The freeze-thaw technique for exfoliation of graphite: A novel approach for bulk production of scroll-free graphene oxide sheets

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Received: 07 January 2016, Revised: 20 August 2016 and Accepted: 22 November 2016

DOI: 10.5185/amlett.2017.6407
www.vbripress.com/aml

Abstract

A freeze-thaw technique is put forth as a novel approach to exfoliating graphene oxide sheets (GO-sheets) in aqueous media. This method does not use shear force or high-temperature treatment at any stage. Avoiding these factors prevents scrolling and promotes defect-free synthesis of the graphitic planes. The research shows how the freeze-thaw technique successfully exfoliates graphitic planes without producing scrolls or defective graphene oxide planes. Further, when compared to conventional exfoliation methods, it was found that the freeze-thaw technique increased the surface area significantly. Copyright © 2017 VBRI Press.

Keywords: Freeze-thaw, graphene oxide, exfoliation, carbon materials, nanoparticles.

Introduction

Graphene and graphene oxide sheets (GO sheets) are 2D materials having outstanding physical and mechanical properties [**1**]. High-tech composite fabrication and synthesis of high surface area material are emerging as a major focus of many researchers [**2,3**]. Previously reported GO sheet bulk production methods involve the use of either mechanical or shear force such as ultrasonication [**4**] or a rapid increase in temperature [**5,6**]. GO sheets are scrolled upon exposure to shear forces such as ultrasonication or stirring [**7**,**8**], ball milling [**9**] or incur backbone plane defects upon thermal shock [**5,6**]. Scrolling and defects in the original planer shape reduce the total surface area and homogeneity of dispersed moiety, and they corrupt the properties of the GO sheets.

In the present research, a novel approach using freeze-thaw cycles was employed to separate graphitic planes in dispersed form. Modified Hummer's method [10] was applied to prepare graphite oxide dispersion. These dispersed graphite oxide particles were exfoliated by freeze-thaw technique. As described in the research, the freeze-thaw cycles use the expansion behavior of water upon freezing and low temperature. No shear force is employed. The results show that the freeze-thaw technique successfully avoids scrolling and the insertion of defects in the material's backbone honeycomb structure, as shown in **Fig. 1**.

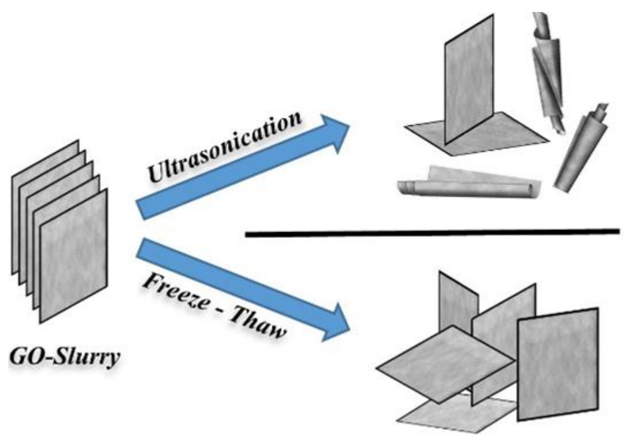

Fig. 1. Exfoliation of graphitic planes by freezing and thawing and ultrasonication.

Proposed theory of the freeze-thaw process

Water exhibits uncommon freezing behavior; it contracts up to 4ºC and slightly expands between 4ºC to 0ºC, and at 0ºC it significantly expands up to 9% upon freezing and is converted into ice [**11**]. This is because of its salient feature - hydrogen bonding between two molecules and the molecular rearrangement leads to expansion upon freezing [**12**]. Graphene oxide planes dispersed in water contain water molecules intercalated between two successive GO planes [**13**]. During freezing, expansion of this inter-planer water causes expansion of inter-planer space. Upon thawing, solidified expanded water melts, and water fills up the increased space by insertion of more water. Repeated cycles of freezing and thawing will separate the graphitic layers from each other considerably.

As an exfoliating agent, water is promising because of its increased viscosity in nano-confinement. Research shows that the viscosity of water dramatically increases when water is confined between two hydrophilic planes with inter-planer space ≤ 1 nm. [**14**]. During expansion, the increased viscosity of the water between the planes prevents the water from coming out of the open space in the planer stacks which helps to overcome the problem of exfoliation agent diffusion [**6**].

Experimental

Graphite flakes were oxidized by the Modified Hummer's Method [**10**]. Special care was taken to avoid scrolling during oxidation of the graphite flakes as a result of rapid stirring, ultrasonication, or vigorous fluid rotation. In each step, shaking with a horizontal bath shaker was substituted for stirring. The bath shaker frequency was kept below 80 cycles per minute to avoid tornado-type fluid rotation. Very slow glass rod stirring was applied whenever necessary. The final product was termed graphene oxide slurry (GO slurry). Thick, viscous GO slurry was diluted with water in 1:9 ratio.

