

leads to lowered cost, improved quality, and minimized viscosity related processing issues. While VARTM is one of the most typical applications which can take advantage of the B-staged epoxy/CNT thin films, this approach can be extended to regular epoxy composites. In particular, it could accommodate tailored design of epoxy composite parts with desired mechanical/functional performance at different locations. Epoxy composites containing multi-layer epoxy/SWCNT thin film interleaves have been fabricated by the VARTM process, which will be reported shortly.

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## Controlled synthesis of few-layered graphene sheets on a large scale using chemical exfoliation

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#### ABSTRACT

The synthesis of few-layered graphene sheets with controlled number of layers (3–4) on a large scale was developed using chemical exfoliation by simply controlling the oxidation and exfoliation procedure. The obtained Few-layered Graphene Oxide (FGO) was characterized by atomic force microscopy, X-ray diffraction, thermal gravimetric analysis and Ultra-violet–visible spectroscopy. It is found that the FGO, which contains less functional groups than single-layered graphene oxide (GO), also has excellent water dispersion. Moreover, after reduction treatments under the same conditions as that used for GO, reduced FGO show a much better electrical conductivity of 108 S/cm, two-orders higher than reduced GO.

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Graphene, a single-atom-thick sheet composed of  $sp^2$ -hybridized carbon, has attracted tremendous attention owing to its strictly two-dimensional structure and outstanding

electronic, thermal and mechanical properties [1–3]. Few-layered graphene (FG), which is composed of several individual graphene layers, is now under intensive investigation as the

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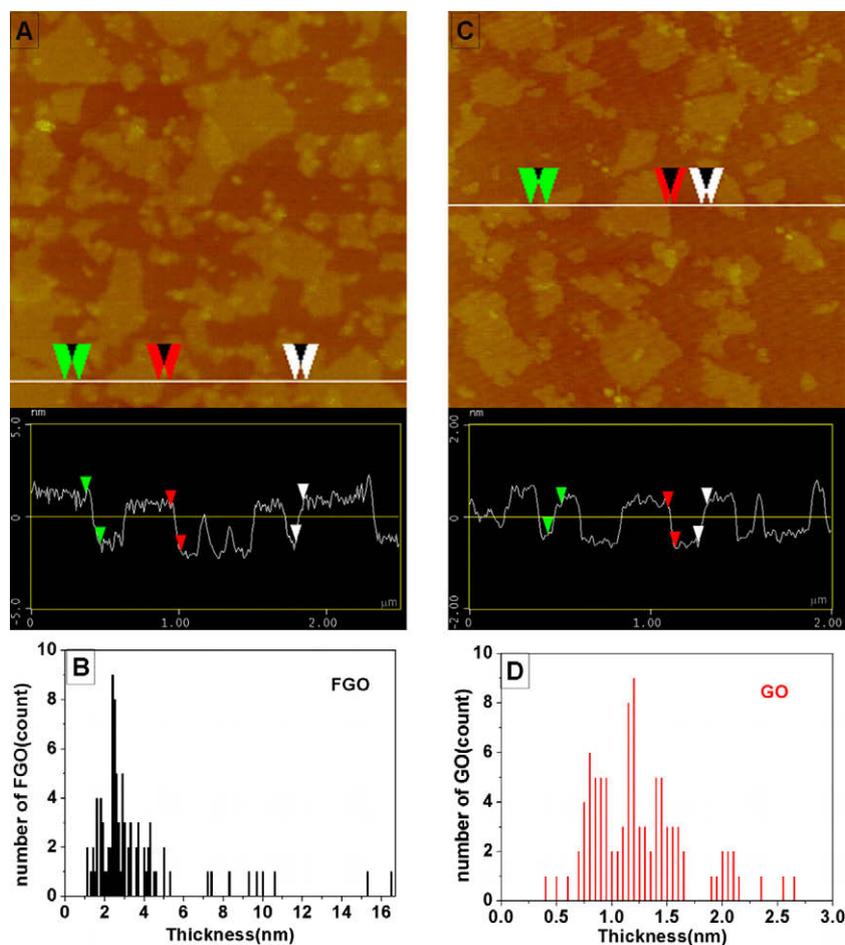
number of graphene layers plays an important role in adjusting their electronic and other properties [1]. Accordingly, in order to study the unique properties of FG and facilitate graphene's practical applications, it is highly important to develop simple and efficient methods for the production of FG with controlled layers and large quantities.

