Facile and size-controllable preparation of graphene oxide nanosheets using high shear method and ultrasonic method

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ABSTRACT
The lateral size of the graphene oxide (GO) nanosheets could be controlled by preparation method, and a simple and effective strategy to adjust the lateral size of GO nanosheets by selecting suitable method is presented. The high shear method was introduced to produce GO nanosheets, and the GO nanosheets (few micrometres) prepared by high shear method is about one order of magnitude larger than GO nanosheets (few hundred nanometres) obtained by ultrasonic method, as evidenced by atomic force microscopy. The FTIR, XPS and Raman analysis revealed that there are no distinct differences in composition and functional groups between the GO nanosheets produced by high shear method and ultrasonic method. The cavitation in the procedure of ultrasonic method is favourable for GO exfoliation, but it also could result in damage to GO nanosheets. The shearing force in the process of high shear method is effective for GO delamination with minimal fragmentation. The results indicated that the high shear method proposed in this paper is an efficient exfoliation means to produce single-layer GO nanosheets.

KEYWORDS
graphene oxide; high shear method; ultrasonic method; size controllable

1. Introduction
The layered materials feature strong in-plane chemical bonds but weak interlayer interactions, and can be easily peeled to multiple or even single-layered nanosheets [1]. Recently, there has been growing interest in exfoliation of layered materials to produce two-dimensional (2D) nanosheets, such as graphene [2-6], graphene oxide (GO) [1,7–10], etc. GO has recently attracted substantial interest as a possible intermediate for the preparation of graphene [11–13] and metal oxide/graphene nanocomposites [14–16]. It also has been used to prepare a strong paper-like material owing mainly to their interesting electrical, thermal, mechanical and optical properties [1,8,10,17–22]. The small area of GO sheets results in high inter-sheet contact resistance in the films due to a large amount of inter-sheet junctions [10,23,24]. So the size control of GO nanosheets is extremely important for certain applications, the large-sized GO nanosheets might be favourable for the
preparation of monolithic materials, and the small-sized GO nanosheets might be favourable for medical applications. In literature, the size of the pristine graphite and the oxidation degree of processed graphite oxide will affect the lateral size of the prepared GO. Zhou et al. [25] reported that the GO size can be easily controlled through the size selection of the graphite material, the exfoliated GO sheets had a lateral size around 15 μm by using the 500 mesh size graphite flakes, and had a lateral size in the order of 100 μm by using the 50 mesh size graphite flakes. Pan et al. [26] showed that GO nanosheets derived from fully oxidised graphite are significantly smaller than those derived from partially oxidised graphite; they attribute this size reduction to the further weakening of graphene sheets resulting from the addition of hydroxyl and epoxy sites. The reduction in GO size with increasing degree of oxidation was also reported by Zhao et al. [10] and Zhang et al. [27]. But Huang et al. [9] observed that GO nanosheets with a large lateral dimension is produced with a higher degree of oxidation; they explained that the complete oxidation of graphite oxide makes the graphite oxide to be exfoliated easily in large pieces.

The most popular method employed for the exfoliation of GO nanosheets is ultrasonic method [8,28–33]. But the sonication also can cause substantial damage to the GO platelets [32], and tend to damage and fragment GO nanosheets [34]. Thus, if the goal is to prepare relatively large-sized GO nanosheets, the milder delamination method is required. So a variety of sonication-free exfoliation methods were used to exfoliate GO nanosheets from graphite oxide, such as thermal method [35,36], mechanical shaking method [25,26], freeze–thaw method [37], etc.

Recently, shear mixer was introduced to exfoliate the graphite into individual graphene nanosheets [3,4,38–40]. Because the oxygen-containing groups binding on carbon atoms will increase the interlayer spacing of graphite oxide, and make the layered graphite oxide easier to cleave [10,41]. It is proposed that the shear mixer is also capable of inducing spontaneous exfoliation of graphite oxide into discrete GO nanosheets without sonication, preserving large lateral dimension of single-layered GO nanosheets. In this paper, the shear mixer was introduced to produce GO nanosheets, and compared with commonly used ultrasonic cleaner. The first aim of the present study was to investigate the difference of the GO nanosheets prepared by ultrasonic method and high shear method. The exfoliation mechanism of GO based on peeling force was studied, and used to analyse the difference of GO nanosheets prepared by ultrasonic method and high shear method. The second aim of the present study was to provide a simple and effective strategy to adjust the lateral size of GO nanosheets by selecting suitable method.

