Synergistic Exfoliation of MoS$_2$ by Ultrasound Sonication in a Supercritical Fluid Based Complex Solvent

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Abstract

Molybdenum disulfide (MoS$_2$) is an extremely intriguing low-D layered material due to its exotic electronic, optical, and mechanical properties, which could be well exploited for numerous applications to energy storage, sensing, and catalysis, etc., provided a sufficiently low number of layers is achieved. A facile exfoliation strategy that leads to the production of few-layered MoS$_2$ is proposed wherein the exfoliation efficacy could be synergistically boosted to $>90\%$ by exploiting ultrasound sonication in supercritical CO$_2$ in conjunction with N-methyl-2-pyrrolidone (NMP) as the intercalating solvent, which is superior to general practiced liquid exfoliation methods wherein only the supernatant is collected to avoid the majority of unexfoliated sediments. The facile and fast exfoliation technique suggests an exciting and feasible solution for scalable production of few-layered MoS$_2$ and establishes a platform that contributes to fulfilling the full potential of this versatile two-dimensional material.

Keywords: Molybdenum disulfide (MoS$_2$), Exfoliation, Supercritical CO$_2$, Ultrasound sonication

Introduction

Two-dimensional (2D) transition metal dichalcogenides (TMD) have attracted substantial attention due to the atomically thin layer as well as unique and versatile electronic properties spanning across being semiconducting to superconducting depending on the particular composition and structure [1–4]. As a quintessential member in the TMD family, molybdenum disulfide (MoS$_2$) consists of hexagonally arranged Mo atoms sandwiched by S atoms in an alternatingly occurring manner. The layered material possesses strong covalent bonds in a plane while the layers out of the plane are held together by weak van der Waals bond, which in principle makes possible the exfoliation of such a material into individually separate thin layers [5]. It has been reported that new physiochemical properties arise accompanying the exfoliation of MoS$_2$ into a few-layered structure such as enhanced-specific surface area, indirect to direct bandgap transition, and improved surface activity [6, 7].

Thus, the great advantages of MoS$_2$ remain hitherto elusive until it is thin enough to induce the aforementioned properties that could make MoS$_2$ very appealing for various applications such as energy storage, catalysis, optical devices, and sensor [7–11].

However, a facile and feasible exfoliation technique that renders scalable production of high-quality few-layered MoS$_2$ remains to be highly sought after in order to fully tap into the huge potential of MoS$_2$ not only for small scale laboratory demonstration or miniature microelectronic applications but also for large scale practical utilization in terms of, say, energy storage applications [12, 13]. These stringent requirements thus rule out currently popular production methods like CVD growth which is time-consuming and involves high temperature and large energy input [14], micromechanical cleavage which suffers extremely low yield and reproducibility [15], ion intercalation method that requires strong reducing intercalants and strict inert reaction atmosphere [16], and hydrothermal reaction that induces defects [17]. This leaves a liquid-phase exfoliation, a compelling strategy that could potentially strike an excellent balance among ease of exfoliation, quality, and scalability. Notwithstanding, in traditional liquid-phase exfoliation, common issues such as the use of surfactants difficult to remove in the post-treatment defiles the purity and the intrinsic electronic property of the 2D material [18] and...
prolonged sonication time in order to enhance layer separation and yield inevitably increase the density of defects under strong cavitation [19].

Herein, an improved liquid-phase exfoliation method is proposed that exploits the unique physiochemical properties and synergistic function of supercritical CO₂ and N-methyl-2-pyrrolidone (NMP), which enables facile intercalation and simultaneously penalty reduction of system enthalpy increase from exfoliation. The novel tactic promotes an effective and rapid exfoliation of MoS₂ into a few-layered 2D structure with a high yield, which sets a highly rewarding demonstration and holds great promise for facile and scalable production of not only exfoliated MoS₂ but also possibly a library of its two-dimensional analogs.

