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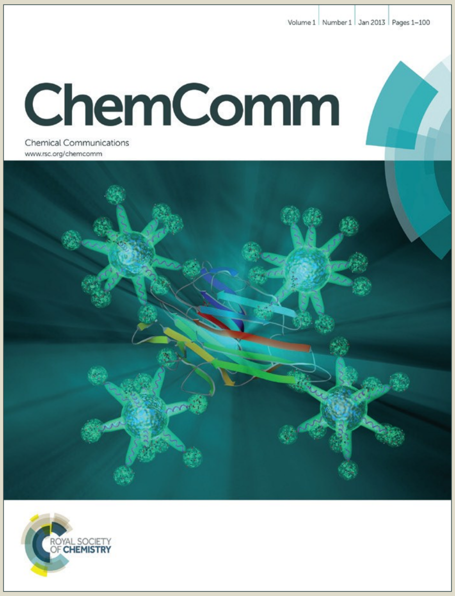

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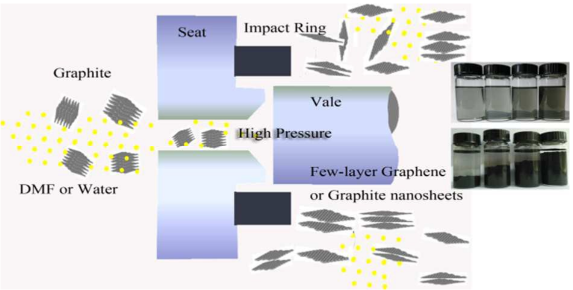

Few-layer graphene and graphite nanosheets were prepared by high pressure homogenization

Graphical Abstract

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Facile fabrication of few-layer graphene and graphite nanosheets by high pressure homogenization

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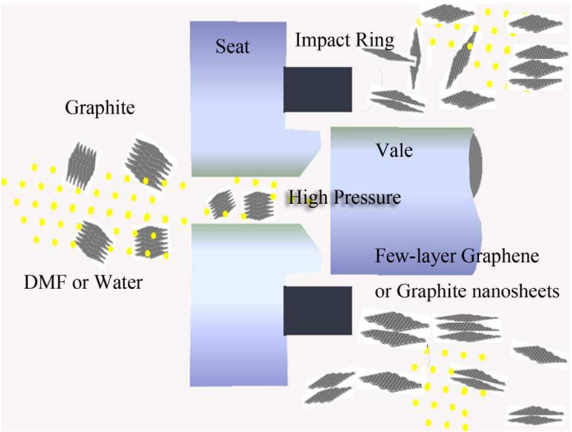
We demonstrated a facile and efficient approach for the fabrication of few-layer graphene in DMF and graphite nanosheets in water with the assistance of high pressure homogenization. This work provides a physical perspective for understanding the exfoliation of other layered materials in liquid phase exfoliation.

Graphene is expected to the most promising and revolutionary material in nanotechnology due to its superior electronic character, exceptional thermal conductivity, remarkable mechanical properties and giant specific surface area.[1-4] Exfoliation of graphite into few-layer graphene requires weakening the van der Waals-like forces between graphite layers. Micromechanical cleavage was firstly used to mechanically split graphite into graphene. [5] Although this method can obtain the high quality graphene, but it has apparent drawbacks in terms of yield and expanded production. Chemical vapor deposition (CVD) has been demonstrated for the synthesis of low-defect, single atomic sheet graphene, [6] but the high-energy consumption and time-consuming make it difficult to scale up. Chemical reduction of graphene oxide disrupts the electronic structure of graphene. [7]