Recently, there have been several reports about the preparation of FG, ranging from chemical vapor deposition [4], arc-discharge [5] to chemical and thermal reduction of Few-layered Graphene Oxide (FGO) [6]. The wet-chemistry method, adopted by using a modified Hummer's method [7], has the advantages to produce FGO in large quantity with excellent solubility which is essential for solution process device applications. In the latest report, Wu et al. prepared FGO and FG by using different starting graphite materials [6]. The lateral sizes and qualities of FGs using this method depend on the different graphite starting materials. Consequently, it is still highly demanded to find an easy way to prepare FG with controlled number of layers on a large scale. In this paper, using a controlled oxidation and intercalation procedure, we are able to produce FGO at large quantity in a controlled manner and obtain FG by chemical and thermal reduction of FGO. More importantly this FGO material has excellent dispersion in both water and dimethylformide (DMF), and the films pre-

pared using its solution process show much better conductivity compared with that of the corresponding graphene oxide (GO) material.

It is well known that GO formation involves the reaction of graphite with strong oxidizers such as sulfuric acid, nitric acid, potassium chlorate, and potassium permanganate. The introduction of oxygen-containing functional groups by fully oxidation results in an increase in the *d*-spacing and complete elimination of the 0.34 nm graphite interlayer spacing [8]. So it is natural to expect that FGO could be obtained by controlled oxidation/exfoliation of graphite. Thus, using a modified chemical oxidation/intercalation process, we studied the effect of the degree of oxidation and exfoliation on the number of layers in FGO sheets. Indeed, we found that both the amount of oxidizers and the time for the oxidation/intercalation process play an important role in the number of layers in FGO sheets and their sizes. With less oxidizers or oxidation time, both the number of layers and size of the FGO are larger. In an optimized process detailed in the Supporting Information, the mean height of fully exfoliated FGO was 2.5 nm, corresponding to FGO with 3–4 layers (see below).

A great number of atomic force microscopy (AFM) measurements were performed to determine the thickness of FGO sheets, together with its corresponding single-layer GO



**Fig. 1** – Typical tapping mode AFM images of (A) FGO sheets and (C) GO sheets deposited on the mica substrate from aqueous dispersion, corresponding height cross-sectional profile. Histograms of the height distribution of (B) FGO and (D) GO obtained from 90 sheets for each sample.

