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Communication

**Production of few-layer MoS₂ nanosheets through
exfoliation of liquid N₂–quenched bulk MoS₂**

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We demonstrate an efficient method for the production of few-layer MoS₂ nanosheets through exfoliation of bulk MoS₂ compounds that were subject to quenching in liquid N₂ and subsequent ultrasonication. This solution-based method, which involves a “quenching cracks” phenomenon, was performed open to the atmosphere. Subsequent ultrasonication of the exfoliated MoS₂ in solution provided us with MoS₂ nanosheets comprising two to four layers.

MoS₂ nanosheets comprising S–Mo–S layers separated by relatively large van der Waals gaps have attracted considerable attention in the field of two-dimensional materials because of their peculiar structural characteristics and potential applications.^[1–10] Several methods have been developed recently for the preparation of MoS₂ nanosheets, including Scotch tape–based mechanical exfoliation,^[11–13] liquid-based exfoliation,^[14–18] and chemical vapor deposition growth.^[19–27] Among them, controllable solution-based exfoliation through Li⁺ ion intercalation and subsequent ultrasonication and exfoliation of the Li⁺-intercalated compounds in water or EtOH is one of the most common approaches for the production of MoS₂ nanosheets.^[2, 28] This method is extremely sensitive to environmental conditions and requires special care during handling, thereby limiting the scalability of the product. Thus, the challenge remains to develop a facile and efficient approach for the production of high-quality MoS₂ nanosheets in large yield. Herein, we describe a highly efficient, green, and facile approach—involving a quenching process and subsequent ultrasonication—for the synthesis of few-layer MoS₂ nanosheets from MoS₂ powder.

Quenching is one of the most fundamental yet complex processes in the heat treatment of metals; it involves the surface of a sample being suddenly cooled in a solution medium, such as oil or liquid N₂.^[29] The instant cooling on the surface induces quenching cracks because of different quenching stresses between the surface and the interior of the sample. In MoS₂, each layer of Mo atoms is sandwiched between two layers of hexagonally close-packed S atoms, with the adjacent layers, bound by weak van der Waals interactions, readily exfoliating into individual MoS₂ nanosheets upon quenching with liquid N₂ and ultrasonication; as a result, we suspected that the quenching cracks phenomenon might be involved in breaking van der Waals force bonded MoS₂ layers in the bulk state to produce MoS₂ nanosheets. Recently, high-quality single and few-layer graphene sheets have been synthesized through rapid quenching of hot bulk highly ordered pyrolytic graphite (HOPG) and expandable graphite (EG) in aqueous solutions of 1.0 wt % NH₄HCO₃ and hydrazine hydrate, respectively.^[30, 31] These processes involve rapid expansion of HOPG/EG at high temperature to weaken van der Waals forces and then rapid quenching of the heated samples in appropriate quenching media to form graphenes. To the best of our knowledge, the quenching approach has not been adopted previously for the production of MoS₂ nanosheets.

In the present study, we stirred a mixture of MoS₂ and KOH at 80 °C for 24 h and then quenched the sample in a matter of a few seconds to low temperature in liquid N₂. The stresses generated from the sudden, large temperature gradient between the surface and the interior of the sample during this quenching process disrupted the van der Waals forces binding these MoS₂ layers and resulted in MoS₂ nanosheets. The resulting liquid N₂–quenched MoS₂ served as a precursor for the production of MoS₂

nanosheets through solution-based exfoliation [see detailed experimental conditions in the Supporting Information (SI)]. Unlike previously employed quenching-based methods,^[30, 31] this approach does not require either a rapid heating process or a special quenching medium. Thus, the major advantages when using this quenching approach for the production of MoS₂ nanosheets from MoS₂ powder are (i) MoS₂ nanosheets can be derived from commercially available MoS₂ powder without the need for Li⁺ intercalation prior to ultrasonication (ii) environmental friendliness, and (iii) facile operation open to the atmosphere.

Figure 1 compares the Raman spectra of the exfoliated MoS₂ with that of bulk MoS₂. The spectrum of the bulk MoS₂ displays bands at 376 and 403.2 cm⁻¹ representing the A_{1g} and E_{2g} modes, respectively, while that of the exfoliated MoS₂ features these bands at 383.8 and 405.2 cm⁻¹, respectively; the frequency difference for of the latter (21.4 cm⁻¹) is smaller than that for the former (27.2 cm⁻¹), consistent with the Raman signature of MoS₂ nanosheets comprising two to four layers.^[11, 23]

