Carbon 101 (2016) 71–76

Contents lists available at ScienceDirect

Carbon

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

Rapid thermal decomposition of confined graphene oxide films in air

Xianjue Chen, Dongli Meng, Bin Wang, Bao-Wen Li, Wei Li, Christopher W. Bielawski, Rodney S. Ruoff*

Center for Multidimensional Carbon Materials (CMCM), Institute for Basic Science (IBS), Ulsan National Institute of Science and Technology (UNIST), Ulsan, 689-798, Republic of Korea

ARTICLE INFO

Article history:
Received 1 November 2015
Received in revised form
14 January 2016
Accepted 19 January 2016
Available online 22 January 2016

ABSTRACT

The ability to scale up the production of chemically modified forms of graphene has led to intense interest in the manufacture and commercialization of graphene-based materials. Free-standing film-like materials comprised of stacked and overlapped platelets of graphene oxide (G-O) or thermally and electrically conductive reduced graphene oxide (rG-O) are potentially useful in various applications including filtration membranes, mechanical seals, protective layers, heating elements and components of batteries or supercapacitors as well as in electronics and optoelectronics. The advances in these applications require efficient and low-cost protocols for fabricating certain types of layered materials and, as such, protocols are urgently needed for the reduced forms of G-O. Here we report an efficient and straightforward method to thermally reduce thin films of stacked G-O platelets while still maintaining their structural integrity. By rapidly heating confined G-O films on a hot plate set to 400 °C under an atmosphere of air, G-O films were readily converted to intact, electrically conductive, reduced thin films. The structure and degree of reduction of the resulting free-standing rG-O films were found to be comparable to those obtained by slow annealing at the same temperature.

1. Introduction

Free-standing thin films composed of stacked and overlapped individual graphene oxide (G-O) platelets that have been converted into electrically and thermally conductive films of reduced graphene oxide (rG-O) upon reduction show promise for use in emerging thin-film based applications [1–7]. The main reduction strategies to obtain rG-O films, while preserving their structural integrity, include thermal, chemical and electrochemical approaches [8]. Reducing agents that are toxic, unstable and/or corrosive, including hydrazine [9], metal hydrides [10] and hydriodic acid [11,12] have been widely used, which typically require additional safety precautions. Reductants such as ascorbic acid may be preferable in certain applications [4]. Electrochemical approaches involving electron exchange between G-O and the electrodes show promise as they normally do not require hazardous chemical reagents [13,14]. Nevertheless, some necessary conditions including an aqueous environment, pre-deposition on substrates, and a means to control pH are potential limitations of this approach. Reducing G-O films by high-temperature annealing may also be considered to be a clean and highly effective method, despite being limited by drawbacks such as high-energy consumption, a reducing environment, and the fact that it can be a time-consuming process [8]. In previous work, the heating process must be slow enough to alleviate the expansion of the structure, as rapid heating leads to a sudden release of intercalated H_2O, and evolution of CO and CO_2 that can rapidly expand the layers, similar to the 'thermal-shock' exfoliation of graphite oxide [15,16]. By exploiting the internal and the applied pressure differential, vacuum has been used to increase the mechanical driving force and promote the thermal exfoliation of graphite oxide [17,18]. In contrast, slowly annealing G-O films between stacked Si wafers under argon suppresses the random interlayer expansion and the movement of the sheets [19]. In this work, we demonstrate that an increase of the environmental pressure by tightly sandwiching the G-O film between two quartz slides while heating at a moderate temperature under an atmosphere of air results in a rapid thermal decomposition yielding a free-standing electrically conductive rG-O film while maintaining its structural integrity.

---

* Corresponding author.
E-mail address: ruofflab@gmail.com (R.S. Ruoff).

http://dx.doi.org/10.1016/j.carbon.2016.01.075
0008-6223/

2. Experimental

Graphite oxide was synthesized from graphite powder (SP-1, Bay Carbon) using a modified Hummers method [20,21]. The graphite powder (6 g) was pretreated with $K_2S_2O_8$ (5 g) and P_2O_5 (5 g) in a concentrated H_2SO_4 (25 mL) solution at 80 °C, and further oxidized with $KMnO_4$ (30 g) in a concentrated H_2SO_4 solution (230 mL) while being continuously stirred. The product was washed with an aqueous H_2O_2 solution (30%, 25 mL) and then an aqueous solution of HCl (10%) to yield graphite oxide. To remove the acid and any remaining salts, the graphite oxide was further washed with DI water followed until the pH of the supernatant reached 6 and then centrifuged. For each centrifugation cycle, the graphite oxide was subjected to bath sonication (30 min) to facilitate its exfoliation and re-suspension. A batch of colloidal G-O dispersion with a concentration of ~1 mg mL^{-1} was made for further use.

G-O paper was prepared by vacuum filtering the G-O dispersion (1 mg mL^{-1}, 10 mL) through a cellulose nitrate membrane filter (47 mm in diameter with 0.2 μm pore size, Whatman). The resulting G-O paper was dried under an atmosphere of air and then carefully peeled from the filter. Each G-O paper was cut into six pieces with a similar size, and one of the pieces was sandwiched between two quartz slides and tightly sealed using polyimide tape. A hotplate was used for supplying heat and its surface temperature was monitored using a digital infrared thermometer. The confined G-O films were placed directly on top of the hotplate for the reduction (see the video in the **ESI**). For the measurement of weight loss, the G-O films were first dried at 50 °C under vacuum, and weighed on a Mettler Toledo StaticDetect balance before and after the confined heating.