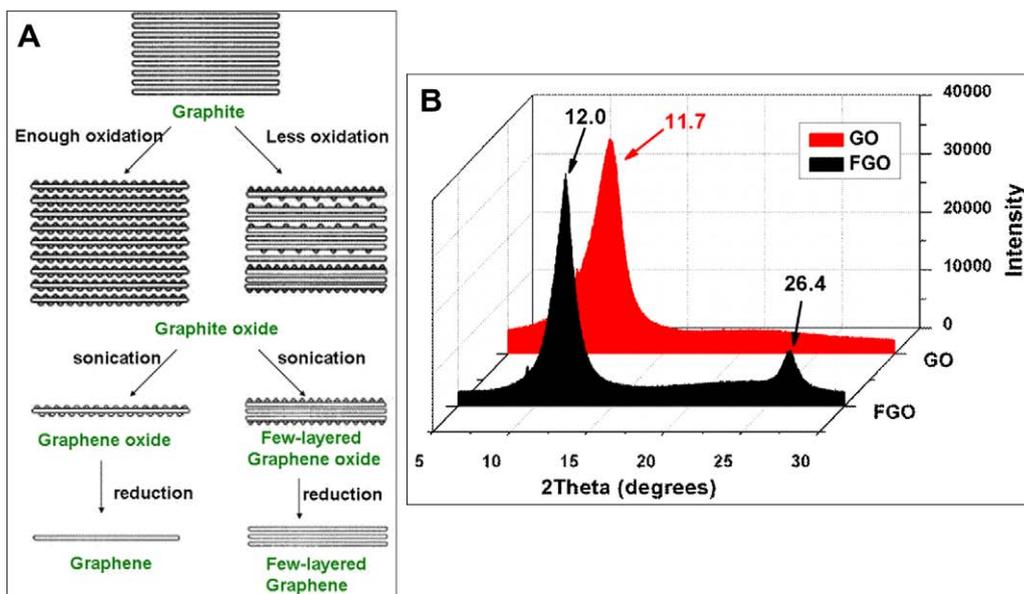


Fig. 2 – (A) Outlined oxidization/intercalation process for the preparation of FGO and GO; (B) XRD patterns of FGO and GO.

for comparison. A typical tapping mode AFM image and the corresponding height cross-sectional profile of FGO sheets deposited on the mica substrate was displayed in Fig. 1A. Based on the AFM height statistical analysis of FGO for 90 sheets, the height of FGO exhibited a Gaussian distribution and the maximum distribution of height is  $\sim 2.5$  nm (Fig. 1B). These are very different from that observed from GO (Fig. 1C and D). Derived from AFM measurements on 90 sheets for GO, the mean height of GO is  $\sim 1.2$  nm, which is characteristic of a single-layer GO sheet as observed in the vast majority of literatures [2,8]. Furthermore, we can also see from the AFM images that FGO has a larger lateral size than GO. That is expected as less oxidizers or oxidation time should introduce less fault lines and cracks in graphite, leading to less unzipping of graphite lattice and resulting in a larger lateral size of sheet [9].

The X-ray diffraction (XRD) of FGO and GO were shown in Fig. 2B. There are two diffraction peaks for FGO at  $2\theta = 12.0^\circ$  ( $d = 0.74$  nm) and  $26.4^\circ$  ( $d = 0.34$  nm). The relatively weak diffraction peak with  $d = 0.34$  nm is corresponding to the normal graphite spacing, and this is consistent with the rather limited ordering for the limited few-layers in FGO. The stronger peak with  $d = 0.74$  nm should come from the inter-FGO diffraction, corresponding to the typical diffraction peak of GO [8]. The reasons for that the peak at  $26.4^\circ$  ( $d = 0.34$  nm) is weaker than that at  $12.0^\circ$  ( $d = 0.74$  nm) are probably because the rather limited ordering (only few-layers) in each FGO and the uneven interlayer spacing (0.34–0.40 nm) in the whole FGO samples and that at the edges due to the fact that each FGO should be slightly different in structure. This XRD result indicates that the limited oxidation/intercalation process results in partial oxidation and incomplete exfoliation of graphite to yield FGO structure as outlined in Fig. 2A. Furthermore, from the high-resolution transmission electron microscopy results, the interlayer spacing in each FGO sheet was still roughly around 0.34 nm, same as that in natural graphite

(Fig. S1). So, in each individual FGO sheet, we believe that the oxygen-containing groups are still mainly attached around the outside edge (including the top and bottom lateral area). This is also supported by the less mass loss in thermogravimetry analysis (TGA) study below, and the Raman results (Fig. S2). Based on this, using the thickness of single-layer GO, we estimate that our fully exfoliated FGO is mainly composed of 3–4 layers.

