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Large-quantity and continuous preparation of two-dimensional nanosheets

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With the increasing demand in two-dimensional (2D) nanosheets, such as graphene, hexagonal boron nitride (h-BN), and MoS₂ and WS₂ nanosheets, finding a simple and feasible method to obtain nanosheets is crucial. Here we show that a high-efficiency exfoliation method to obtain abundant and superior graphene, h-BN, MoS₂, and WS₂ nanosheets in aqueous solution. The obtained 2D nanosheets are very thin, especially MoS₂ and WS₂ nanosheets, and below 1 nm.

Two-dimensional (2D) nanosheets, such as graphene, hexagonal boron nitride (h-BN) nanosheets, and MoS₂ and WS₂ nanosheets, possess unique and outstanding properties, including optical¹⁻⁴, magnetic^{5, 6}, electrical⁷⁻⁹, and electrochemical properties¹⁰⁻¹². In addition, graphene and h-BN nanosheets also have high temperature stability¹³, good mechanical strength¹⁴, good catalytic ability¹⁵, and so on. Moreover, they can “graft” many functional inorganic and organic groups and can be embedded in glass, ceramics, or polymers to produce materials with superior performance¹⁶⁻²⁰. Therefore, studying these 2D nanosheets is gradually becoming the focus in the material fields. This causes the demand of 2D nanosheets is becoming more and more. And finding a simple and feasible method to obtain nanosheets is crucial.

Thereinto, numerous studies have been conducted on the exfoliation of layered materials and functionalization of nanosheets in recent years.²¹⁻²⁸ For example, previously, we proposed “molten hydroxides”²¹ and “chemical”²⁹ exfoliation methods for peeling h-BN, and for fluorinating boron nitride nanosheets.⁶ Lopez-Sanchez et al.⁴ designed an ultrasensitive photodetector based on monolayer MoS₂, and Lukowski et al.¹⁵ to enhanced hydrogen evolution catalysis by using MoS₂ nanosheets. Zhao et al.²⁰ proved that emissions from WS₂ monolayers are 100 to 1000 times stronger than those from bulk

materials. Further, the works about functionalization of graphene are much beyond measure.^{1, 2} In these two dimensional nanosheets, transition metal sulfides (TMDs) nanosheets, h-BN and graphene are the most intensively studying materials. Molybdenum disulphide (MoS₂) is a typical semiconductor, and monolayer MoS₂ can be used as catalyst in hydrogen evolution reaction.¹⁵ Further, it can also be used as a semiconducting channel in phototransistors because of its direct bandgap⁴. Graphene, arranged in a honeycomb pattern, is the thinnest, strongest, and stiffest material, and it is an excellent conductor of both heat and electricity³⁰. H-BN (white graphite) nanosheets (h-BNNSs) are also extensively used currently in versatile technological applications because of their exceptionally mechanical³¹, thermal^{13, 32}, and electronic properties.³³ Tungsten disulfide (WS₂) nanosheets possess many characteristics similar to those of MoS₂ nanosheets, it also has great research value in future. Furthermore, the combination of thin layers of WS₂ with other two-dimensional (2D) nanosheets produces a large category of 2D heterostructures. These studies show that the 2D nanosheets prepared from layered materials exhibit unique properties, and have broad application prospects. However, stripping these 2D layers is very difficult because of the van der Waals interaction force. And by now there still has been no one way that can be utilized to prepare all kinds of nanosheets. How to peel of layered materials to prepare two-dimensional (2D) nanosheets is currently a hot research topic.^{6, 21-24}

Here we show that a high-efficiency exfoliation method to obtain abundant and superior graphene, h-BN, MoS₂, and WS₂ nanosheets in aqueous solution. Through various tests, prove that these 2D nanosheets have been successfully prepared via this method, and the production rate is very high. Compared with the other methods^{6, 21-24}, this method possesses many advantages including fast, efficient, continuous, and thorough. Besides, this study also theoretically demonstrates why the proposed method is efficient for fabrication of nanosheets. This theory signifies that the method can be applied to exfoliate a range of other layered materials.