2. Experiment

2.1. Materials

Graphite flakes (~325 mesh, 99.8%) were purchased from Alfa Aesar; and sulphuric acid (H2SO4, 98%), potassium permanganate (KMnO4, 99.9%) and hydrogen peroxide (H2O2, 30%) were purchased from Beijing Beihua Fine Chemicals Co., Ltd. All the agents were used without further purification.

2.2. Graphite oxide synthesis

The study here uses the pressurised oxidation method [42] to oxidise the graphite flakes for the synthesis of GO. Typically, graphite flakes, KMnO4, H2SO4 and Teflon reactor
(100 ml) were cooled in a refrigerator at 0–4 °C for 8 h. Then, the cooled graphite flakes (1 g), KMnO₄ (5 g) and H₂SO₄ (50 ml) were added quickly into the Teflon reactor. After this, the reactor and stainless steel autoclave were covered, fastened and kept at 0–4 °C for 4 h and then heated at 75 °C in an oven for 4 h. Subsequently, the obtained mud was diluted with 500 ml water, and H₂O₂ (30%) was dripped into the suspension until the slurry turned golden yellow. Finally, the resulting suspension was washed with water for five times, and the humid graphite oxide was obtained.

2.3. Graphene oxide preparation

The ultrasonic method and high shear method were used to exfoliate the as-prepared graphite oxide. In typical ultrasonication procedure, 25 ml as-prepared graphite oxide suspension (1 mg/ml) was loaded in a 30-ml glass beaker, and then sonicated by an ultrasonic bath cleaner (100 W, KX-1620, Beijing Kexi technology Co. Ltd., China) for 1, 2, 3 and 4 h (hereon denoted as u1, u2, u3, u4). In order to control the temperature of the water, the water was changed every half hour. In high shear exfoliation procedure, 350 ml as-prepared graphite oxide suspension (1 mg/ml) was loaded in a 500-ml double-walled glass beaker, which was outside cooled by ice water. The dispersion was then treated by AE300S-H high-speed shear mixer (Angni Instruments, China) at the speed of 10,000 rpm for 1, 2, 3 and 4 h (sampled as h1, h2, h3, h4), which are shown in Figure S1. In experiment, 20 ml GO samples were collected by straw every hour from the beaker. All samples were centrifuged at 4000 rpm for 1 h in L600-type centrifuge (Xiangyi Instruments Factory of Hunan, China). After centrifugation, the supernatant was carefully removed and retained for further characterisation.

2.4. Characterisation

The morphology of graphite flakes and graphite oxide was examined using JSM-6700F field-emission scanning electron microscope (JEOL, Japan) with an accelerating voltage of 5 kV. The samples were sputter-coated with gold before imaging. The chemical bonding of graphite flakes, graphite oxide and GO was characterised by Nicolet iS10 Fourier transform infrared (FTIR) spectrometer (Nicolet Instrument Crop., USA) in the range of 400–4000 cm⁻¹, accumulating 32 scans at a resolution of 4 cm⁻¹. The samples were mixed with KBr at a 1:160 mass ratio and pressed into pellets. The surface composition and element analysis for graphite flakes, graphite oxide and GO were analysed by X-ray photoelectron spectra (XPS) on ESCALAB 250 system (Thermo Scientific, UK), using Al-Kα radiation as the excitation source (1486.6 eV). The crystallographic structural analysis for graphite flakes, graphite oxide and GO were carried out by X-ray diffraction (XRD) on XPert Pro MPD (PANalytical, The Netherlands), using Cu-Kα radiation. Raman spectra of graphite flakes, graphite oxide and GO were obtained on Renishaw 2000 Raman spectrometer (Renishaw, UK) utilising a laser beam of 514 nm. Atomic force microscopy (AFM) was performed on Nanoman AFM (Veeco Metrology Group, USA), and tapping mode was employed to determine the thickness and lateral dimension of GO nanosheets at ambient temperature. In the sample preparation, a drop-let of diluted GO suspension was dropped onto a freshly cleaved mica substrate. AFM can easily give high-resolution images of the GO nanosheets, and the image processing was
used for the direct measurement of area and thickness of GO nanosheets in the present study.

3. Results and discussion

3.1. Scanning electron microscopy analysis

Scanning electron microscopy (SEM) images of graphite flake and graphite oxide are shown in Figure 1. From the figure it can be seen that the surface of highly crystalline graphite flakes is smooth (Figure 1(a)), and the surface of graphite oxide is rough with micrometre-long wrinkles (Figure 1(b)) [18,26,43]. The formation of the wrinkles on the graphite oxide surface indicates that the graphite flakes are oxidised successfully, which may be due to the undulation of the sheet as epoxy and hydroxyl sites form [26,36].

