



Solvothermal reduction of graphene oxide in dimethylformamide



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ABSTRACT

The reduction of graphene oxide (G-O) is one of the most promising methods for the large scale production of graphene-based materials. In this paper, we report a simple and non-toxic method to produce reduced graphene oxide (rG-O) by refluxing G-O in *N,N*-dimethylformamide without the aid of a reducing agent. The rG-O materials with high degrees of reduction are prepared and the levels of reduction are controlled using reflux time. Successful reduction is confirmed by combustion-based elemental analysis and X-ray photoelectron and Fourier transform infrared spectroscopy.

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1. Introduction

Graphene is composed of a one atom thick sp^2 carbon network, and exhibits excellent performances in various applications, such as, batteries [1–3], supercapacitors [2,4], fuel cells [5], sensors [6], and nanocomposites [3,7] due to its excellent physical and electrical properties and high surface area. Chemical modification of solution-processable graphene oxide (G-O), which is exfoliated from graphite oxide as individual layers, offers a promising route to the mass production of graphene-based materials and introduction of functionality into the carbon network [8,9]. G-O is electrically insulating because the sp^2 network is disrupted during chemical oxidation. Chemical, thermal, solvothermal, and electrochemical reduction methods that can remove oxygen containing groups from G-O and restore the sp^2 network have been intensively reported [10–17]. However, non-toxic novel methods are required to produce reduced graphene oxide (rG-O).

Chemical reduction is one of the most frequently used methods to reduce G-O and typically requires the use of reducing agents, such as, hydrazine, sodium borohydride, NH_4OH , BH_3 , or NH_3-BH_3 [4,10,18–20], but most reducing agents described to date are corrosive, explosive, or hazardous. On the other hand, solvothermal methods can effectively reduce G-O without the aid of reducing agents [14,15]. Recently, it was reported that refluxing a G-O suspension in water provides an extremely useful, simple, environment friendly way of controlling levels of oxygen in rG-O [21].

However, the process is time consuming and the degrees of reduction achieved are mediocre. In this work, we found refluxing G-O for relatively short time in *N,N*-dimethylformamide (DMF) provides a means of producing rG-O with a high degree of reduction.

2. Experimental

2.1. Sample preparation

Graphite oxide was synthesized from natural graphite (SP-1, Bay Carbon, USA) using the modified Hummers method [22]. A homogeneous aqueous colloidal suspension of G-O (3 mg of graphite oxide per 1 mL of purified water) was produced by sonicating graphite oxide particles using a Branson 8510 ultrasonic cleaner (250 W) until the brown suspension became clear without visible graphite oxide particles. This brown suspension was then diluted with DMF (9 mL per 1 mL of G-O suspension, 99.8%, Daejung, Republic of Korea), immersed in an oil bath, and refluxed with stirring for designated times (12 h (rG-O-DMF-12), 24 h (rG-O-DMF-24), and 72 h (rG-O-DMF-72)). Resulting mixtures were filtered through an Anodisc membrane filter (47 mm of diameter, 0.2 μm of pore sizes, Whatman). The filtrate was further washed with DMF, H_2O , and ethanol several times then dried under vacuum at room temperature for 12 h.

2.2. Instruments and measurements

Elemental analysis for C, N, H, and O was conducted using a

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FLASH EA1112 instrument (Thermo Electron, Italy). X-ray photoelectron spectroscopy (XPS) of powder samples was performed using an angle-resolved X-ray photoelectron spectrometer (Theta Probe AR-XPS, Thermo Fisher Scientific, U.K.) equipped with a MXR1 Gun 400- μm 15 keV spectrometer. Fourier transform infrared (FT-IR) spectra were obtained from KBr pellets containing powder samples using a FT-IR Vacuum Spectrometer (Bruker VERTEX 80 V, Bruker, Germany). X-ray diffraction (XRD) patterns were obtained using a micro-area X-ray diffractometer (D/MAX-2500, Rigaku, Japan). Specific surface areas were determined using the Brunauer-Emmett-Teller (BET) method and a Tristar 3000 analyzer (Micromeritics, USA). Scanning electron microscope (SEM) images were obtained using a field emission scanning electron microscope (S-4300SE, Hitachi, Tokyo) at an accelerating voltage of 15 kV.

3. Results and discussion

Suspensions of G-O in DMF were produced as previously described [9]. The brown G-O suspensions were refluxed with stirring for the designated times (12, 24, or 72 h) (Fig. 1). It has been previously reported refluxing G-O suspensions in water for 24 h produced homogeneous colloidal suspensions containing rG-O (Fig. S1) [21]. In the present study, reflux for 12, 24 or 72 h in DMF produced black precipitates of rG-O-DMF-12, rG-O-DMF-24, and rG-O-DMF-72. Importantly, these DMF systems required less time to produce rG-O than aqueous systems. Usually, higher degrees of reduction lead to greater hydrophobic character, and in turn, the generation of more aggregated rG-O materials.