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Electronic Supplementary Information (ESI) available: SEM images of large quantities of exfoliation of layered nanosheets; SEM images of raw materials; Experiment instrument; Specific preparation time of exfoliation of 2D materials; Solvents influence at the same exfoliation time. See DOI: 10.1039/x0xx00000x

In this study, in order to peel off 2D layered materials more conveniently and directly, ultrasonic method was firstly taken into consideration. However, stripping these 2D layers using ordinary ultrasound is very difficult because of the “Magdeburger Halbkugeln” phenomenon: In ordinary ultrasound, when 2D layered materials are dispersed in aqueous solution after a certain period, most of the 2D material will be in a state level with the ultrasound, as shown in Figure 1a. The force analysis of the monolayer of 2D layered materials in ordinary ultrasound is shown in Figure 1b. Besides the upward force of ultrasonic (F), monolayer still has very strong outside pressure (P_1). The strong outside pressure is caused by the water molecules sealing the pores between the layers, thereby forming a vacuum condition (as shown in Figure 1a). Just like Magdeburger Halbkugeln experiments, it need large amount of power to separate the layered structures. But with ordinary ultrasound method no strong enough energy is supplied to separate the layered structures, as shown in Figure 1c. Moreover, because the needed power is so strong that even the power won't separate the layered structure, but break layered structure to form some pieces.

To solve this problem, we searched for all kinds of ultrasound machines and ultimately design an ultrasonic instrument with magnetic stirring. The experimental instrument is displayed in Figure 1g. In the ultrasonic process, 2D layered materials undergo tilted rotation with magnetic stirring. The force analysis of the two-layer and monolayer of 2D layered materials in the designed ultrasound is shown in Figures 1d and 1e. Monolayer also has the upward ultrasonic force (F) and very strong outside pressure (P_2). The upward ultrasonic force (F) can be divided into the upward force perpendicular to the surface of the layer strength (F_1) and along the surface force (F_2). The F_1 is very difficult to divide the lamella because of strong outside pressure (P_2). However, the along the surface force (F_2) is very easy to make layer sliding separate (Figure 1f), because water molecules act as lubrication, thereby reducing the friction (f) between the layers (Figure 1e). Therefore, large quantities of nanosheets can be obtained using this the method (Figure 1h). But other solvent exfoliation effect of large molecules is no better than that of water in Figure S8, because it is difficult for them to enter the molecular layer.

Restricted by the size of the instrument (Figure 1k), 0.1 to 0.2 g of raw materials can be completely separated within 24 h of ultrasonic processing (40 KHz). Excessive amounts of raw materials (more than 0.2 g) can also be stripped fully by adding the aqueous solution. The as-obtained samples are dispersed in aqueous solution (Figure 1j). Figure S1 shows that large quantities of uniform nanosheets were obtained using this method. Comparing the morphology in Figure S1 with the raw materials (Figure S2), we can clearly see that several 2D materials were stripped and became nanosheets. Thus, we conclude that the proposed method is very fast, efficient, and continuous, and can peel off 2D materials fully. Their production rate is about 96% (graphene nanosheets), 95.5% (MoS_2 nanosheets), 95% (WS_2 nanosheets) and 97% (h-BN nanosheets), respectively (The production yields of these 2D nanosheets are as high as 95% or more. Losses of nanosheets

are only from a small amount of broken and filtrated-losses). More specific morphology was characterized as below. The more specific preparation time of exfoliation of 2D materials is put in the supporting materials (Figure S4-S7).