Twenty-five mL of diluted GO slurry was pipetted out and slowly poured into a one-sided close-ended glass tube having a two cm inner diameter and a one mm thick glass wall. The glass tube was immersed in a chiller bath pre-chilled to -10ºC. To ensure freezing of the whole mass, the GO slurry mixture was chilled to -5ºC. The frozen mass was then removed from the chiller bath and kept in a water bath at 25ºC until the temperature of the GO slurry reached 15ºC. The freezing and thawing cycles were repeated 10 times. The mixture in the tube was found to be yellowish-brown, cluster-free, and uniformly distributed. It was directly analyzed without any additional treatment such as ultrasonication, stirring, or vigorous shaking. For comparison, graphitic planes were also exfoliated by ultrasonication for 20 min in a bath ultrasonicator, as described in the literature [**10**].

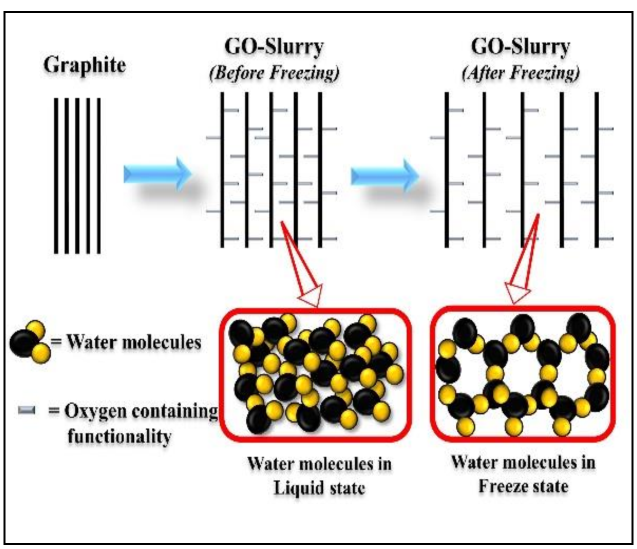

Fig. 2. Mechanism of exfoliation during freeze-thaw cycles.

Results and discussion

Oxidized graphite is a planer-stacked group of GO sheets having oxygen containing functionalities [**13**]. The d-spacing between planes was found to be 8.44 Å corresponding to 2θ=10.47º by the X-ray diffraction method. The total oxygen-containing functionality in oxidized graphite was found to be 59% by weight by Thermo Gravimetric Analysis (carried out from 110ºC to 400ºC in an inert atmosphere).

Before exfoliation, large particles of graphite oxide consisting of a group of planes were observed during TEM analysis, as shown in **Fig. 3(a)**. After freezing and thawing treatment, the planes separate out resulting in a single or a few graphitic plane layers, as shown in **Fig. 3(b)**. While they seem wrinkled, they are noticeably scroll free, **Fig. 3(c)** show that mild ultrasonication results in significant scroll formation. To ensure disruption of planer stacking, SAED patterns were observed. The SAED images in **Fig. 3(d)** indicate large crystallite structures. As shown in **Fig. 3(e),** the SAED image of graphite oxide exfoliated by freezing and thawing shows a planer structure with a single layer or only a few layers that probably are layers caused by folding and wrinkling. In contrast, the electron diffraction of ultrasonication seen in **Fig. 3(f)** shows polycrystalline behavior, probably because of scrolled planes attached with each scroll behaving as a separate crystal. Raman spectroscopic analysis was carried out to ensure exfoliation of planes.

