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# Synthesis and systematic characterization of functionalized graphene sheets generated by thermal exfoliation at low temperature

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#### Abstract

We describe the low-temperature thermal exfoliation of graphite oxide to obtain functionalized graphene sheets (FGSs). Graphite oxide, which is highly oxidized graphite produced by a nodified Brodie method, is further exfoliated by a simple heat treatment at 270–275 °C under ambient Ar. The FGSs that are generated have fewer defects and less oxygen content than in commercial graphene sheets (GSs) prepared at high temperatures (>900 °C). X-ray photoelectron spectroscopy demonstrates a clear  $\pi$ -plasmon peak in the FGSs of the type that is seen in precursor graphite, but not in commercial GSs. Thus, our FGSs exhibit high 2D crystallinity and minimal defects.

(Some figures in this article are in colour only in the electronic version)  $\equiv$ 

### 1. Introduction

Graphene, a single layer of graphite, has an ideal twodimensional structure as evidenced by its excellent electrical properties. These properties make graphene suitable for use in field-effect transistors, transparent conducting films, lithiumion batteries, supercapacitors and ultra-sensitive sensors [1–7]. GSs can be obtained by several routes: (i) micromechanical cleavage of highly ordered pyrolytic graphite (HOPG) [1], (ii) chemical vapour deposition (CVD) [8, 9] or (iii) exfoliation (thermal or chemical) [10–16]. Micromechanical cleavage is simple, but mass production using this method is limited and it is difficult to control the number of layers that are produced. The CVD method seems to be an ideal approach but layer control is still difficult. The thermal exfoliation method not only provides high quality graphene layers, but the graphene layers are also cheap to produce in large quantities [15] and graphene ribbons can be obtained relatively easily compared with other methods [16].

Thermal exfoliation in general uses natural graphite as a starting material. It is well known that in the graphite the interlayer interaction is mediated by weak van der Waals forces with a separation distance of 3.4 Å. The preparation of graphene involves three steps: (i) oxidation of the starting graphite to synthesize graphite oxide (GO), (ii) hightemperature thermal expansion/exfoliation of the as-prepared GO to obtain exfoliated graphite and (iii) ultrasonication and centrifugation of the obtained exfoliated graphite to obtain monolayer or multilayer graphene sheets (GSs) [10-15]. Oxidants with strong electron affinity can attack exposed  $\pi$ -electrons between layers and intercalate to extended interlayers to form graphite intercalation compounds (GICs). When the GICs are exploded by thermal treatment, the high pressure accumulated due to the decomposition of functional groups can exfoliate graphite by expanding the interlayer distances by several hundredfold. On the other hand,

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Figure 1. Schematic of experimental procedures used to produce FGSs at low temperatures.

ultra-smooth graphene nanoribbons have been also fabricated by combining thermal exfoliation of expanded graphite with chemo-mechanical breaking of the resulting GSs by sonication [16]. These approaches involve strong oxidants such as KMnO<sub>4</sub>, peroxide or nitric acid mixed with sulfuric acid to obtain intercalated H<sub>2</sub>SO<sub>4</sub>-graphite (or GO). This GO was further exfoliated at a high temperature by rapid thermal treatment, typically 900-1050 °C for 10-60 s under ambient Ar [10–16]. Because this process involves explosive expansion, low-temperature operation is highly desirable due to safety considerations. Due to this reason, alkali metal-intercalated graphite synthesized at low temperature had already been exfoliated successfully to produce scrolled GS. However, in this case, numerous graphitic layers still remained due to incomplete exfoliation [17, 18]. Recently, exfoliation of graphite oxide at high vacuum and low temperature has been tried. High vacuum was necessary to enhance exfoliation due the presence of insufficient functional groups in the pristine raphite oxide [19].

In this study, the precursor graphite was directly mixed with sodium chlorate and fuming nitric acid at room temperature without introducing sulfuric acid, a method known as the modified Brodie method [20-22]. The generated GO has several functional groups such as hydroxyl, carboxyl and epoxide functional groups and an expanded interlayer distance of 6–7 Å [20–22]. The GO was further heat-treated under ambient Ar at low temperature (270-295 °C). The exfoliated graphite had a specific volume of  $535 \text{ cm}^3 \text{ g}^{-1}$ , which is similar to the maximum value of the available expanded graphites at high temperature [23, 24]. Comprehensive analysis of the samples was performed using thermogravimetric analysis (TGA), x-ray diffraction (XRD) analysis, Raman spectroscopy, Fourier-transform infrared spectrometry (FTIR), x-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). All analyses indicated that our low-temperature functionalized graphene sheets (FGSs) are exfoliated with negligible (002) peak and furthermore have high 2D crystallinity with fewer defects nd lower oxygen content than commercially available hightemperature products.