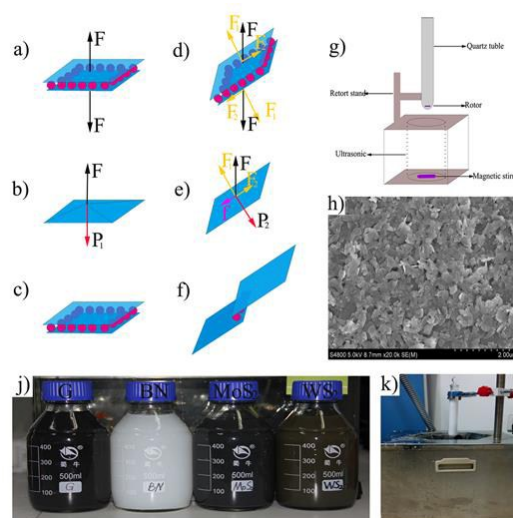


Figure 1. (a and b) Force analysis of 2D layered materials in ordinary ultrasound. (c) Results of ordinary ultrasound. (d and e) Force analysis of 2D layered materials in designed ultrasound. (f) Results of designed ultrasound. (g) Designed experiment instrument drawing. (h) Large quantities of exfoliation of the layered MoS_2 (SEM). (j) The as-obtained samples dispersed in 500ml aqueous solution. (k) Experimental instrument.

Scanning electron microscopy (SEM) was used to study the morphologies of the as-obtained samples dispersed in the aqueous solution (Figure 1j). As shown in Figure 2, the 2D materials were peeled off using the proposed method (The morphologies of the raw materials are shown in Figure S2). In Figure 2a, numerous folds of graphene nanosheets were observed in the image. Compared with the raw graphite powders (Figure S2a), graphite has been peeled off.

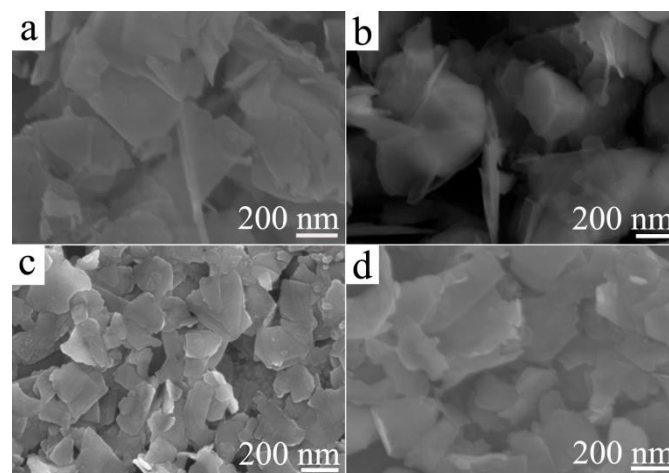


Figure 2. SEM images of the exfoliation of nanosheets: (a) Graphene; (b) h-BN nanosheets; (c) MoS_2 nanosheets; (d) WS_2 nanosheets.

Figure 2b shows that the corrugated surface of the h-BN nanosheets is more evident than that of graphene, and the size of h-BNNSs is approximately 2 μm to 3 μm . The background is distinctly visible through the folds and the completely transparent main body. The MoS₂ nanosheets were also effectively obtained, with sizes ranging from 300 nm to 600 nm, as shown in Figure 2c. Moreover, the morphology is different from that of the raw materials (Figure S2c). Large and thin WS₂ nanosheets are shown in Figure 2d, which are approximately 500 nm to 1 μm in size. These SEM images intuitively show that the method is very effective for exfoliating 2D layered materials.