Consequently, new alternatives for producing graphene have been proposed. For different approaches, the liquid phase exfoliation (LPE) presents several advantages due to its simplicity and potential scalability. [8] In addition, the stable suspensions of graphene can be employed to produce graphene-based composites or films, such as thin-film transistors and conductive transparent electrodes. [9-11] LPE can be done mainly with the assistance of ultrasonic and ball-milling. [12-15] Coleman used high-shear mixing method to exfoliate two-dimensional layered materials.[16] Texter and Samori had comprehensively reviewed the graphene dispersion for the previous work.[17, 18] Ager reported graphene dispersions in water at up to 5% by weight (166-fold compared with previous work) using triblock copolymers and copolymeric nanolatexes.[19] Researchers had used ionic liquid [20, 21] to exfoliate graphite to improve the concentration currently. Adding the surfactants or stabilizers such as carbon quantum dots (CQDs) are used to enhance the concentration and yield. [22,23] Texter has reported a kinetic model which appeared to quantitatively fit graphene exfoliation data and illuminated mechanistic aspects of exfoliation.[24] It has been found that the excessive ultrasonic and ball-milling and the high temperature could destroy the graphene sheets. Thus, it is advisable to design new methods to prepare large quantities of graphene.



Scheme1 Schematic illustration for the preparation of graphene in DMF and graphite nanosheets in water through high pressure homogenization

High pressure homogenization (HPH) is one of the most encouraging methods in mechano-chemical. It's widely used in food production and dairy industries in which the homogenization plays a vital role in improving the product quality.[25-27] In addition, researchers used it for the preparation of a nanosuspension of a solid pharmaceutical active principle.[28] The homogenization process occurs in a homogenization valve comprising an impact ring and a valve seat which is the main component of a homogenizer device. During this process, the pressurized fluid is allowed to flow through a narrow gap valve which is subjected to three

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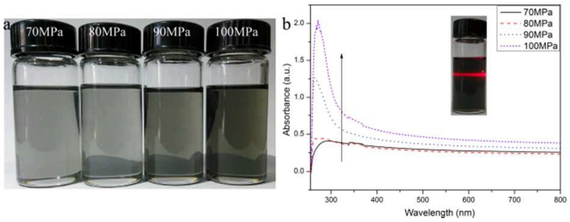

Fig. 1 (a) Photographs of dispersion of graphene under different pressure. (b) UV-Vis spectra of the graphene under different pressure. Inset: The Tyndall effect when passing a 635 nm red laser light through the exfoliated graphene in DMF.

simultaneous mechanisms, cavitation effect, impact effect and high shear stress effect. [29, 30] The combination of these three effects helps to emulsify, disperse, and mix the products. Because of this facile method, HPH has an enormous advantage over the others, for example, simplicity of the process, cost saving, ease of large scale production and reducing product contamination. According to the above facts, we have reasons to believe that HPH can provide enough energy to exfoliate graphite.

In this report, we used high pressure homogenizer to exfoliate layered graphite in the pure solvent without adding any surfactants under 100MPa for 10min at 25 ⍰ to give stable dispersions of graphene in DMF. By the same experiment condition, we could prepare the graphite nanosheets in pure water after the high pressure homogenization (Scheme 1). On one hand, the exfoliated graphite produced a suspension of few-layer graphene flakes in DMF that were stable up to several weeks. The graphene dispersion exhibited obvious Tyndall phenomenon and showed characteristic absorption in UV-Vis spectrum. Using techniques from the Raman, transmission electron microscope and atomic force microscopy, we revealed that the graphene dispersion had only few layers. On the other hand, we likewise found that thick layer of graphite can largely by exfoliated to ultra-thin graphite nanosheets after homogenizing the graphite bulk in the pure water. The detailed experimental method could be found in Electronic Supplementary Information (ESI†). In addition to promoting the fundamental understanding of liquid phase exfoliation, this versatile and effective method would also be ideal for large-scale production of graphene dispersions, graphite nanosheets and the nanoparticles for other layered materials.