The TGA analysis (Fig. 3) of FGO showed a mass loss of  $\sim 15\%$  in the range of 110–230  $^\circ\text{C}$ , while TGA of GO showed a mass loss of more than 30% in the same range, suggesting a much lower content of oxygen-containing groups in FGO than in GO. Besides, smaller amounts of water are lost in FGO than in GO during the initial heating stage. This phenomenon is clearly consistent with the results of XRD discussed above

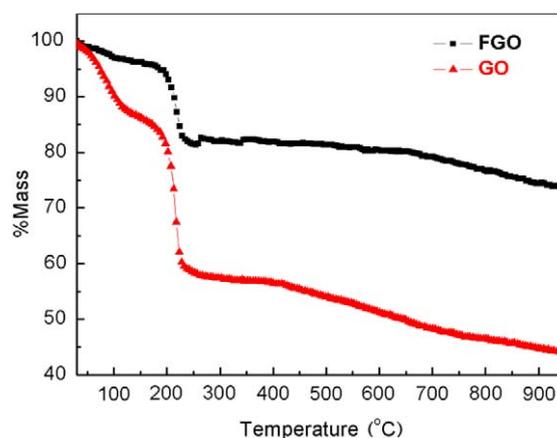


Fig. 3 – TGA curves of FGO and GO at a heating rate of  $5^\circ\text{C min}^{-1}$  from room temperature to 1000  $^\circ\text{C}$  in  $\text{N}_2$  atmosphere.

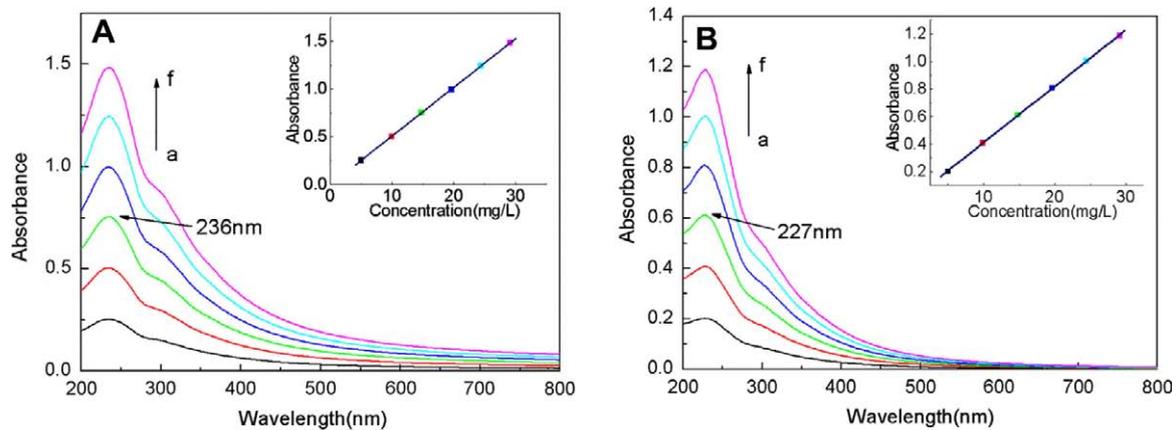


Fig. 4 – UV-vis spectra of (A) FGO and (B) GO dissolved in water (concentrations are 5.0, 9.9, 14.8, 19.6, 24.4, 29.1 mg L<sup>-1</sup>, from a to f, respectively). The inset shows the linear relationship between the absorbance and the concentration.

Table 1 – Conductivity and sheet resistance of reduced FGO and GO films using different reduction treatments.

Sample	Reduction treatments	Thickness (nm)	Conductivity (S/cm)	Sheet resistance (ohms/sq)
Reduced FGO films	Hydrazine vapor + annealing at 800 °C under argon flow	12	4.76E+02	1.75E+03
	Hydrazine vapor + annealing at 400 °C under argon flow	72	1.08E+02	1.28E+03
	Annealing at 800 °C under argon flow	66	1.09E+01	1.40E+04
	Hydrazine vapor	25	3.23E-02	1.24E+07
Reduced GO films	Hydrazine vapor + annealing at 800 °C under argon flow	28	3.83E+01	9.32E+03
	Hydrazine vapor + annealing at 400 °C under argon flow	29	3.95E+00	8.72E+04
	Annealing at 800 °C under argon flow	18	1.10E+01	5.07E+04
	Hydrazine vapor	33	5.32E-06	5.69E+10

and the results from Fourier transform infrared spectroscopy (Fig. S3).