Atomic force microscopy (AFM) was used to study the thicknesses and fine structures of the nanosheets, which were unobservable in SEM characterization. Figure 3a shows a single flat graphene nanosheet with a thickness of approximately 1.8 nm (the corresponding height profile is also shown in Figure 3e). Similarly, the thicknesses of the h-BN, MoS₂, and WS₂ nanosheets are approximately 2.8, 0.6, and 0.8 nm, respectively (Figures 3f–h). The bright spots of Figure 3b indicate the corrugated layers of small h-BN nanosheets. The edge of the h-BN surface exhibited gaps, and the structure is conducive for the functionalization of h-BNNSs. As shown in Figures 3c and 3d, a large number of MoS₂ and WS₂ nanosheets with very thin layers (below 1 nm) were obtained through the proposed exfoliation method. Thin MoS₂ or WS₂ nanosheets are often used in the piezoelectric^{9, 34} and optical³ fields. Moreover, the sizes of nanosheets were similar to those observed in the SEM images (Figure 2). The AFM images also illustrates that the proposed method is effective for peeling off 2D layered materials.

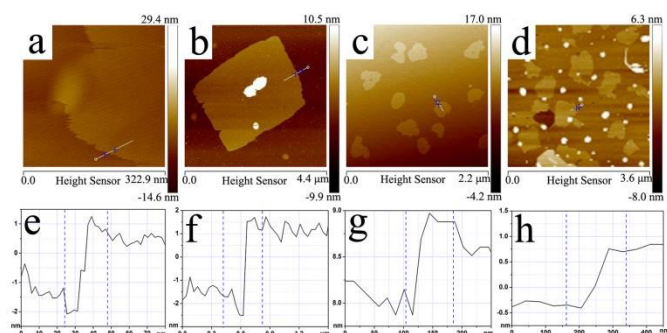


Figure 3. AFM images of exfoliation of nanosheets: (a) Graphene; (b) h-BN nanosheets; (c) MoS₂ nanosheets; (d) WS₂ nanosheets. The corresponding height profile: (e) Graphene; (f) h-BN nanosheets; (g) MoS₂ nanosheets; (h) WS₂ nanosheets.

Raman spectroscopy was used to characterize bulk powders and nanosheets with 532 nm. As shown in Figure 4a, The Raman spectra of graphite and graphene includes the G peak located at $\sim 1580\text{ cm}^{-1}$ and 2D peak at $\sim 2700\text{ cm}^{-1}$, caused by the in-plane optical vibration and second-order zone boundary phonons, respectively. According to previous reports, 2D peak high or low could be used to distinguish the quality of graphene. And blue shift of G and 2D peaks can show

graphene's layered structure.³⁵ Based on Raman spectra of graphite and graphene, high quality graphene nanosheets can be obtained by this method. Similarly, Raman spectra of h-BN nanosheets are

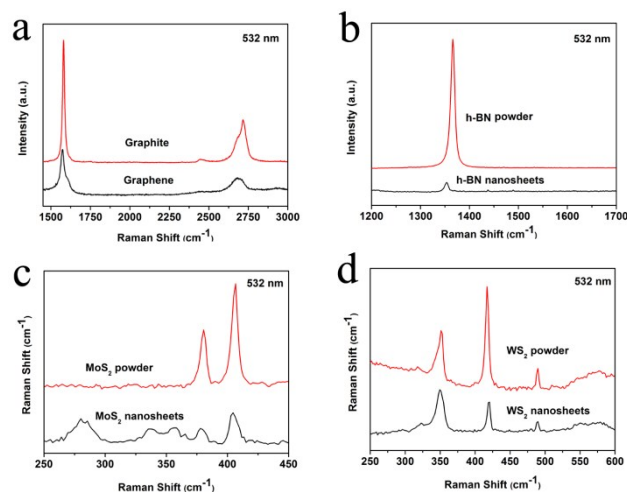


Figure 4. Comparison of Raman spectra at 532 nm: (a) bulk graphite and graphene; (b) h-BN powder and nanosheets; (c) MoS₂ powder and nanosheets; (d) WS₂ powder and nanosheets.

found peaks shift to low wavenumbers, and this is similar to previous reports.^{6, 21} Exciting find is shown in Figure 4c, obtained MoS₂ nanosheets is belonged to 1T@2H-MoS₂ nanosheets. This kind of mixed phase can show excellent ferromagnetism and electrochemical performance.^{36, 37} Figure 4d show that the softening of the A_{1g} (Γ , 417 cm^{-1}) mode of WS₂ nanosheets is lower than that of WS₂ powders resulted from weaker interlayer contributions to the phonon restoring forces, this is similar to previous reports.³⁸ In a word, Raman results exhibit high quality 2D nanosheets were prepared by this simple and effective method.