3.2. Atomic force microscopy analysis

To elucidate the formation of GO nanosheets and achieve size-controllable synthesis, we investigated the effects of exfoliation time and method on the size of GO nanosheets. Figure 2 shows the typical AFM images of the GO nanosheets obtained by ultrasonic exfoliation from four different exfoliation times (1, 2, 3, 4 h). The AFM images revealed the presence of irregularly shaped GO nanosheets and the lateral sizes of the GO nanosheets decreased severely with increasing sonication time, as previously observed in [24,44]. The GO nanosheets with lateral sizes of a few micrometres can only be observed in a small amount in sample u1, and most GO nanosheets with sizes of few hundred nanometres can be seen in samples u2, u3 and u4. On the basis of AFM measurements (more than 150 GO nanosheets for each sample), the statistical area distributions are obtained and shown in Figure 3. From the figure it can be seen that only 3% GO nanosheets in sample u1 are larger than 1 μm². When the sonication time increased to 2, 3 and 4 h, no GO nanosheet is larger than 1 μm², much smaller GO nanosheets are obtained, 75% of GO nanosheets in sample u2, 83% in sample u3, and 82% in sample u4 have an area less than 0.01 μm². This phenomenon can be attributed to the cracking of large GO nanosheets under ultrasonic exfoliation condition. Based on the AFM height profile analysis, the cross-sectional contour lines (inset) of GO nanosheets are shown in

![Figure 1](image_url)  
**Figure 1.** SEM images of (a) graphite flake and (b) graphite oxide.
The thickness of 20 measured GO nanosheets is typically between 0.8 and 1.3 nm (Figure S2), which is consistent with the thickness of the characteristic single-layer GO reported [9,10]. As a result, GO nanosheets with a small lateral size (few hundred nanometres) can easily be formed by ultrasonic method, and the longer sonication time results in smaller GO nanosheets.

Figure 4 displays the AFM images of GO nanosheets prepared by high shear method at different shear times (1, 2, 3, 4 h). The GO nanosheets with lateral sizes of a few micrometres can be observed in all samples and some GO fragments can also be found in AFM images, these fragments might be derived by inevitable breakage during the exfoliating process. Based on the analysis of the AFM images for more than 150 nanosheets for each sample (more AFM images of GO nanosheets are provided in the Supporting Information, Figure S3), the respective area distributions are shown in Figure 5. The percentage of
GO nanosheets larger than 10 $\mu$m$^2$ are 20% in sample h1, 11% in sample h2, 9% in sample h3 and 3% in sample h4, which indicates that the area of GO nanosheets decreases with the increasing shear time. Based on the AFM height profile analysis, most of the GO nanosheets obtained are 0.8–1.4 nm in thickness (Figure S4), indicating that these GO nanosheets are monolayer, which indicates the successful exfoliation of graphite oxide by high shear method.

We define the GO with an area of 1 $\mu$m$^2$ corresponding to the GO with a lateral size of 1 $\mu$m by assuming that the GO nanosheets is square. Because of the percentage data were calculated based on the number of GO nanosheets in this paper, the weight of 10 GO nanosheets of 1 $\mu$m$^2$ equal one GO nanosheet of 10 $\mu$m$^2$. The percentage of GO nanosheets larger than 1 $\mu$m$^2$ is 83% in sample h1, 60% in sample h2, 48% in sample h3 and 49% in sample h4, which means that the GO nanosheets with the lateral sizes of a few micrometres can be obtained by high shear method. The results indicate that GO nanosheets prepared by high shear method had been exfoliated with minimal fragmentation. The size reduction of GO nanosheets obtained with sonication is more significant than that of the GO nanosheets obtained with shear exfoliation, and the lateral size of GO

Figure 3. Histograms of respective areas of the GO nanosheets after (a) 1-h, (b) 2-h, (c) 3-h and (d) 4-h exfoliation by ultrasonic method.
nanosheets (few micrometres) prepared by high shear method is about one order of magnitude larger than GO nanosheets (few hundred nanometres) obtained by ultrasonic method.