#### 2. Experimental methods

In this work, the process of preparing FGSs consists of two steps, as shown in figure 1: (i) room-temperature oxidation

to generate GO and (ii) low-temperature exfoliation to obtain FGSs.

The GO was produced by a modified Brodie method using precursor graphite as a starting material. One gram of precursor graphite (99.999%, 200 mesh, Alfar Aesar, USA) was mixed with 8.5 g sodium chlorate and 20 ml fuming nitric acid at room temperature and stirred for 24 h. The mixed solution was then neutralized with deionized water and dried at 80 °C for 12 h. The completely dried GO was transferred to a chamber with a temperature-programmed furnace. Ar gas was pumped into the chamber at a flow rate of 3000 ml min<sup>-1</sup> and the temperature was increased at a ramping rate of 9.0 °C min<sup>-1</sup> from room temperature to 300 °C. Exfoliation took place in a temperature range 270–295 °C. Various structural properties of the obtained FGS were compared with those of commercially available GSs prepared by the conventional high-temperature exfoliation with sulfuric acid (N-BARO TECH, Korea).

Here, the interlayer distance of the samples was analysed by powder x-ray diffraction (XRD, Rigaku Rotaflex D/MAX System, Rigaku, Japan). The surface morphology was examined by FE-SEM (JSM 700F, JEOL, Japan). TGA (Q500, TA Instruments, USA) was used for structural and composition analysis. Raman spectroscopy was performed with a micro-Raman system (Renishaw, RM1000-In Via) with an excitation energy of 2.41 eV (514 nm). The presence of functional groups was also confirmed by FT-IR (IFS66/S, Bruker). XPS (ESCA2000, VGmicroteach, England) was used for chemical analysis of samples. Each powder sample was dispersed in ethanol and sonicated for 20 min and sprayed on the Au substrate. The I-V characteristics of the samples were measured by a source-measure unit (Keithley 236, 237) using a probe station. FE-TEM (JEM 2100F, JEOL, Japan) images were also obtained for the generated FGS. The selected area electron diffraction (SAED) pattern as well as the TEM morphology of the samples were recorded.

#### 3. Results and discussion

Figure 2 shows FE-SEM images of various samples. The precursor graphite comprised well-defined layered graphite (figure 2(a)). After oxidation, the layered structures were severely distorted and some layers were completely separated from the remaining layers. The irregular shape of layers seen in figure 2(b) is clear evidence of the expected interlayer expansion due to oxygen-related functional groups, which will be discussed in more detail below. After low-temperature





Figure 2. FE-SEM images of (a) precursor graphite, (b) GO, (c) FGS and (d) commercial GS.



Figure 3. TG and DTG of (*a*) typical GO and (*b*) FGS.

exfoliation, the volume of the layers expanded to  $535 \text{ cm}^3 \text{ g}^{-1}$ . As a consequence, worm-like GSs were obtained, as shown in figure 2(c). Their morphology was very similar to that of commercially available GSs (figure 2(d)).

Figure 3 shows the TGA and differential thermogravimetric (DTG) curves of GO and FGS. The temperature was increased from room temperature to 1000 °C at a ramping rate of 5 °C min<sup>-1</sup> under air atmosphere. For the GO sample (figure 3(a)), two characteristic DTG peaks were observed near 292 and 649 °C, corresponding to the burning temperatures of functional groups such as hydroxyl, carboxyl and epoxide roups, and the burning of the carbon backbone, respectively [21]. In the TGA curve, the actual burning temperature began at 260 °C and ended at 305 °C for GO at our experimental condition. This implies that exfoliation could occur near his temperature range. We also found that the exfoliation temperature may vary on the heating rate. The relative amount of functional groups was obtained by integrating each DTG urve, which was estimated to be 32%. These pre-existing functional groups can be decomposed at low temperature and give rise to endothermic explosion, resulting in full

exfoliation of graphene layers at low temperature under Ar ambient. The high content of functional groups in our work is in good contrast with the previous work, where vacuum environment (<1 Pa) was required for full exfoliation due to low content (about 20%) of functional groups in the pristine GO [19]. Therefore, the abundance of functional groups in the pristine GO is a necessary condition for full exfoliation at low temperature and atmospheric pressure. Furthermore, we note that the exfoliated GSs did not show appreciable functional groups; only one peak was observed near 569°C, which indicates burning of the carbon backbone, as shown in figure 3(b). We suppose that some of the FGS samples still had layered structures with relatively larger interlayer distances than the GO samples, as will be shown later. At the same time from SEM images, we found that the sample has a porous structure consisted of separated GSs. As a consequence, the kinetics for air to reach the reactive sites was enhanced, resulting in the lower burning temperatures observed in this study.