Supplementary video related to this article can be found at http://dx.doi.org/10.1016/j.carbon.2016.01.075.

Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were performed on a JEOL JEM-2100 instrument at an accelerating voltage of 200 kV. The TEM samples were prepared by dip coating 200-mesh holey carbon copper grids (#2450-AB, SPI Supplies) in the G-O aqueous solution. Atomic force microscopy (AFM) images were acquired in air using a Bruker Dimension Icon instrument operating in the Tapping mode. The G-O solution was drop-casted onto freshly cleaved highly ordered pyrolytic graphite (HOPG, #498HP-AB, SPI Supplies) and dried in air prior to AFM analysis. Scanning electron microscopy (SEM) imaging was conducted on an FEI Verios 460 High Resolution Field Emission instrument, with an accelerating voltage of 5 kV and working distance of 10 mm. The TEM and SEM images were processed using the Image J software package, and the AFM image was analyzed using the Gwyddion free SPM software package. X-ray diffraction (XRD) was carried out on a Rigaku SmartLab powder X-ray diffractometer. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Fisher Scientific ESCALAB 250XI system with a 90 μm beam size, and the data was processed using CasaXPS software. Raman spectra were acquired by a Wi-Tec micro Raman with a 532 nm excitation laser at ambient temperature. Tensile tests were carried out using a Q800 Dynamic Mechanical Analyzer (DMA; TA instruments). The sheet resistance of the free-standing G-O and rG-O films was measured on a CMT2000N surface resistivity measurement system with a four-point-probe head unit. Three measurements were made for each sample.

3. Results and discussion

As shown in Fig. 1a–c, monolayer G-O sheets ranging from 200 nm to 2 μm in a lateral dimension and ~1.2 nm in thickness were observed by TEM and AFM. A piece of freestanding G-O film peeled off from the cellulose nitrate filter after drying in air is shown in Fig. 1d. The G-O film was further dried in vacuum at 50 °C prior to the rapid heating [22]. Cut pieces of the G-O film were tightly confined between two quartz slides using polyimide tape as shown in the inset of Fig. 1d. The confined G-O films were then directly placed on the hotplate at temperatures ranging from 100 °C to 400 °C for a fixed processing time of 5 min, or for different processing times from 20 s to 10 min at a fixed temperature of 400 °C. The G-O film pieces were from the same G-O film for each set of control experiments. The temperature on the top of the quartz slide was monitored over time with an infrared thermometer. As shown in Figure S1, the temperature of the slide increased from room temperature to 120 °C in the first 5 s, and then gradually reached 300 °C within 60 s. Photographs of the resulting film pieces, Fig. 1e and f, show the appearance of the films treated under different conditions, and that all of the films retained their structural integrity. The change in mass of the materials after heat treatment was also measured; key data are summarized in Table S1. The G-O film pieces lost roughly half of their weight after being heated at 300 °C for 5 min or at 400 °C for 2 min, and the weight remained nearly unchanged afterwards. The film prepared at 100 °C (Fig. 1e) appeared to be darker than the original G-O film, whereas films heated to 200 °C and above had a metallic luster. As shown in Fig. 1f, the films had a metallic luster after heating for only 20 s at 400 °C.

XRD analysis revealed the evolution of the structure of the films under different conditions (Fig. 2) and a summary of the corresponding d (002) interlayer spacing and full width at half maximum (FWHM) for each XRD pattern is given in Table S2. As shown in Fig. 2a, the original G-O film shows a typical XRD pattern featuring a strong and sharp (002) peak with a d (002) value of 0.84 nm and a FWHM of 0.60°. After heating at 100 °C for 5 min, the 2θ value of the (002) peak increases slightly, with a small decrease in d (002) value to 0.83 nm and an increase in its FWHM to 0.61°. When the temperature reached 200 °C and above, the two (002) peaks were observed to shift to higher angles, indicating a decrease in the interlayer spacing and a broadening of the FWHM. According to previous studies, the smaller angle peak may be due to the removal of intercalated H_2O molecules in the films, and the larger angle peak may be because of the elimination of oxygen containing groups [23]. For samples heated at 200 °C, the two peaks subsequently recorded at 17.3° and 23.2° (2θ) correspond to d-spacings of 0.51 nm and 0.38 nm and FWHM values of 2.0° and 4.7°, respectively. The decrease of the interlayer spacing was attributed to the removal of intercalated water and main oxide groups [23]. The average size of the G-O crystals was also reduced because the decomposition of oxygen-containing groups involved removal of carbon atoms from the basal plane, which split the G-O sheets into smaller pieces. As the temperature increased, the two peaks continued to shift to higher angles, with an apparent sharpening of the lower angle peak. At 400 °C, the lower angle peak, corresponding to a d (002) value of 0.40 nm, appeared to combine with the other peak that featured a d (002) value of 0.36 nm. The FWHM decreased from 2.0° to 1.2° for the lower angle peak and from 4.7° to 4.0° for the higher angle peak when the temperature was increased from 200 °C to 400 °C. A similar trend of (002) peak shifts can be observed for the processing time experiments (Fig. 2b). For the sample heated at 400 °C for 20 s, signals were recorded at 18.1° and 23.2° upon analysis of the resulting material. The values of d (002) and FWHM appeared to be stable after heating for 5 min. In a control experiment, a similar piece of G-O film was reduced in a furnace thermostatted to 400 °C for 1 h under an atmosphere of argon. The XRD pattern of the resulting rG-O film (red curve in Fig. 2a) showed signals that appeared to be combined and was attributed to a d (002) value of 0.38 nm and FWHM of 1.3°, which