Methods
Materials
The molybdenum disulfide powders (MoS₂, 99.5%) and N-methylpyrrolidone (NMP, 99.9%) were purchased from Aladdin Reagent (Shanghai) and used without further purification. Absolute ethanol (99.5%) was purchased from Chengdu Kelong chemicals. Purified water was purchased from Sichuan Uppulta-pure Technology. CO₂ with 99.5% purity was purchased from Chengdu Qiyu Gas.

Exfoliation process
The exfoliation device mainly consists of a high-pressure chamber which can be pressured up to 20 MPa and an ultrasonic probe. All exfoliation experiments were performed in the stainless-steel reactor chamber with a maximum volume of 250 mL. In a typical experiment, MoS₂ powder (100 mg) was added and dispersed in a specified solvent (150 mL), then the device was heated up to a preset temperature by an electric heating jacket before CO₂ was subsequently pumped into the reactor up to 14 MPa using a manual pump. After the temperature and pressure reached the preset level, the ultrasonic probe was started for 1 h under the power of 600 W. After exfoliation, the pressure was released and the chamber was opened, and the obtained MoS₂ nanosheets were thereafter repeatedly washed and collected via filtration before drying.

Characterization
The crystal structure was examined by X-ray diffraction (XRD, Rigaku Co., Japan) analysis under CuKα radiation at 10–80° with a scan rate of 10°/min. Raman spectra were recorded on a laser Raman spectrometer (Thermo Fisher Co., America) with a He-Ne laser at 532 nm at room temperature. The number of layers and topography of the exfoliated samples were probed by atomic force microscopy (ANSYS, Co., America) in a tapping mode with the sample prepared from solution-casting of MoS₂ nanosheets dispersion onto mica. The Brunauer–Emmett–Teller (BET) surface areas were analyzed from a Tristar 3020 apparatus (Micromeritics Instrument Co., America) over a P/P₀ range automatically determined by
Quadrawin. Sample surface chemistry was investigated using X-ray photoelectron spectroscopy (XPS) with monochromated Al K\textsubscript{α} X-ray source (excitation energy of 1486.6 eV) on XPS ESCALAB 250Xi. High-resolution transmission electron microscopy (HRTEM, Quanta America) was carried out to determine the surface morphology and thickness. The examined sample was prepared by dropping diluted dispersion of exfoliated MoS\textsubscript{2} onto a holey carbon-covered copper grid.

**Results and discussion**

A schematic showing the exfoliation procedure is presented in Fig. 1, and the detailed description could be found in the experimental section. Briefly, bulk MoS\textsubscript{2} is suspended in a complex solvent made up of supercritical CO\textsubscript{2} and NMP followed by ultrasound sonication to initiate exfoliation. The critical factor that determines effective exfoliation lies in the employment of a complex solvent constituted by supercritical CO\textsubscript{2} and NMP. For one thing, once the supercritical state is reached, CO\textsubscript{2} delivers unique properties that straddle between gas and liquid wherein a low viscosity, zero surface tension, and high diffusivity resembling those of gas set in, and at the same time, it bears a certain density and behaves as a liquid solvent. This peculiar combination makes supercritical CO\textsubscript{2} a surprisingly outstanding intercalating molecule that inserts between MoS\textsubscript{2} layers to weaken the Van der Waals interaction between adjacent layers given its small molecular size in conjunction with the unrestrained mobility. On the other hand, it is established by Coleman that in order to facilitate liquid-phase exfoliation, a careful choice of solvent with matching surface tension to the surface energy of the layered material so as to compromise the gain in enthalpy of mixing during exfoliation is of paramount significance \cite{19, 20}. Besides, according to Hansen solubility parameter theory \cite{21, 22}, solvents that enable successful exfoliation ought to contain dispersive, polar, and H-bonding components of the cohesive energy density within a certain reasonable range. The end result points to NMP as a matching solvent that reduces barrier for solvent intercalation and improves the dispersion of MoS\textsubscript{2} \cite{23–25}. Considering NMP is miscible with supercritical CO\textsubscript{2}, the concerted function of the dual solvent system not only thermodynamically reduces the exfoliation threshold but also weakens the interlayer force

**Table 1** A summary of the exfoliation figure of merits (F.O.M) under different processing conditions

| SC CO\textsubscript{2} pressure | NMP     | F.O.M  |
|-------------------------------|---------|--------|
| 1                             | 14 MPa  | 150 ml | 0.152  |
| 2                             | 14 MPa  | None   | 0.676  |
| 3                             | 0 MPa   | 150 ml | 0.778  |
between MoS$_2$ to accelerate exfoliation, which results in facile and rapid exfoliation as will be delineated below.