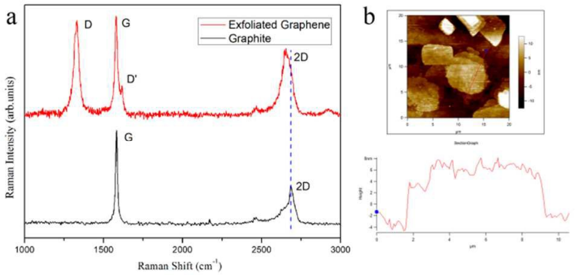

Fig. 2 (a) Raman spectra at 633nm for graphite bulk and exfoliated graphene. (b) AFM image of the graphene

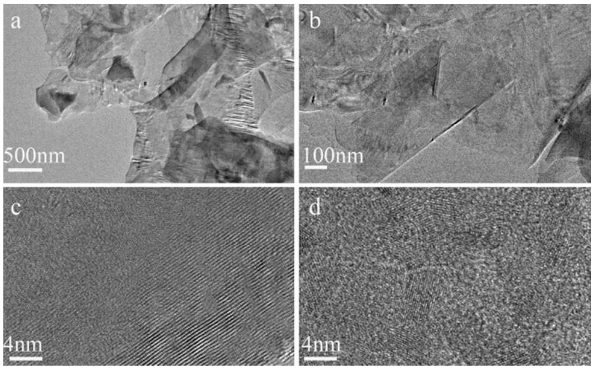

Fig. 3 (a, b) TEM images of exfoliated graphene. (c, d) HR-TEM images of exfoliated graphene

All the resulting supernatants were transparent and grayish in color as shown in Fig. 1a. The dispersions of exfoliated graphene were characterized by UV-Vis absorption spectroscopy (Fig. 1b). A prominent peak was found for all samples at around 270 nm corresponding to the π to π^* transition of graphene. [31] Different homogeneous pressure show different absorbance and the highest pressure of 100Mpa corresponded to the largest absorbance. As shown in Fig. 1b inset, when the red laser light (632 nm) passed through the DMF dispersion of exfoliated graphene, it exhibited the obvious Tyndall phenomenon whereby the light scatters along a straight path. [32] It's a representative phenomenon that was widely applied to probe the colloidal dispersion and certify the presence of nanometric structure. The absorption coefficient of graphene dispersion followed the Lambert–Beer law (Fig. S1, ESI†) with an average absorption coefficient of α_{660nm}=3463 mL/(mg.m) which is a little difference from other reference.[17-19]

Further proof of the exfoliated graphene in DMF was achieved by Raman spectroscopy with He–Ne laser (633 nm) as the irradiation light source. It was also employed to characterize the structural differences between graphite and graphene. The spectroscopy showed that the graphene produced by the HPH method consisted of few layers. Fig. 2a compared the Raman spectra of the exfoliated DMF dispersion of graphene and bulk graphite. For pristine graphite, a G band (1580 cm^{-1}), a 2D band (2680 cm^{-1}) and no D band can be observed. The G band is the result of first-order scattering of an E_{2g} mode of graphite and is related to vibration of sp^2-bonded carbon atoms. However, D and D` peaks have significant intensities in the graphene dispersion besides the G and 2D peaks. D` band appearing as a shoulder around 1615cm^{-1} on the G band is the feature of few-layer and defect of graphene, but not found in graphite. The D band around 1331 cm^{-1} is associated with disorder-induced scattering resulting from imperfections or loss of hexagonal symmetry of disordered graphite. It was found that the 2D peak shifts to a low wave number. Researchers reported that the peak location was strongly affected by the number of layers. The phenomenon was highly consistent with their results. What's more, the $I_{2D/G}$ ratio equaling about 0.7 could also be the characteristic feature of few-layer graphene as previously reported. [33-35] The exfoliation of graphene was confirmed by tapping mode atomic force microscopy (AFM) to measure the thickness of the synthesized graphene sheets. The sample was

