechs Sonosmasher ULH-700S at 19.82 kHz. X-ray photoelectron spectroscopy (XPS) was performed using an ESCA2000 instrument with an Al Kα X-ray source (1486.6 eV) under ~10^{-10} torr vacuum pressure. The pass energy was set at 50 eV for wide and 20 eV for narrow scanning. The X-ray take off angle was fixed at 56°.

3. Results and discussion

In the first step, graphite was converted to graphene oxide by reaction of a potassium permanganate, sulfuric acid, and phosphoric acid mixture. As mentioned, the treated graphite contains a number of oxygen containing groups, and is thus readily dispersed in water, i.e., GO acts as an oxygenated graphene layer.

Based on the physical appearance of graphite, GO and graphene, they could be separated. Graphite was grey in color whereas the GO was brownish, and graphene had a very dark color. The mass of each of these species was another distinguishing feature. GO contained a large quantity of water, thus the mass was increased relative to that of graphite. However, after reduction, the mass was low compared to that of GO because of the loss of oxygen during the reduction process. Approximately 50 mg of grey-colored graphite yielded 100 mg of GO, which, upon reduction, yielded 52 mg of graphene.

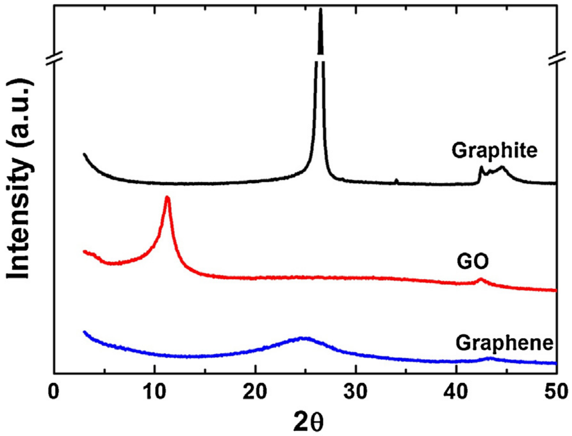

Fig. 1. XRD patterns of graphite, graphene oxide and graphene.

Fig. 1 shows the XRD patterns of graphite, graphene oxide, and graphene. In the XRD pattern of GO obtained via the improved Hummers' method, the (0 0 1) crystal plane of GO was evident, with a spacing of 8.33 Å, which is typical for GO. The spacing was 3.36 Å for graphite. The increased distance in the former was due to the introduction of a number of oxygen-containing groups on the edge of each layer, which increased the distance between the layers. After hydrothermal treatment of GO, the spacing again decreased to 3.70 Å, which is still slightly higher than that of graphite. This suggests the presence of some remaining oxygen functional groups in the prepared graphene. From the observed peak broadening, it is inferred that the stacking of graphene was not well ordered.

To evaluate the degree of exfoliation of the GO into graphene, an aqueous suspension of both GO and graphene was spin coated onto a Si/SiO_2 substrate and inspected by means of FE-SEM. The SEM image in Fig. 2(a) shows that GO flakes were distributed on the substrate. From the FE-SEM image, the average size of GO was estimated at ~500 nm. Graphene flakes of various sizes are observed in the SEM image in Fig. 2(b), derived from overlapping with each other as a result of the three spin-coating cycles. Ultrasonication (700 W) for a long time (1 h) may reduce the size of the graphene flakes. The average size of the prepared graphene was ca. 200–500 nm. Transmission electron microscopy (TEM) is also a very important tool for investigating the quality of exfoliated graphene. Fig. 2(c) shows the TEM image of a graphene sheet, acquired by dropping a small quantity of the graphene dispersion on a holey carbon grid, followed by drying. A very thin film of graphene is observed in this image.

AFM, an effective method for determination of the thickness of graphene, confirmed that the resulting graphene sheets deposited on the Si/SiO_2 were flat and had a thickness of around 1.0–1.5 nm (Fig. 2(d)). Given that the pristine graphene sheet is flat with a well-known van der Waals thickness of ~3.70 Å, and the XRD analysis demonstrated that the inter-sheet distance was around 3.70 Å, the data suggest that the hydrothermally treated graphene consists of two to four layers. The size and shape of the graphene produced in this method varied, as confirmed by the AFM data.

The prepared GO and graphene were characterized from their Raman spectra (Fig. 3), which allow for consideration of the conjugated and carbon–carbon double bonds, which lead to high-intensity peaks in the Raman spectrum. The typical Raman spectrum of GO is characterized by a G band at ca. 1605 cm^{-1}, which corresponds to the E_{2g} phonon of the sp^2 C atoms, and a D band at 1353 cm^{-1}, which corresponds to the breathing mode of κ-point phonons of A_{1g} symmetry. Here, the G band of graphene was