To ascertain the critical role of NMP in promoting more intense exfoliation and the involved fundamentals, a series of control experiments were conducted under the condition of fixed sonication power, time, and the presence of supercritical CO$_2$. Their corresponding XRD patterns were recorded as shown in Fig. 2a. The XRD peak intensity is here adopted as the major indicating parameter to reflect the exfoliation extent based on the knowledge that with the reduction in the number of layers of such 2D materials, the loss in long-range order leads to weakened coherent scattering which in turn results in the reduction in the reflection intensity. It is found that when no co-solvent is used the exfoliation effect is weak, with the corresponding XRD peak intensity showing almost no change compared to the bulk MoS$_2$ sample, which suggests the difficulty of supercritical CO$_2$ alone to surmount the enthalpy gain barrier resulting from exfoliation. Given that water poorly mix with supercritical CO$_2$, the corresponding result suggests the phase separation between the two solvents prevents any joint action on MoS$_2$ and this barely leads to any obvious exfoliation. The adoption of ethanol and NMP with excellent miscibility with supercritical CO$_2$ results in improved exfoliation. NMP shows the best exfoliation efficacy reflected by the largely suppressed XRD peak intensity. This leads to the conclusion that both an excellent miscibility with supercritical CO$_2$ and a matching surface tension to MoS$_2$ that leads to reduced enthalpy gain thus promoting facile exfoliation, need to be guaranteed so as to achieve efficient exfoliation.

A synergistic contribution from supercritical CO$_2$ and NMP to MoS$_2$ exfoliation is discovered (Fig. 2b). To quantitatively characterize the exfoliation efficiency from each exfoliation condition, a figure of merit (F.O.M) is defined as the retention rate of the XRD peak intensity of plane (002) at 14.5° after exfoliation with respect to that of the bulk sample, i.e., $I_{\text{exfoliated}}/I_{\text{bulk}}$ (the lower the better exfoliation). It is particularly worth mentioning that even the multiplied F.O.M value obtained from the exfoliation where NMP and supercritical CO$_2$ were employed alone (0.526) is still much bigger than the F.O.M for when they were adopted simultaneously (0.152) (Table 1). This clearly verifies a strong synergistic effect wherein the two miscible solvents are enhancing each other in the exfoliation process with NMP lowering
the exfoliation energy barrier while concurrently supercritical CO$_2$ facilitates the subsequent intercalation between layers to initiate facile exfoliation.

Raman spectroscopy was conducted on the bulk sample as well as the exfoliated MoS$_2$ from the complex solvent. The bulk sample exhibits typical $E_{2g}$ and $A_{1g}$ bands with their respective full width at half maximum (FWHM) of 4.37 and 5.62 cm$^{-1}$ (Fig. 2c). The reduced peak intensity of the exfoliated sample along with the enlarged FWHM to 13.44 and 13.56 cm$^{-1}$ for $E_{2g}$ and $A_{1g}$ peaks due to phonon nanoconfinement by facet boundaries [26, 27] indicates the decrease in the number of layers of MoS$_2$ which tallies with the results from XRD analysis.

XPS analysis has been conducted to study the chemical state of the exfoliated MoS$_2$ sheets. High-resolution XPS spectra for de-convoluted Mo (3$d$) and S (2$p$) peaks have been shown in Fig. 3a and b. The peak positions at 229.2 eV and 232.3 eV refer to Mo 3$d_{5/2}$ and Mo 3$d_{3/2}$, respectively, confirming the Mo$^{4+}$ state [28, 29]. Meanwhile, the doublet peaks for S 2$p_{3/2}$ and S 2$p_{1/2}$ at 161.0 eV and 163.2 eV, respectively, confirm the sulfide S$_2^-$ state [29, 30].