UV-vis spectroscopy measurements were also used to compare the degree of oxidation of FGO with GO (Fig. 4). The absorption peaks of FGO and GO are at 236 and 227 nm, respectively, indicating a blue shift of the absorption peaks from FGO to GO. This is expected for the stronger oxidation and more serious disruption of the  $\pi$ -conjugation in GO. Surprisingly, FGO can be readily exfoliated in water under a mild ultrasonic treatment to form a stable colloidal suspension of individual sheets as its single-layer counterpart GO [9], even though it has much less functional groups than GO. This is demonstrated in the inset of Fig. 4A, the absorbance of FGO aqueous solutions are well in line with the relative concentrations, obeying Beer's law, which reveals the excellent solubility and stability of FGO in water.

Finally, we obtained FG by either chemical or thermal reduction of FGO and evaluated the effect of different reduction treatments on the electrical conductivity of FG transparent films. Hydrazine vapor reduction was utilized as chemical reduction. For thermal treatments, we have tested the annealing of our films under argon flow at different temperatures ranging from 400 to 800 °C. The different treatment and the conductivity of the films, together with that from GO as comparison, are summarized in Table 1. It is important to note that, with the same reduction method, the reduced FGO films show much higher electrical conductivity than

the reduced GO films. For example, FGO film reduced by hydrazine vapor and then annealing at 400 °C under argon flow shows a conductivity as high as 108 S/cm (sheet resistance 1280 ohms/sq), which is two-orders of magnitude higher than that of GO film reduced by the same method. The higher electrical conductivity of FG may be attributed to its less disrupted  $\pi$ -conjugation due to less functionalization, larger sheet size, and probably its multilayered structure too.

In conclusion, an easy and efficient approach has been demonstrated for the preparation of FG sheets on large scale with a controlled thickness. It is important to find that FGO, with less oxygen-containing groups but still excellent water dispersion, show a much better electrical conductivity than its single-layered counterpart after the same reduction treatment. These results should facilitate the studies and applications for graphene materials with different layers and properties. Furthermore, its solution processing capability and excellent conductivity of the reduced films indicate that it should offer great advantages for some large scale and low-cost applications compared with its single-layered counterpart.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbon.2010.02.035.

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# Lithographically defined site-selective growth of Fe filled multi-walled carbon nanotubes using a modified photoresist

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### ABSTRACT

Partially Fe filled multi-walled carbon nanotubes (MWCNTs) were grown by chemical vapor deposition with propane at 850 °C using a simple mixture of iron (III) acetylacetonate (Fe(acac)<sub>3</sub>) powder and conventional photoresist. Scanning electron microscopy revealed that catalytic nanoparticles with an average diameter of 70 nm are formed on the Si substrate which governs the diameter of the MWCNTs. Transmission electron microscopy shows that the nanotubes have a multi-walled structure with partial Fe filling. A site-selective growth of partially Fe filled MWCNTs is achieved by a simple photolithographic route.

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Carbon nanotubes (CNTs) exhibit a unique combination of electronic, thermal, mechanical and chemical properties, which promise a wide range of potential applications in key industrial sectors. In the last few years, chemical vapor deposition (CVD) has been the preferred method among different CNT growth methods because of its potential advantage to produce a large amount of CNTs growing directly on a desired substrate with high purity, large yield and controlled alignment. The CVD synthesis of CNTs on plain substrates gener-

ally requires catalyst metal deposition over the substrate, which is time consuming and the deposited area is also finite. These limitations can be easily overcome by employing the spin-coating of the catalyst material on the desired substrate. Moreover, in recent times, magnetic metal encapsulated CNTs are of huge interest as it has demonstrated widespread applications in magnetic force microscopy [1], high-density magnetic recording media [2] and biology [3]. However, there are many technical barriers to achieve magnetic metal

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