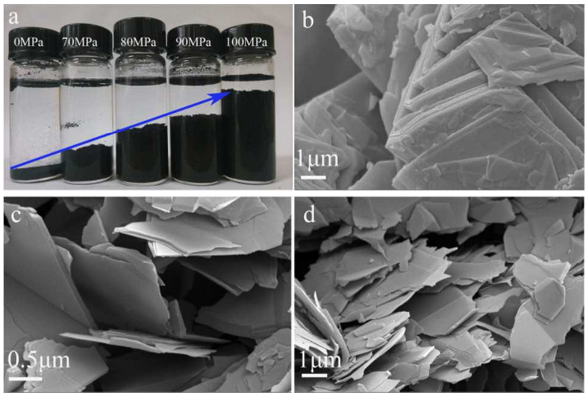

Fig. 4 (a) Photographs of graphite nanosheets under different pressure. (b) SEM images of graphite. (c, d) FE-SEM images of exfoliated graphite nanosheets

prepared by drop casting the graphene dispersion onto fresh cleaved mica surface. The AFM images (Fig. 2b) showed plate-like structures and the height image indicated that the thickness of the graphene sheets was less than10nm corresponding to few-layers, which was in agreement with the height observed elsewhere for few-layer graphene sheets. [36]

The pristine graphite powder had micro-scale graphite with thick layers. The sizes and thickness of graphite particles were apparently reduced and the graphene sheets were formed (Fig. S2, ESI†) after homogenization. Fig. 3a and 3b showed the representative TEM images of the graphene sheets observed by drop casting from these dispersions onto a micro-grid copper covered with carbon film. The TEM images revealed that the graphene sheets were transparent under the electron beam, suggesting a very small thickness of the graphene sheets.[4] It was possible to observe the large flakes of graphene form wrinkles and some flakes fold over or stack together gave a disordered multilayer structure. Furthermore, as shown in the high-resolution transmission electron microscopy (HRTEM) image in Fig. 3c and 3d, we can identify the few-layer graphene on the folded edges owing to the fact that the folded graphene sheets were locally parallel to the electron beam.[4] Overall, by comprehensive consideration of the results of UV-Vis, Raman spectra, AFM, SEM and TEM, we demonstrated that few-layered graphene had been successfully achieved. It is a pity that the graphene concentration was about 0.084mg/mL and the resulting yield was only 2.68% approximately that is the limitations of our study. Now, we are trying some methods to enhance the yield.

The volume changes of graphite after homogenization under 70-100MPa in the pure water may be caused by the reason that the structure of layered graphite was delaminated apparently. During this homogenizing, the volume of the sample was expanded more than ten times (Fig. 4a). In addition, under the condition of the same quality, the higher pressure of the homogenization could get the greater volume of the exfoliated graphite nanosheets which is attributed to the fact that the higher pressure can cause more severe exfoliated energy. Fig. 4b was the SEM images of graphite bulk and Fig 4c and 4d were the exfoliated graphite nanosheets respectively. It was clear that the layer's structure was destroyed seriously and the layer numbers of the graphite nanosheets decreased visibly. The graphite bulk was vividly delaminated to the ultrathin graphite nanosheets. The crystal structure was not changed after homogenization according to the XRD research (Fig. S3, ESI†) and the FT-IR spectra (Fig. S4, ESI†) showed no peaks around 1700cm^{-1} that indicated the graphite nanosheets were not oxidized during the procedure.

In summary, we have reported a facile and practical exfoliation of graphite by a new method. The HPH can break of the van der Waals interactions allowing graphite bulk to be exfoliated easily. By HPH of graphite with DMF or water, few-layered graphene or graphite nanosheets can be prepared. As a common technique, the HPH method offers an opportunity for high yield production of few-layered graphene sheets and graphite nanosheets on a large scale. This technique for the preparation of exfoliated graphene and graphite nanosheets might be potentially extended into energy storage, catalysis, biomedical, electronics applications, ink-jet-printed graphene film and nanohybrid.

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