Atomic force microscopy (AFM) analysis was conducted in tapping mode on exfoliated MoS$_2$ nanosheets solution-casted on mica substrate to identify their topography and layer thickness. It is observed that the obtained MoS$_2$ nanosheets were exfoliated into sizes ranging from 100 to 450 nm (Fig. 4a). The exfoliation end result could be properly adjusted by tuning sonication power and time to avoid strong cavitation and in-plane cracking of MoS$_2$ sheets while increasing the chamber pressure to induce stronger intercalation of supercritical CO$_2$ and weakening of interlayer van der Waals force. Therefore, the maximum
dimension could be possibly enhanced to micrometer range. Line scannings for the cross-sectional height profile on exfoliated MoS 2 nanosheets reveal different layer thicknesses from ~3 to ~9 nm as shown in Fig. 4a inset, which indicates the number of layers distributed from 5 to 15 considering the thickness of a single layer MoS 2 being 0.61 nm [31]. The number of layer distribution plot for exfoliated MoS 2 is shown in Additional file 1: Figure S1 with the majority number sitting between 12 and 20 layers. Besides, HRTEM was employed to directly probe into the layer thickness and number of layers by checking the lattice fringes on exposed nanosheet edges. The number of layers of 18–19 is identified which corresponds to a thickness of ~11 nm (Fig. 4b).

To estimate the average number of layers, Brunauer–Emmett–Teller (BET) tests were conducted on the dried sample collected from each exfoliation condition. It has to be highlighted that neither centrifugation nor decanting the upper clear supernatant was employed to collect the exfoliated sample, but rather, the whole entity of product from the exfoliation chamber was taken for the test. This results in a remarkably high product percentage yield that easily surpasses 90% with the minor loss resulting from sample washing and collection. As such, the herein proposed exfoliation technique represents a truly viable approach for scalable exfoliation. This is in steep contrast to generally practiced liquid exfoliation method wherein only the supernatant is garnered to avoid the majority of unexfoliated sediments, which inevitably brings about a low yield [24, 32]. Efficiency-wise, the exfoliated product from the complex solvents delivers the highest specific surface area among all processing conditions with 36.86 m 2/g, which is congruent with previous discussions (Fig. 5). This corresponds to an average exfoliated number of layers of 17 by taking account of the theoretical specific surface area of single layer MoS 2 of 636 m 2/g [33]. Considering the large overall quantities of MoS 2 exfoliated, it is sound to deem this approach highly efficient.

When the exfoliated powders are re-dispersed in fresh NMP, a stable dispersion without sedimentation in 5 h is observed (Fig. 6a, c). This implies the existence of stable fine colloidal particles, whereas when the re-dispersed MoS 2 of the same concentration was prepared in NMP from the sample exfoliated in supercritical CO 2 alone, a conspicuous amount of settled particles could be identified after 5 h settlement (Fig. 6b, d). Furthermore, due to the synergistic exfoliation effect that intensively prompts the exfoliation, the whole process is completed rapidly in 1 h which is substantially faster than some reported intercalation-based exfoliation process that could even last up to 48 h [34].

**Conclusions**

A modified liquid phase exfoliation approach benefiting from the synergistic effect from supercritical CO 2 and NMP for facile MoS 2 exfoliation into a few-layered structure is realized. The concerted function of the complex solvent system reduces the exfoliation energy barrier while simultaneously promotes easy insertion of supercritical CO 2 into MoS 2 interlayers to initiate facile exfoliation. This technique is not only highly efficient but also permits scalable production of few-layered MoS 2 with a high yield (>90%), and thus, it creates a prospectively valuable opportunity to promote the versatile applications of MoS 2.
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