Figure 2 presents an AFM image of a sample prepared by spin-coating a diluted solution (0.05 wt%) of exfoliated MoS₂ onto the surfaces of a Si/SiO₂ substrate and then drying in air. The lateral dimension of this exfoliated nanosheet was approximately 3.0 μm; its thickness was approximately 1.5 nm, corresponding to approximately two layers, based on the thickness of a single MoS₂ layer being 0.7 nm—again, consistent with our production of few-layer MoS₂ nanosheets. AFM images of other individual nanosheets (see SI) revealed that the thickness varied from 1.5 to 3.5 nm and the lateral dimensions from 0.5 to 3.5 μm. For further examination of an individual sheet-like nanostructure, Figure 3 presents a TEM image of an exfoliated MoS₂ product. It indicates that the sheets were flat, folded, and slightly transparent to the electron beam. A selected-area electron diffraction pattern (SAED) of the flat area of the nanosheet (inset to Fig. 3) reveals the typical six-fold symmetry of MoS₂, indicating that the MoS₂ sheets obtained using this method had good crystallinity; furthermore, point energy dispersive X-ray spectroscopy (EDS) from the same area revealed the presence of Mo and S atoms in a 1:2 ratio, further confirming the formation of MoS₂ nanosheets. We consider a possible two-step mechanism for the exfoliation of the liquid N₂-quenched MoS₂ powder. The first step of the quenching process involved gradual heating of the bulk MoS₂ powder at a moderate temperature (80 °C, 24 h),

resulting in a uniform dispersion of MoS₂ flakes. The hot flake-like MoS₂ particles were then cooled rapidly to low temperature in liquid N₂. Because the surfaces of the hot flake-like MoS₂ particles cooled faster than their interiors, quenching stresses occurred instantly upon contact with the liquid N₂, leading to cracking of bonds between the layers of weakly bonded MoS₂ layers, instantly freezing the cracks within the liquid N₂ medium.

The interaction between the hot flake-like MoS₂ particles and the liquid N₂ quenching medium resulted in quenching-cracked layers that allow further ultrasonic-facilitated exfoliation. Then, the detachment of MoS₂ layers preferentially occurs at these quenching-cracked layers via ultrasonication and subsequent re-dispersion in chloroform. To further identify the mechanism behind this quenching approach, we exfoliated MoS₂ solutions in both DI water and in aqueous KOH with and without the quenching process. The MoS₂ nanosheets prepared from exfoliation of bulk MoS₂ in DI water with and without quenching are termed MoS₂-DIQ and MoS₂-DI, respectively, and the MoS₂ nanosheets prepared from exfoliation of bulk MoS₂ in aqueous KOH with and without quenching are termed MoS₂-KOHQ and MoS₂-KOH, respectively. Tables 1, S.1, and S.2 provide details of the experimental methods and the obtained results. We observed that exfoliation of MoS₂ in aqueous KOH was greater than that in DI water. We suspect that aqueous KOH created better conditions for uniform dispersion of the flake-like MoS₂ particles than did DI water, leading to more-uniform quenching on the surfaces of the hot flake-like MoS₂ particles. One possible reason for the more uniform dispersion of flake-like MoS₂ in the presence of KOH is that KOH can dissociate into K⁺ and OH⁻ ions, and K⁺ ion might intercalate into the layered MoS₂ in bulk, which facilitates exfoliation.

In conclusion, we have synthesized MoS₂ nanosheets from commercially available bulk MoS₂ through a two-step process involving quenching in liquid N₂ and subsequent exfoliation through sonication. To the best of our knowledge, this paper provides the first example of the use of quenching technology for the preparation of MoS₂ nanosheets at low temperature and under atmospheric pressure. This method is quite promising because of its highly efficient, green, and facile operation.

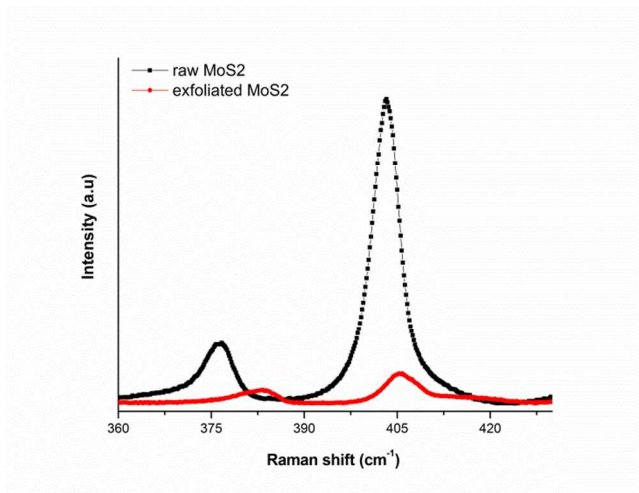


Fig. 1 Raman spectra of bulk MoS₂ and exfoliated MoS₂ nanosheets processed using the liquid N₂-exfoliation process.