3.3. X-ray diffraction analysis

XRD patterns of graphite flake, graphite oxide and GO nanosheets are shown in Figure 6. Graphite flake exhibits a basal reflection (002 plane) peak at $2\theta = 26.6^\circ$ (d-spacing = 0.335 nm) [45]. After oxidisation of graphite flake, the 002 reflection peak shifts to the lower angle ($2\theta = 9.9^\circ$, d-spacing = 0.89 nm), which clearly indicates the formation of graphite oxide. The increase in d-spacing is due to the formation of oxygen-containing functional groups between the layers of the graphite. The 002 reflection peaks of GO u4
and GO h4 shift to the lower angle $2\theta = 7.2^\circ$ and $2\theta = 5.8^\circ$ (d-spacing = 1.23 nm and 1.52 nm, respectively), and the increase in d-spacing is due to the exfoliation of graphite oxide. From the figure, it also can be seen that the diffraction peak of u4 is much broader than that of h4. From the well-known Scherrer equation [46], it is known that the

![Figure 5](image)

**Figure 5.** Histograms of respective areas of the GO nanosheets after (a) 1-h, (b) 2-h, (c) 3-h and (d) 4-h exfoliation by high shear method.

![Figure 6](image)

**Figure 6.** XRD spectra of graphite flakes, graphite oxide, GO u4 and GO h4.
crystallite size is a reciprocal ratio to the half peak width at 2θ, so the sheet size in u4 is smaller than that in h4.

3.4. Fourier transform infrared analysis

Figure 7 shows the FTIR spectra of graphite flake, graphite oxide, GO u4 and GO h4. For graphite flake, there is no distinct peak detected in the spectrum of graphite flakes. In the GO spectrum, a strong and broad band at 3410 cm⁻¹, which is due to the O–H stretching vibrations [47,48], and the presence of peaks between 1000 and 1750 cm⁻¹ corresponding to a large number of functional groups. The bands at 1743 cm⁻¹ [47,49,50] are related to the C=O stretching vibrations, the peak at 1637 cm⁻¹ [50,51] is ascribed to C=C stretching vibration, and the bands at 869 [52], 1054 [52], 1230 [53] and 1400 cm⁻¹ [54] are attributed to C–O stretching vibrations. No distinct differences are found between the spectrum of GO u4 and GO h4, indicating that the relative functional groups of GO nanosheets are similar and not affected by exfoliation method.

3.5. X-ray photoelectron spectra analysis

In order to study the composition of graphite, graphite oxide and GO nanosheets, XPS spectroscopy of all samples were measured and shown in Figure 8. Consistent with the FTIR results, the high-resolution C1s spectrum of graphite (Figure 8(a)) exhibits a sharp peak characteristic of single-phase (284.6 eV), and the C1s spectrum of graphite oxide (Figure 8(b)), u4 (Figure 8(c)) and h4 (Figure 8(d)) include three chemically shifted components, that correspond to non-oxygenated C (284.8 eV) [55], C in C–O bonds (287.1 eV) [55], and C in C=O bonds (288.9 eV). From the figure, it also can be seen that the intensity of the non-oxygenated C peak increases a little after 4-h high shear exfoliation, which may be due to the reduction of GO nanosheets during the high shear exfoliation procedure. The XPS survey analysis (Figure S5) also indicates the C/O atomic ratios of graphite flake (23.8) is much higher than that of graphite oxide (1.89), confirming the
successful oxidation of graphite oxide. The C/O atomic ratios of graphene u4 and graphene h4 are 1.90 and 1.93, respectively, indicating that the relative elements were similar and not affected by exfoliation method.

3.6. Raman analysis

Raman scattering is a useful tool to characterise graphite and GO. Figure 9 shows the Raman spectra of graphite flake, graphite oxide, GO u4 and GO h4. For graphite flake, the Raman spectrum contains the G-peak at 1578 cm$^{-1}$ and the 2D-peak at 2700 cm$^{-1}$. In sharp contrast, the Raman spectra of graphite oxide, GO u4 and GO h4 exhibit the characteristic spectrum of GO, featuring by the broad and merged D- and G-bands. In the figure, it also can be seen that there are no distinct differences between the spectrum of graphite oxide, GO u4 and GO h4, which was consistent with the results of FTIR and XPS.

3.7. Exfoliation mechanism

On the basis of the above observations and analyses, the exfoliation methods play a key role in controlling the size of GO nanosheets. We suggest that the synthesis of GO nanosheets with selected lateral size is essentially attributed to the different peeling forces
during exfoliation procedure, which provides useful information on the size-controllable preparation of GO nanosheets by different method. The mechanism of graphite oxide exfoliation is much more complex in different methods due to the different modes of peeling force, and the previous knowledge of graphene preparation can provide much more insight into the mechanism of GO nanosheets preparation in ultrasonic method and high shear method.