The interlayer distance changes were obtained from the XRD data. The interlayer distance in the GO samples

expanded from 3.4 Å (precursor graphite) to 5.7 Å due to the presence of functional groups. After exfoliation, the expanded GO peak shifted to 7.5 Å, but the peak intensity was reduced significantly. The intensity of FGS was very small, as shown in the inset of figure 4. The areal intensity of the FGS peak was only 0.8% compared with that of the precursor graphite (002) peak. These results indicate that most of the graphene layers were exfoliated randomly while a small portion of the sample still remained as layered structures with further expansion of the interlayer distances to 7.5 Å [25]. This peak position was also similar to that of the commercially available sample. Thermal expansion occurred instantaneously, as documented previously [10–16]. Gases, including oxygen gas, form due to the decomposition of functional groups in the GO structure. The accumulated gas explodes and thereby exfoliates the layers, resulting in expansion of the volume of FGS by several hundredfold. The pre-existing functional groups in GO that decompose around 290 °C, as shown in figure 3(a), invoke low-temperature exfoliation.

For Raman spectroscopy, the powder was mixed in ethanol and sonicated for 5 h and dropped on the Si substrate. The D-band intensity near  $1350 \text{ cm}^{-1}$ , which represents sp<sup>3</sup> hybridization, was normalized with respect to the G-band



**Figure 4.** XRD data of precursor graphite, GO, FGS and GS. The inset shows small remaining peaks of FGS and GS.

intensity in figure 5(a). After oxidation of precursor graphite for 24 h, the D-band intensity became stronger due to the presence of functional groups on the planar carbon backbones (figure 5(b)) [25–27]. The D-band intensity decreased after exfoliation due to removal of functional groups and recovery of sp<sup>2</sup> hybridization in the carbon backbone. Another interesting feature is the G-band peak shift, shown in figure 5(b). The G band of the GO sample was upshifted from 1580 cm<sup>-1</sup> (precursor graphite) to  $1604 \text{ cm}^{-1}$ . This is evidence of a strong charge transfer from the carbon backbones to oxygenrelated functional groups, inducing p-type doping in GSs [28, 29]. This peak position was downshifted to  $1589 \,\mathrm{cm}^{-1}$ after exfoliation, which indicates recovery of the structures to  $sp^2$  by the desorption of oxygen-related functional groups. This peak position was even lower than the  $1599 \,\mathrm{cm}^{-1}$  peak observed for the commercial product; in other words, there were fewer remaining functional groups in our FGS than the commercial product.

Changes in the functional groups during exfoliation were identified by FT-IR spectra. For FT-IR, the sample was ground with KBr and pelletized. Precursor graphite had small water-related peaks preferentially located at the edges of flakes. Oxidation involved severe content of oxygen-related functional groups in GO (figure 6(a)). In the case of FGS, the number of functional groups was reduced significantly to levels similar to those seen in the precursor graphite. Furthermore, the peak intensities of the functional groups in FGS were consistently lower than those of the commercial product. For instance, the E peak near 1064 cm<sup>-1</sup> representing epoxide was the dominant peak in GO, but this peak almost disappeared after exfoliation, as shown in figure 6(b).

A quantitative analysis of the functional groups in the graphene backbone was provided by XPS. Since the samples were sonicated in ethanol for 20 min during the sample preparation, samples could be oxidized unintentionally and introduce hydroxyl and carboxyl groups at the edges of even precursor graphite. Figure 7 shows C1s XPS spectra of each sample. The curves were deconvoluted into four or five peaks depending on the sample. The precursor graphite clearly shows a sp<sup>2</sup> carbon peak near 285.0 eV with an asymmetric line shape which might be exaggerated due to the sample treatment mentioned above, as shown in figure 7(*a*). One thing



Figure 5. (a) Raman spectra of precursor graphite, GO, FGS and GS at an excitation wavelength of 514 nm. (b) Position of the G band and the intensity ratio of the D band to the G band of each sample are indicated.



**Figure 6.** FT-IR curves of precursor graphite, GO, FGS and GS. (*a*) Full range. Peaks H1 and H2 originated from the hydroxyl group. Peaks W1 and W2 originated from water. E and CX stand for the epoxide and carboxyl groups, respectively. (*b*) Portion of epoxide groups.



**Figure 7.** XPS spectra of C1s. The FGS spectra were deconvoluted into the five peaks of sp<sup>2</sup>, COOH, C–OH, C–O–C and  $\pi$ -plasmon groups. The spectra of GO and GS were deconvoluted into the four peaks of sp<sup>2</sup>, COOH, C–OH and C–O–C groups.

**Table 1.** XPS data of C1s of each sample deconvoluted into four or five peaks of C–C, C–OH, C–O–C, COOH, and  $\pi$ -plasmon groups; binding energies (area percentages of peaks). The area percentages were normalized by subtracting values of the precursor graphite.

