Research Article

Preparation of Bulk ^{13}C-Enriched Graphene Materials

Leilei Tian,[1] Xin Wang,[1] Li Cao,[1] Mohammed J. Meziani,[1] Chang Yi Kong,[1, 2] Fushen Lu,[1] and Ya-Ping Sun[1]

[1] *Department of Chemistry and Laboratory for Emerging Materials and Technology, Clemson University, Clemson, SC 29634-0973, USA*

[2] *Department of Materials Science and Chemical Engineering, Faculty of Engineering, Shizuoka University, 3-5-1 Johoku, Naka-ku, Hamamatsu 432-8561, Japan*

Correspondence should be addressed to Ya-Ping Sun, syaping@clemson.edu

Arc-discharge has been widely used in the bulk production of various carbon nanomaterials, especially for structurally more robust single-walled carbon nanotubes. In this paper, the same bulk-production technique was applied to the synthesis of significantly ^{13}C-enriched graphitic materials, from which graphene oxides similarly enriched with ^{13}C were prepared and characterized. The results demonstrate that arc-discharge is a convenient method to produce bulk quantities of ^{13}C-enriched graphene materials from relatively less expensive precursors (largely amorphous ^{13}C powders).

1. Introduction

Graphene nanosheets (GNs) consisting of a single or few layers of hexagonally arrayed sp^2-bonded carbons in a two-dimensional lattice have attracted tremendous amount of recent attention for their interesting and/or unique properties, with a long list of predicted technological applications [1–10]. For example, individual GNs have been found to possess superior electronic properties arising from the confinement of electrons in two dimensions [3], and as a zero-bandgap semiconductor to feature long-range ballistic transport and high carrier mobility at room temperature [8, 11, 12]. GNs also exhibit excellent thermal transport properties [10], with their dispersion into polymeric matrices resulting in record-setting thermal conductive performances [13–15].

The preparation or production in larger quantities of GNs has been actively pursued in the research community [16, 17]. Among widely investigated methods are those based on the micromechanical cleavage of graphite [11], epitaxial growth [18], and chemical exfoliation of graphite [13, 19], especially the exfoliation through the route of graphene oxides (GOs) [20]. For structural characterization and other purposes, ^{13}C-enriched GNs (or GOs as precursors) are

particularly valuable. However, the ^{13}C-enrichment in bulk quantities of graphene materials has hardly been a routine task. There are only a few relevant studies in the literature (all based on the same sample source), despite their obviously high impact in the graphene research field [21–23]. The sample of ^{13}C-enriched graphite films in the available studies was synthesized by using cold-wall chemical vapor deposition (CVD) onto nickel substrate, with isotopically enriched methane as the ^{13}C source [22].

Beyond CVD, arc-discharge under inert atmosphere has been widely used in the bulk production of various carbon nanomaterials, including especially carbon nanotubes [24–28]. In fact, single-walled carbon nanotubes from arc-discharge production are generally structurally more robust [26, 27]. Therefore, it is desirable to apply the same bulk-production technique to the synthesis of graphite from amorphous carbon powders (such as commercially supplied ^{13}C powders). Here, we report the use of arc-discharge for the production of significantly ^{13}C-enriched graphitic materials, from which graphene oxides (GOs) similarly enriched with ^{13}C were prepared and characterized. The results demonstrate that arc-discharge is a convenient method to produce bulk quantities of ^{13}C-enriched graphene materials from relatively less expensive precursors (^{13}C powders).