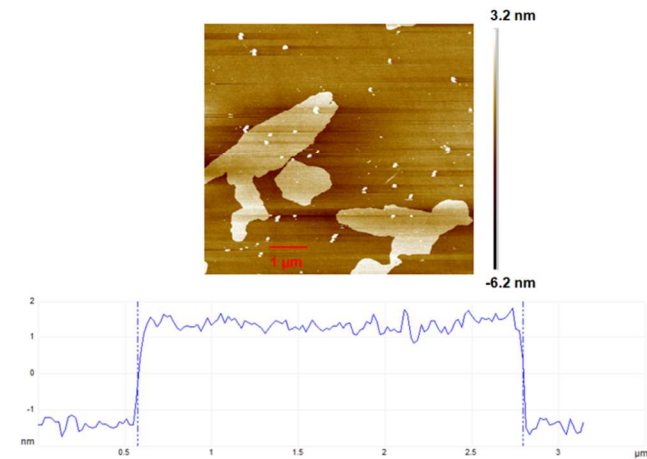


Fig. 2 AFM image and height profile of MoS₂ samples processed from a dispersion of exfoliated MoS₂.

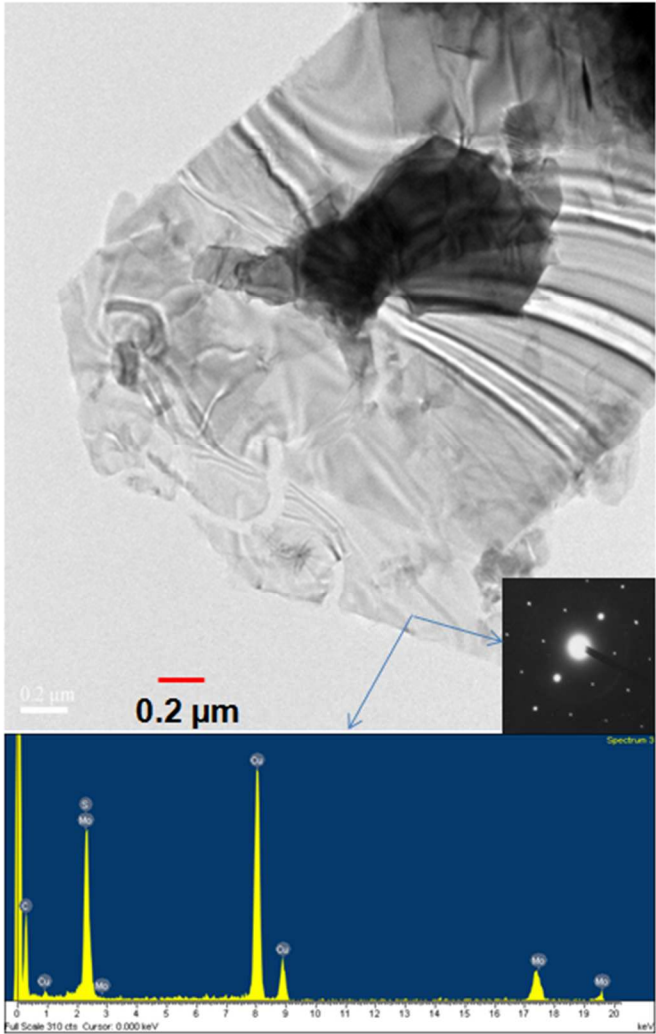


Fig. 3 TEM image of a MoS₂ sample processed from a dispersion of exfoliated MoS₂; inset: SAED pattern and EDS spectrum of the in situ-recorded area. The Cu signal arose from the TEM support grid.

Table 1: Exfoliation of solutions with and without quenching treatment

Exfoliation	Results	
	With quenching	Without quenching
Solution of MoS ₂ in DI water	Large amounts of exfoliated sheets having a thickness of 3 nm; difference in frequency between the A _{1g} and E _{2g} signals of ca. 22.2 cm ⁻¹ , but not uniform among sheets.	Small amounts of exfoliated sheets having a thickness of 5 nm; difference in frequency between the A _{1g} and E _{2g} signals of ca. 25.4 cm ⁻¹ . Flake-like MoS ₂ particles did not fully exfoliate and remained on the surfaces of the sheets. Obtained sheets were relatively thick, with a lack of uniformity among them.
KOH-based MoS ₂ solution	Large amounts of uniformly exfoliated sheets having a thickness of 2 nm; difference in frequency between the A _{1g} and E _{2g} signals was ca. 21.4 cm ⁻¹ .	Small amounts of exfoliated sheets having a thickness of 5 nm; difference in frequency between the A _{1g} and E _{2g} signals was ca. 25.8 cm ⁻¹ . Obtained sheets were relatively thick, with a lack of uniformity among them.

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Notes and references

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Table of Contents

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