A C/O atomic ratio, which was calculated by combustion-based elemental analysis, has been frequently used to determine the degree of reduction of rG-O materials [23–25]. The C/O atomic ratio of graphite oxide is 1.4 and this ratio gradually increased as DMF refluxing time was increased (Table S1 and Fig. 2a). After 12 h of reflux, the C/O ratio (7.4) significantly increased relative to graphite oxide then slightly increased with further reflux (7.4, 7.7, and 8.4 for rG-O-DMF-12, rG-O-DMF-24, and rG-O-DMF-72 respectively). These results indicate that refluxing G-O in DMF provides an efficient means of producing rG-O materials in the absence of an additional reducing agent. As shown in Fig. 2a and Table S2, the C/O ratios of rG-O materials produced by DMF reflux were higher than those produced by water reflux. Fig. S2 compares deconvoluted XPS C1s spectra of rG-O samples refluxed in DMF or water with the same reflux time. XPS C1s components, corresponding to O-containing functional groups, were found with higher intensity in the DMF system than water system. These data clearly indicate that the DMF process is the more effective than water process to achieve high degree of reduction [21]. The high boiling point of DMF (153 °C) probably explains this difference.

Fig. 2b shows deconvoluted XPS spectra for graphite oxide and a series of rG-O-DMF samples. The deconvoluted XPS C1s spectra of graphite oxide and rG-O-DMF samples showed several peaks at 284.6, 285.6, 286.6, 287.8, and 289.0 eV, corresponding to sp^2 carbon, hydroxyl, epoxy, ketone, and carboxyl groups, respectively [8,22,23]. The peak intensity for C–O moieties in the spectra of rG-O-DMF samples were markedly lower than those in the spectrum of

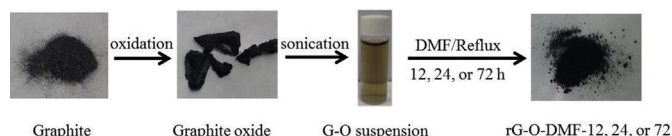


Fig. 1. Schematic of the production of rG-O samples by DMF-reflux.

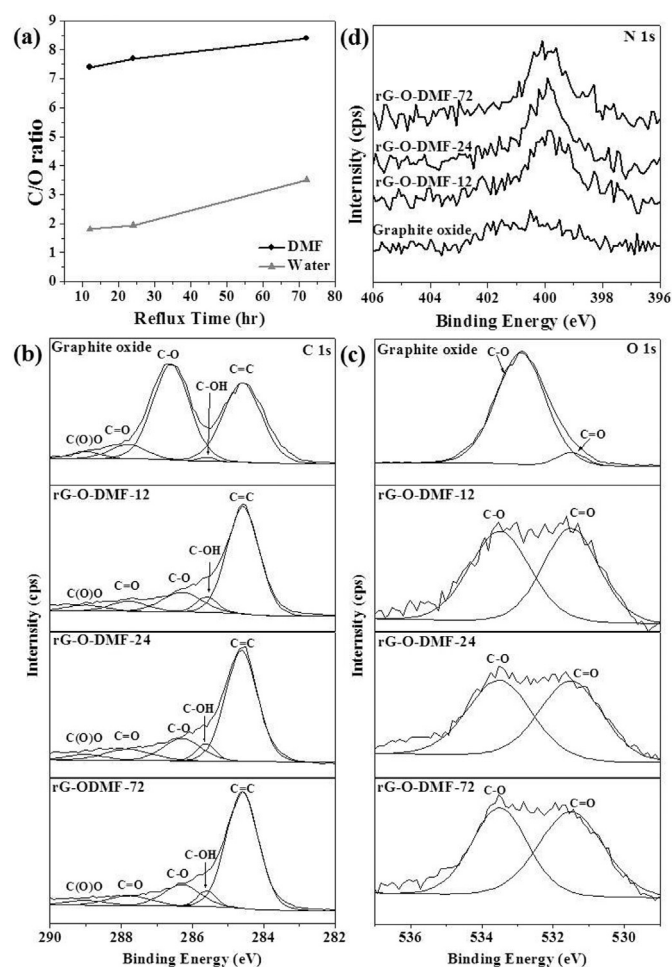


Fig. 2. (a) C/O ratios of DMF- and water-refluxed samples as determined by elemental analysis and XPS spectra of graphite oxide and rG-O-DMF samples (b) C1s spectra, (c) O1s spectra, and (d) N1s spectra.

graphite oxide, confirming that oxygen-containing functional groups of G-O were successfully removed by DMF reflux. The deconvoluted XPS O1s spectrum of graphite oxide shows two components at 531.5 and 533.5 eV, corresponding to C=O and C–O, respectively (Fig. 2c) [23,26]. Furthermore, the relative intensity of the C–O peak to the C=O peak significantly decreased with reflux, suggesting C–O moieties, such as, hydroxyl and epoxy on basal planes were removed more selectively than C=O. A small amount of nitrogen, which could have originated from the DMF, was detected by elemental analyses and XPS measurements (see

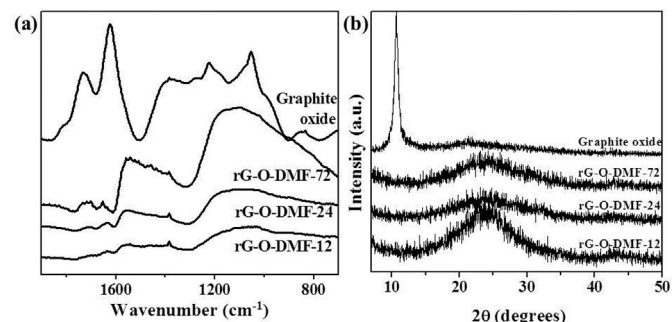


Fig. 3. (a) FT-IR spectra and (b) XRD patterns of graphite oxide and rG-O-DMF samples.

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