2. Results and Discussion

The sample containing ^{13}C-enriched graphite was synthesized in an arc-discharge chamber. For the electrodes, the anode was a hollow graphite rod completely filled with a mixture of ^{13}C powder (largely amorphous) and graphite. The total ^{13}C content in the anode rod was targeted to be about 20%. The cathode was a solid graphite rod. In a helium atmosphere, the arc-discharge was at a high current to render a high temperature for the carbon evaporation, thus to facilitate the formation of more graphitic carbon materials. In principle, arc-discharge (or sometime called plasma arcing) creates a high-temperature (up to 3,000°C) condition that evaporates and ionizes the carbon electrode materials. The ultrahot carbon vapors and ions serve as precursors to spontaneously form the targeted nanostructures (fullerenes, carbon nanotubes, or graphite sheets) upon condensation in the arc-discharge chamber. In the experiment reported here, there was a significant amount of black deposit on the cathode, which was determined as being more graphitic than the soot-like material in the chamber according to thermogravimetric analysis (TGA). The deposit was collected as a sample containing ^{13}C-enriched synthetic graphite. According to spectral shifts in the Raman spectroscopy evaluation, the estimated ^{13}C content in the sample was on the order of 15%, slightly lower than the original ^{13}C loading in the anode rod.

The X-ray diffraction pattern for the ^{13}C-enriched sample was generally similar to that of the commercially supplied natural graphite (Figure 1), with diffraction peaks at 2θ of 26.2°, 42.7°, 54.0°, and 78.0°, corresponding to (002), (10), (004), and (110) diffractions, respectively, in the graphitic framework. However, the ^{13}C-enriched sample was likely more complex morphologically, as reflected in the significantly broader (002) diffraction peak (Figure 1), though the complexity should have little effect on the preparation of graphene oxides (GOs) in terms of the Hummers method [1, 29]. The extreme processing conditions associated with the Hummers method would push all surviving species toward the well-exfoliated GOs.

In the Hummers method treatment of the ^{13}C-enriched sample, the same experimental conditions as those for natural graphite were applied. A similarly homogeneous aqueous dispersion of GOs was obtained (Figure 2), which was stable over the duration of the project (several months).

The optically transparent aqueous dispersions were used in UV/vis absorption measurements. Shown in Figure 2 is a comparison of optical absorption spectra between GOs from precursor samples with and without the ^{13}C enrichment. Both spectra exhibited the characteristic absorption bands at 230 nm and 300 nm, corresponding to the well-established π-π^* (due to the remaining graphene structure) and n-π^* transitions in GOs, respectively [30], suggesting that the ^{13}C-enriched GOs were structurally similar to those from natural graphite.

The ^{13}C-enriched GOs from the Hummers method in aqueous dispersion were deposited onto a solid substrate for characterization by Raman spectroscopy. As shown in Figure 3, the Raman spectrum of the ^{13}C-enriched GOs
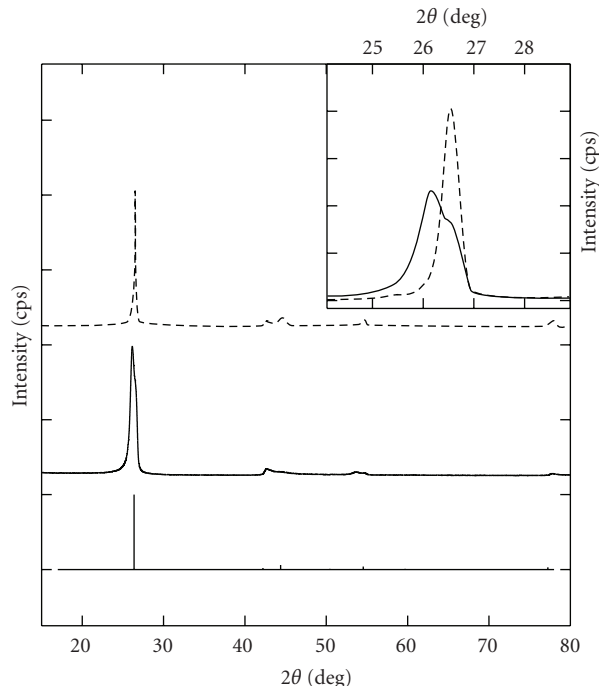

FIGURE 1: X-ray diffraction patterns of the ^{13}C-enriched sample produced in arc-discharge (solid line) and the as-supplied natural graphite (dashed line), along with the standard from JCPDS database.