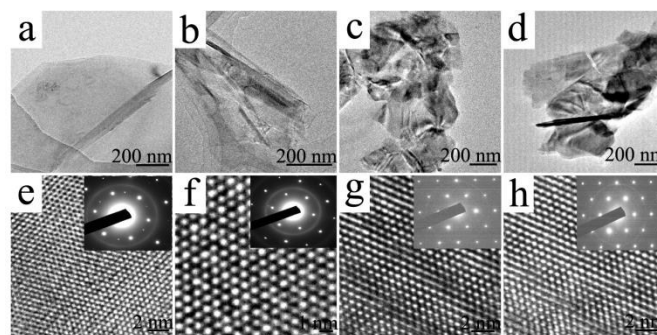


Figure 5. TEM and HRTEM images of exfoliated nanosheets: (a, e) Graphene; (b, f) h-BN nanosheets; (c, g) MoS₂ nanosheets; (d, h) WS₂ nanosheets. The inset shows the electron diffraction pattern implying a single undistorted lattice.

To better understand the exfoliation effect, transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were used to characterize the morphology and structure of the nanosheets.^{39, 40} In Figure 5a, the TEM image of the graphene nanosheets is similar to those observed in the SEM and

AFM images. However, the TEM images of h-BN, MoS₂, and WS₂ nanosheets (Figures 5b–d) exhibited a small change compared with those observed in the SEM and AFM images. This finding is attributed to the fact that the samples are very thin (especially MoS₂ and WS₂ nanosheets); hence, when high energy beam irradiates on the nanosheets surface, nanosheets will form crimp and gather, as shown in Figures 5b–d. In Figures 5e–f, hexagonal lattice and lattice fringes can be clearly observed. The electron diffraction patterns (shown in the inset) show the six-fold symmetric structural characteristic of the 2D layered materials, which indicates that the well-crystallized structure of the obtained nanosheets are not destroyed by the proposed exfoliation method. These results signify that the quality of obtained nanosheets is very high and fine. In summary, as a new preparation method, this proposed skillfully modified ultrasound exfoliation can be used to prepare abundant and fine quality 2D nanosheets in aqueous solution.

Conclusions

In this study, abundant and fine quality 2D nanosheets of graphene, h-BN, MoS₂, and WS₂ were successfully prepared in aqueous solution by the ingenious method. Through mechanism analysis and morphology characterization, prove that this method is very fast, efficient, continuous. The obtained 2D nanosheets exhibit high quality and very thin specialty. The mechanics analysis also proves that other layered materials can also be directly peeled off using this practical exfoliation method. Moreover, the simple and feasible method can solve the lack of 2D nanosheets problem in basic science research.

Experimental Section

Preparation Method: Graphite powders, h-BN and MoS₂ were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai). WS₂ was purchased from Alfa Aesar. All reagents were used as received.

In a typical experiment, 0.1 to 0.2 g of raw materials was dissolved in 100 mL of distilled water. The samples were ultrasonic processed 24 hours under magnetic stirring at 30 °C. Then the solutions were sampled and centrifuged (1,000 rpm for 30 min) to remove any aggregated sheets of materials. Finally, the upper solutions were stored in a small 500mL bottle for characterization.

Material Characterization: SEM was performed with a Hitachi S-4800 SEM. HRTEM images were obtained with a Philips Tecnai 20U-Twin high-resolution TEM at an acceleration voltage of 200 kV. AFM 3100 Digital Instruments Dimension was used to investigate surface morphology.

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performance of materials. All the authors discussed the results and commented on the manuscript.

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