Samples	C–C	C-OH	С-О-С	СООН	$\pi$ – plasmon
GO	285.0 (68.9)	286.3 (25.3)	287.8 (5.0)	289.0 (0.8)	291.2 (4.5)
FGS	285.0 (82.4)	286.5 (5.8)	288.0 (3.5)	289.0 (3.8)	
GS	285.1 (74.1)	286.7 (14.3)	288.1(6.2)	289.2 (5.4)	

to note is the existence of a  $\pi$ -plasmon peak near 291.2 eV [30–33]. The  $\pi$ -plasmon peak is ascribed to  $\pi - \pi^*$  shake-up transitions, which is a characteristic of aromatic ring structures [34–36]. Therefore, the existence of this peak further testifies to the abundance of aromatic ring structures. In the case of GO, the sp<sup>2</sup> carbon peak was significantly reduced and

instead, the oxygen-related sp<sup>3</sup> carbon peak increased. The oxygen-related functional groups such as epoxide, hydroxyl and carboxyl groups were dominant in this case. As shown in table 1, the content of oxygen-related functional groups is 31%, which is consistent with the value (32%) obtained from TGA. Moreover, the  $\pi$ -plasmon peak disappeared. In the case



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Table 2. Elemental analysis of GO, FGS and GS samples.

Samples	Carbon (wt%)	O/C ratio	H/C ratio
GO	64.33	0.40	0.26
FGS	91.87	0.06	0.04
GS	90.07	0.08	0.12

)f FGS, functional groups were removed and therefore, the sp<sup>2</sup> carbon peak increased significantly compared with that of the commercial product (GS), as shown in table 1. All the data of area percentages in table 1 were normalized by subtracting the area of the edge-related functional groups in the precursor graphite to avoid unintentional oxidation effect that might be introduced during sample preparation. The existence of a long tail indicates that the exfoliated graphene still contains some amount of functional groups (figure 7(c)). Hence, this material is called 'functionalized' graphene sheet. Interestingly, the aromatic ring structure-related  $\pi$ -plasmon peak reappeared after exfoliation. This is in contrast with the commercial product that did not show this peak. All these results are congruent with the results from Raman analysis. Shown in table 2 is the elemental analysis for three samples. The content of hydrogen and oxygen atoms in three samples shows similar trend to those of XPS data.

Figures 8(a)–(c) are TEM images, and the corresponding SAEDs are shown in figures 8(d)-(f). In this case, the samples were sonicated in ethanol for 2h and dropped in a 200 mesh Cu TEM grid. As expected, the GO sample was rather thick, as evidenced by its dark colour. The FGS sample was rather transparent and uniform over a large observation area compared with the commercial product. The SAED of the GO sample showed hexagonal symmetry, which indicates good stacking order of the layered structures (figure 8(d)) [20]. The distinction between peaks was less obvious after exfoliation. Furthermore, the diffraction pattern was rather polycrystalline, indicating no obvious stacking order and a lower film thickness (figure 8(e)) [10, 11]. The diffraction pattern of the commercial product showed more distinct peaks and better defined peak positions than our exfoliated sample (figure 8(f)). This again suggests that our sample is better exfoliated than the commercial product.

Figure 9 shows the I-V curve of the FGS and GS at a zero gate bias. The FGS powder was pelletized by a press method at 20 MPa for 10 s at room temperature. The apparent density is  $0.9 \text{ g cm}^{-3}$  The I-V curve shows a clear linear relationship, indicating typical metallic behaviour. The conductivity of the FGS paper is 12.3 S cm<sup>-1</sup>. This value is higher than that  $(0.05-2 \text{ S cm}^{-1})$  of the reduced GO [37] and is similar to that  $(8.1 \text{ S cm}^{-1})$  of the commercial GS.

#### 4. Conclusions

FGSs were obtained by low-temperature thermal exfoliation near 275–295 °C using graphite oxide as a pristine material. The low-temperature exfoliation was made possible because of the preexisting oxygen-related functional groups in graphite oxide that accumulate explosive gases at low temperature. The FGSs generated consisted mostly of randomly exfoliated GSs



**Figure 8.** TEM images (a)–(c) and the corresponding SAED (d)–(f). The GO (a), (d) shows a hexagonal stacking order. However, no stacking order was evident in FGS (b), (e) or GS (c), (f).



**Figure 9.** The room-temperature I-V curve of the FGS (solid line) and GS (dotted line) pellet.

and only a small portion of layered structures with an expanded interlayer distance of 7.5 Å. The generated FGSs showed high 2D crystallinity with fewer defects and less oxygen content than the commercial high-temperature product. The ability to produce FGSs at low reaction temperature indicates that mass production of GSs is feasible.

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