featured the same G-band and D-band as those typically found in GOs from natural graphite (Figure 2) [31], except that the Raman bands of the ^{13}C-enriched GOs were at lower frequencies (due to ^{13}C being heavier than ^{12}C). The Raman results confirmed that the aqueous dispersion from the Hummers method was indeed a dispersion of ^{13}C-enriched GOs. More quantitatively, the Raman spectral shifts were used to estimate the ^{13}C content in the enriched sample. Under the assumption of same force constants for ^{12}C and ^{13}C bonds, the observed frequencies of a specific Raman mode for the ^{13}C-enriched sample (ω) and regular ^{12}C sample (ω_{12}) are related to the ^{13}C content in the enriched sample (x) as follows [32, 33]:

$$\omega = \omega_{12}\sqrt{\frac{m_{12}}{m_{12}(1-x) + m_{13}x}}, \qquad (1)$$

where m_{12} and m_{13} are atomic masses of ^{12}C and ^{13}C, respectively. The Raman spectral shifts from different batches of GOs were slightly different, so were the shifts of G-band versus D-band between the ^{13}C-enriched and regular GOs. On average, however, the estimated ^{13}C content in the enriched sample was 18.5%, comparable with the targeted ^{13}C enrichment in the anode used in arc-discharge (about 20%).

The presence of GOs in the ^{13}C-enriched sample after Hummers method treatment was further confirmed and their morphology probed in electron microscopy analyses. The specimen of the ^{13}C-enriched GOs was prepared by depositing a few drops of a diluted aqueous dispersion
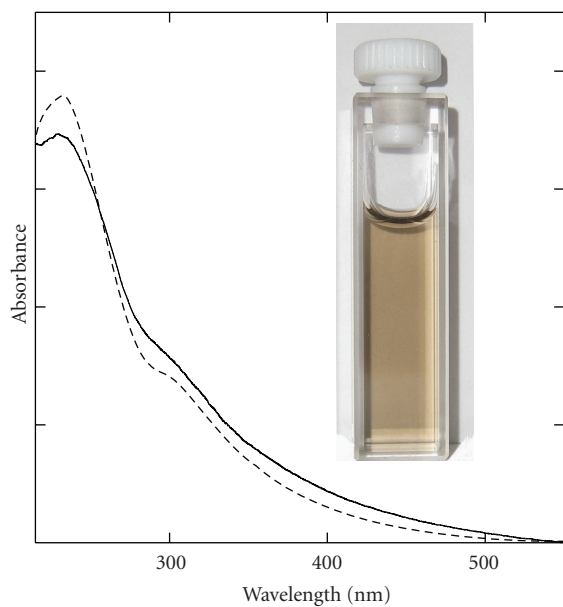
FIGURE 2: UV/vis absorption spectra of aqueous dispersions of the ^{13}C-enriched GOs (solid line, a photo of the dispersion in the inset) and GOs from the natural graphite (dashed line).
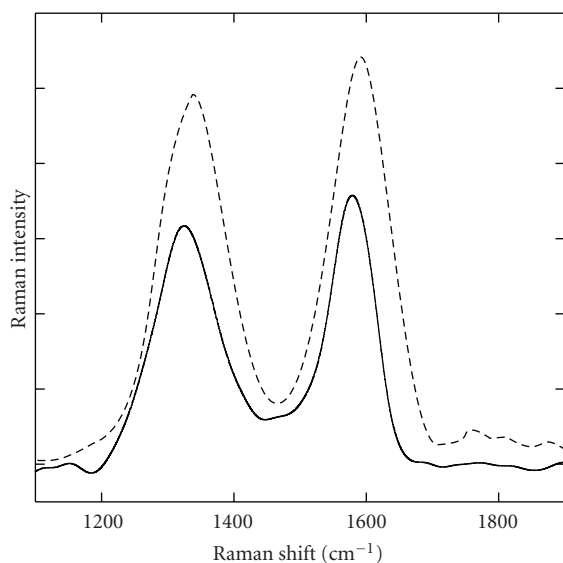

FIGURE 3: Raman spectra of the ^{13}C-enriched GOs (solid line) and GOs from the natural graphite (dashed line).

FIGURE 4: TEM images of the ^{13}C-enriched GOs (a) and GOs from the natural graphite (b) on holey carbon-coated copper grid; and the ^{13}C-enriched GOs in the Z-contrast mode (c).