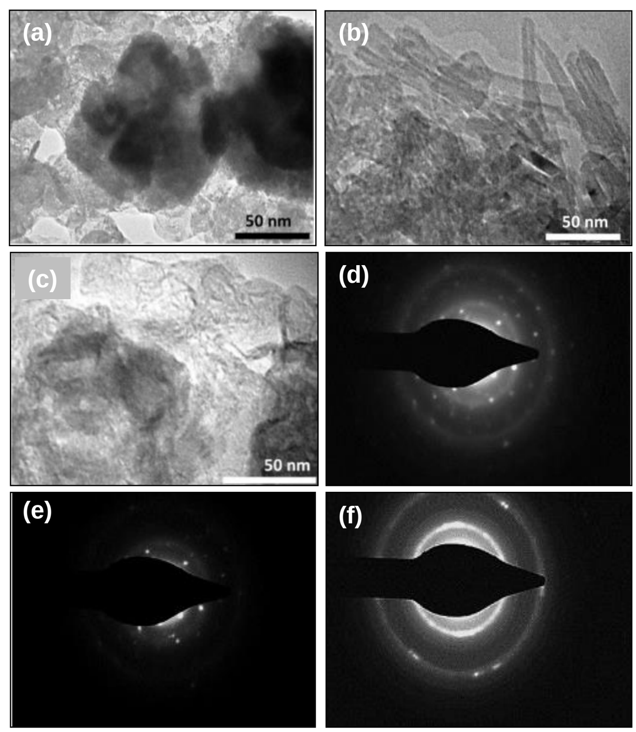

Fig. 3. TEM images of (a) GO-slurry, (b) exfoliated graphitic planes and scrolls by ultrasonication, (c) exfoliated graphitic planes by freezing and thawing, and SAED images of (d) GO slurry, (e) exfoliated graphitic planes and scrolls by ultrasonication, and (f) exfoliated graphitic planes by freezing and thawing.

Raman spectroscopy, as shown in **Fig. 4** gives a better illustration about scrolling behavior of both techniques. Raman spectrum of dispersed graphene sheets after freeze-thaw cycles shows strong D band at 1328 cm^{-1} and a G band at 1607 cm^{-1}. This G band is shifted from 1582 cm^{-1} as its actual position in pristine graphite due to extensive defects or functionality generated by oxidation. Because of the scroll formation in ultrasonication technique, the G band shifts at 1595 cm^{-1} which is towards its position in the pristine state, probably as a result of overlapping of the graphene planes due to scrolling.[**15**] The ratio of the intensity of the D band and G band that is I_D/I_G, was found to be ~ 1, indicating good exfoliation [**16,17**].

A very high surface area is a significant feature of graphene planes. Indeed, scrolling reduces the effective open surface area. The methylene blue dye probing method was used to determine the surface area of the functionalized graphene planes in an aqueous dispersion. As such, the graphite oxide particles showed a surface area of 730 m^2/g; this is consistent with previous reports [**18**]. The surface area of the GO sheets produced by the freeze-thaw technique ranged from 1900 to 1950 m^2/g in various batches. These results show significant separation of graphitic layers, while in the conventional method of ultrasonication the surface area was found to range from 1300 to 1400 m^2/g. No significant change was found upon increased exposure time to ultrasonic waves. The methylene blue probing study shows that dispersed graphitic sheets produced by freezing and thawing exhibit a greater surface area compared to sheets produced by conventional methods. Probably, the absence of scrolling in the presented method may provide more surface area for dye molecules to be absorbed. Indeed, using freezing-thawing cycles produces a greater surface area, but it is less than the theoretical surface area of graphene, which is 2630 m^2/g. Practically, this theoretical value cannot be achieved because of folding and wrinkling of planes.

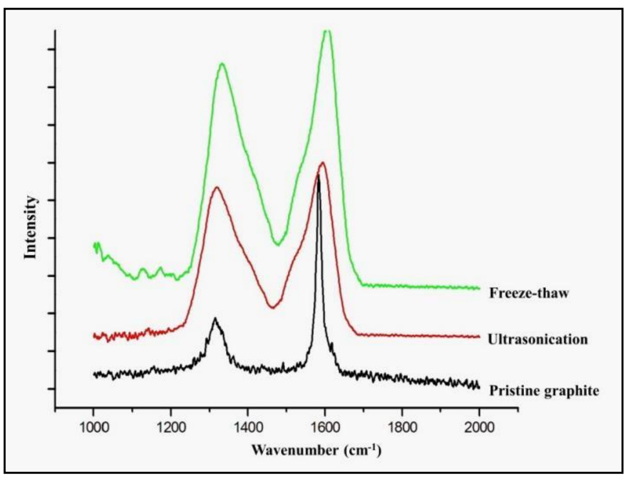

Fig. 4. Raman spectrum of exfoliated graphene oxide by Freeze-thaw technique in comparison with ultrasonication technique and pristine graphite.

Conclusion

The freeze-thaw technique presented herein is a novel approach for the scalable synthesis of graphene and graphene oxide sheets without scrolling of the graphitic planes. Major scrolling factors such as shear force were avoided. Results show good concordance with theory. TEM and SAED images show that freezing and thawing prevents scrolling of planes, which cannot be avoided using conventional methods. Raman spectra I_D/I_G ~ 1 signifies complete exfoliation. The methylene blue dye probing shows good improvement in the surface area. The freeze-thaw technique can emerge as a potential method to synthesize scrolling-free and planer defect-free graphene or GO sheets.

Author's contributions

Conceived the plan: VM, LM, SM; Performed the experiments: VM, HG; Data analysis: VM, LM, SM; Wrote the paper: VM. Authors have no competing financial interests.

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