As graphite oxide was exfoliated by ultrasonic method, the graphite oxide will be exfoliated by the force induced by cavitation bubble collapse. When the cavitation-induced bubbles collapse with enormous energy, micro-jets and shock stress waves will act on the graphite oxide particles instantly [2]. Actually, there are two effects responsible for the exfoliation of graphite oxide. The first one, the compressive stress waves emitted by implosion of cavitation bubbles, can exert on the surface of the graphite oxide stack and propagate to the opposite side surface, a tensile stress wave will be reflected back to the graphite oxide body and the GO nanosheets will be peeled from the bulk graphite oxide (Figure 10(a)) [56,57]. The second one, the micro-jets induced by cavitation, could not only exfoliate the graphite oxide into GO, but also break the graphite oxide or GO

Figure 9. Raman spectra of graphite flakes, graphite oxide, GO u4 and GO h4.

Figure 10. The illustration of the effects of ultrasonication: (a) the compressive-stress-induced exfoliation, (b) micro-jets-induced exfoliation and scission.
nanosheets into small pieces (Figure 10(b)). If the micro-jets act at the edge of graphite oxide, the jet impact force may split the graphite oxide stack along their interlayer spacing as a wedge. If the micro-jets exert on the surface of graphite oxide, they will cause punching effect and leave holes or pits on the graphite oxide [57], which could break larger crystallites into smaller crystallites, result in the fragmentation of the graphite oxide or GO nanosheets. Typically, more micro-jets will act on GO surface than at GO edge because of the high aspect ratio of GO. In a word, the cavitation is favourable for GO exfoliation, but it is also a relatively harsh process which could result in damage to GO nanosheets.

When graphite oxide was exfoliated in high-speed shear mixer, the rotor revolves quickly, because of the narrow gap between the rotor and the stator, the combined action between rotor and stator generate shearing, impacting, pressing, turbulence and cavitation [2,4]. Therefore, the graphite oxide will be exfoliated and broken. Two main forces which can peel and tear the graphite oxide in shear mixer are shown in Figure 11. The first one is the shear force, which was induced by the mechanical rotating of the rotor directly, and the field of shear flow in the narrow slot between a couple of stator and rotor. The second one is the impact force, which was generated by the mechanical impact against the rotor directly, the impact to stator by the acceleration of the fluid, and the frequent and random collisions between graphite oxide particles [4,58,59]. Shear force is one of the effective mechanical forces that lead to material exfoliation, but impacting force is more effective in material breakage because it tends to accentuate the tendency for the residual cracks in the material to propagate. Typically, under the shear force, preferential cleavage happens mainly along the weak inter-plane bonds so that the thin GO nanosheets were able to be mechanically peeled off from the graphite oxide particles [60]. The shear force can cleave graphite oxide from their outer surface [61] (Figure 11(a)), while the impacting force peels off thin GO nanosheets from the edge of graphite oxide [62] (Figure 11(b)). Concurrently, the impacting force also can lead to the in-plane fracture of the GO [63] (Figure 11(b)), which will reduce the area of the GO nanosheets. In a word, high-speed shear mixer is the shear-dominated mixer, which can effectively break van der Waals forces between adjacent GO layers without breaking them, and lead to the fabrication of GO nanosheets with large area, similar to the scotch tape in micromechanical exfoliation process [5,63].

For the evidence of lateral exfoliation induced by shearing force, some GO nanosheets prepared by high shear method at high magnification are shown in Figure 12. Apparently, the existence of the edge warping in these GO nanosheets presents an edge peeling
configuration (Figure 12), indicating that lateral exfoliation really happens induced by shearing force (Figure 11(a)).

4. Conclusion

A simple and effective strategy to control the lateral size of GO nanosheets by selecting suitable method is presented. The high shear method was introduced to produce GO nanosheets, and the mild high shear treatment proposed in this paper is an efficient exfoliation means to produce single-layer GO nanosheets. The GO nanosheets (few micrometres) prepared by high shear method is about one order of magnitude larger than GO nanosheets (few hundred nanometres) obtained by ultrasonic method. The FTIR, XPS and Raman analysis revealed that there are no distinct differences between the GO u4 and GO h4, indicating that the composition and surface functional groups of GO cannot be changed by exfoliation method, only the lateral size of the GO could be adjusted by preparation method. The exfoliation mechanism of GO based on peeling force in ultrasonic method and high shear method was studied. The cavitation in the procedure of ultrasonic method is favourable for GO exfoliation, but it also could result in damage to GO nanosheets. The shearing force in the process of high shear method is effective for GO delamination with minimal fragmentation.

Disclosure statement

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