($\sim$0.05 mg/mL) onto a holey carbon-coated copper grid, followed by drying under ambient conditions. With the use of a scanning transmission electron microscope (S-TEM), the images obtained for the specimen in different imaging modes (transmission and Z-contrast) exhibited consistently a primary morphology of well-exfoliated sheets, which appeared to be transparent to the electron beam (Figure 4). The ^{13}C-enriched GOs in TEM images were generally similar to those from natural graphite (Figure 4), except for the former appearing somewhat more wrinkled with less regular edges (Figure 4). While the TEM results alone
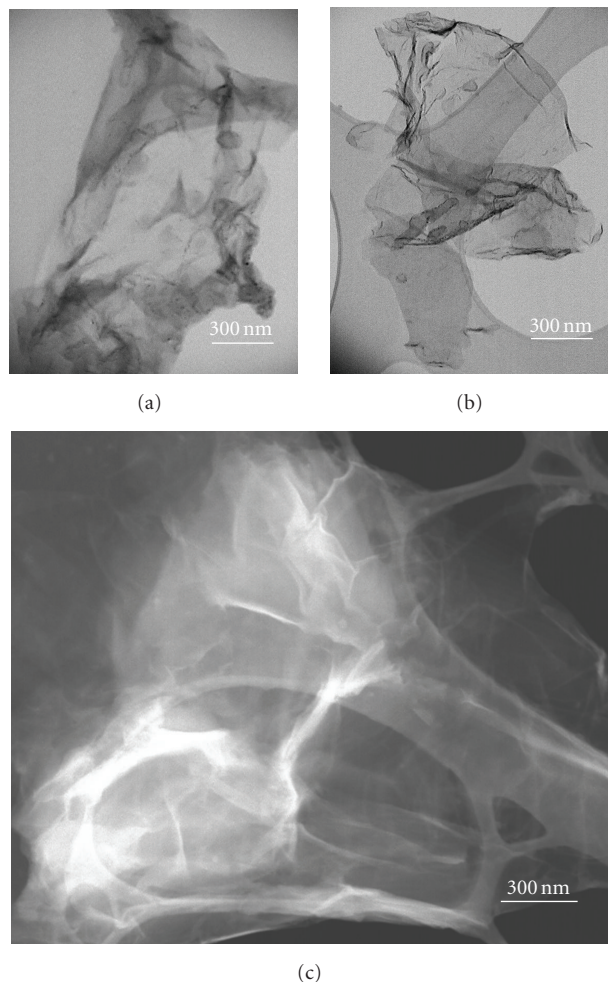
were hardly sufficient for any conclusions, the possibility existed that the graphite material (as precursor to the GOs) from the arc-discharge production had a smaller grain size and contained more defects. Nevertheless, the production conditions were not optimized, thus still more rooms for significant improvements in arc-discharge production for structurally more robust graphite precursors.

The results presented above clearly demonstrate that ^{13}C-enriched GOs in bulk quantity can be obtained from the graphite precursor produced in an arc-discharge chamber. A major advantage of this production approach is the use of relatively less expensive ^{13}C powders as starting material. The overall yield from ^{13}C powders to GOs was on the order of 10% in terms of ^{13}C conversion, and improvements may be expected when the production conditions are optimized. The soot-like material (also with significant ^{13}C content) collected from arc-discharge chamber could be recycled (for graphite materials of lower ^{13}C enrichment). Another improvement to be pursued is the quality of the graphite precursor and the resulting GOs, as it is well-established that

arc-discharge is a preferred method to produce structurally more robust carbon nanotubes.

The correlation between the ^{13}C enrichment in the final GOs and that in the starting anode rod for arc-discharge is interesting and useful, as it may allow more predictable production of graphene materials of various targeted ^{13}C enrichment ratios for different applications. Efforts on such predictable production and on the optimization of production conditions are in progress.

3. Experimental Section

3.1. Materials. The graphite sample, referred to as "natural graphite", was the surface-enhanced flake graphite (Grade 3805) supplied by Asbury Carbons. ^{13}C powders (largely amorphous, ^{13}C content 97%) were purchased from Icon Isotope, Inc. Fine-extruded graphite rods (carbon content >99.9%, 6.4 mm in diameter and ~30 cm in length) were acquired from Graphitestore.com, Inc. Sulfuric acid (93%), nitric acid (73%), hydrochloric acid (36%), hydrogen peroxide (35%), and phosphorus pentoxide (P_2O_5) were obtained from ACROS, ammonium persulfate ($(NH_4)_2S_2O_8$) from Aldrich, and postassium permanganate ($KMnO_4$) from Fisher Scientific. PVDF membrane filters (0.45 μm pore size) were supplied by Fisher Scientific, dialysis membrane tubing (MWCO ~ 3,500) by Spectrum Laboratories, and holey carbon-coated copper grids by SPI Supplies. Water was deionized and purified by being passed through a Labconco WaterPros water purification system.

3.2. Measurements. Thermogravimetric analysis (TGA) was performed on a TA Instruments Q500 analyzer. Optical absorption spectra were recorded on a Shimadzu UV-3600 UV/vis/NIR spectrophotometer. Raman spectra were obtained on a Jobin Yvon T64000 Raman spectrometer equipped with a Melles-Griot He-Ne laser (35 mW) for 632.8 nm excitation, a triple monochromator, an Olympus BX-41 microscopy, and a liquid nitrogen-cooled symphony detector. Transmission electron microscopy (TEM) images were acquired on Hitachi HD-2000 S-TEM systems.

3.3. Arc-Discharge. The arc-discharge production was carried out in a water-cooled stainless steel chamber equipped with an arc length controller (ALC-401, Jetline Engineering). For the anode, a commercially supplied graphite rod was cut in half to ~15 cm in length and then drilled to become hollow, with an inner diameter of ~4 mm. The hollow cavity was filled with a mixture of the natural graphite (0.54 g) and ^{13}C powders (0.64 g). The targeted ^{13}C content in the anode rod was ~20%. A solid graphite rod was used as cathode. The arc-discharge, under helium atmosphere (1 atm), was at a direct current of 70 A (28 V). The anode was consumed in about 40 min. The black deposit (~2 g) on the cathode containing ^{13}C-enriched graphite was collected.

3.4. Graphene Oxides. The Hummers method [29] with minor modification was used for the preparation of graphene oxides (GOs) from the arc-produced graphite sample.

Briefly, concentrated H_2SO_4 (10 mL) in a 500 mL flask was heated to 80°C, to which $(NH_4)_2S_2O_8$ (0.9 g) and P_2O_5 (0.9 g) were added. The mixture was stirred until the reagents were completely dissolved. The ^{13}C-enriched graphite sample (1 g) from the arc-discharge production was added, and the resulting mixture was heated at 80°C for 4.5 h. Upon being cooled to room temperature, the reaction mixture was diluted with water (250 mL) and kept for ~12 h. It was then filtrated and washed repeatedly with water, followed by drying in a vacuum oven. The solid sample was added to concentrated H_2SO_4 (40 mL) in a 500 mL flask cooled in an ice bath. To the mixture was added slowly $KMnO_4$ (5 g over 40 min), during which the temperature was kept at <10°C. The reaction mixture, with a change in color from black to greenish brown, was heated at 35°C for 2 h, followed by dilution with water (85 mL—Caution: the temperature must be kept at <35°C throughout) and further stirring for 2 h. The reaction mixture was poured into a large beaker, to which water (250 mL) and then aqueous H_2O_2 (30%, 10 mL) were added. Bubbles from the aqueous mixture along with a color change to brilliant yellow were observed. The mixture was allowed to settle for ~12 h. The clear supernatant was decanted, and the sediment was washed repeatedly with aqueous H_2SO_4 (5 wt%)-H_2O_2 (0.5 wt%) and HCl solution (10 wt%), followed by washing repeatedly with water until no layers observed in centrifuging. The sample was then dialyzed (MWCO ~ 3,500) against water for 7 days to yield a clean aqueous dispersion of GOs.

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