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Rapid preparation of single-layer transition metal dichalcogenides nanosheets via ultrasonication enhanced lithium intercalation

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In this report, we developed a rapid and versatile ultrasonication enhanced lithium intercalation (ULI) method to prepare single-layer transition metal dichalcogenides nanosheets (TMDCs NSs, including MoS_2, WS_2, and TiS_2) by using n-butyllithium (n-BuLi).

As inorganic analogue of graphene, two-dimensional (2D) transition metal dichalcogenides (TMDCs) have attracted great attention of researchers from all over the world during recent years. TMDCs usually have X-M-X sandwich-type layered structure, in which X refers to chalcogen atoms (S, Se or Te) and M stands for transition metal atoms (Ti, Zr, Hf, Nb, Ta, Mo, W, and so on).[1] The interaction of chalcogen and transition metal atoms in a X-M-X layer is strong covalent bonding, while the X-M-X layers form bulk material via relatively weak van der Waals force.[2] When bulk TMDCs materials are exfoliated to ultrathin nanosheets (NSs), their electronic structure changes significantly.[1b] For example, bulk MoS_2 has an indirect band gap about 1.3 eV, while the single-layer MoS_2 NSs have a 1.9 eV direct band gap.[3] The ultrathin 2D structure renders the TMDCs with unique electronic, optical, chemical, and catalytic properties, which has opened up large numbers of opportunities for novel applications, such as field effect transistors, light emitting devices, photodetectors, solar cells, hydrogen evolution catalysts, lithium batteries, biosensors, drug delivery, bioimaging, phototherapy, and so on.[4]

Various methods have been developed to prepare ultrathin TMDCs NSs. Chemical vapour deposition (CVD) has been successfully used to synthesize high quality TMDCs NSs in controllable manner with different compositions and number of layers.[5] However, this method has low yield and is not easy to scale-up. Mechanical exfoliation is another method to prepare single-layer TMDCs NSs, but the yield is also very low and needs long time labour work.[6] Coleman et al. developed an ultrasonication assisted liquid exfoliation method to prepare nanosheets from various TMDCs bulk materials.[7] However, single-layer or few-layer nanosheets are hard to be obtained by this method. Compared with those methods mentioned above, chemical exfoliation is a simple and versatile method to prepare single-layer TMDCs NSs. The mostly used chemical exfoliation method is conventional lithium intercalation (CLI) using n-butyllithium (n-BuLi) as lithiation agent, which was developed by Joensen and co-workers in

the 1980s.[8] One troublesome issue of this method is that the lithium intercalation rate is low and often needs more than 48 hours or high temperature to complete the reaction.[8-9] Zeng et al. explored an electrochemical lithium intercalation method to significantly improve the efficiency and controllability of lithium intercalation.[10] Although very effective, this method needs complicated lithium battery system and not easy to scale-up. Therefore, though great progress in the preparation of single-layer TMDCs NSs has been achieved, novel preparation methods, which are even more facile, rapid, and versatile, are still in great need.
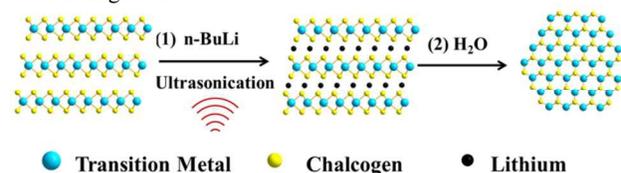
Scheme 1 Ultrasonication enhanced lithium intercalation method to prepare single-layer TMDCs NSs.

Ultrasonication assisted synthesis has been widely used to prepare various nanomaterials, since ultrasonication can provide several unconventional reaction conditions due to acoustic cavitation effect.[11] Although being used in liquid exfoliation method,[7a] ultrasonication has merely been studied for chemical intercalation of TMDCs, especially for lithium intercalation.[12] Miremadi et al. showed that ultrasound can be used to exfoliate the inert WS_2 using n-BuLi, however, the morphology of the products and reaction mechanism were not well studied.[13] In this communication, we report an ultrasonication enhanced lithium intercalation (ULI) method to prepare single-layer TMDCs NSs with high yield and short time, and investigate the possible reaction mechanism.

In a typical reaction for preparing MoS_2 NSs by ULI method, MoS_2 powder and n-BuLi hexane solution was sealed in a Schlenk tube under Ar atmosphere and then sonicated in a commonly used ultrasonic cleaner. Enhanced by ultrasonication, lithium intercalates into the interlayer of MoS_2 matrix by ion-electron transfer topotactic reaction.[14] The as-formed lithiation intermediate Li_xMoS_2 reacts vigorously with H_2O and forms H_2 gas, which drives MoS_2 layers to separate with each other and form single-layer nanosheets. In order to compare the morphology and structure of MoS_2 NSs prepared by ULI with those of CLI method, we used strict centrifugation procedures before

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characterization. After the exfoliation with H_2O, ethanol was first added into the opaque slurry of MoS_2 NSs to wash the organic residues and centrifuged at 12000 rpm. The sediment was dispersed in ethanol and centrifuged again. After the washing steps, MoS_2 NSs was dispersed in water and centrifuged at 5000 rpm to remove the thick nanosheets. Then the supernatant was collected and centrifuged at 12000 rpm to obtain the single-layer MoS_2 NSs. In order to guarantee the purity, at least two more centrifugation cycles were proceeded to remove any residual large contents remained in MoS_2 NSs suspension.

The morphology and structure of MoS_2 NSs prepared by ULI and CLI method were characterized in more details. Transmission electron microscopy (TEM) was used to investigate the morphology of the MoS_2 NSs. Fig. 1a shows that MoS_2 NSs prepared by CLI method have uniform sheet-like morphology. As shown in the high-resolution TEM (HRTEM) image (Fig. 1f), the crystal lattice spacing is about 2.7 Å and can be assigned to (100) plane, which is identical to other studies.[9a, 10, 15] Selected area electron diffraction (SAED) pattern (Fig. 1k) indicates the MoS_2 NSs prepared by CLI have hexagonal symmetry structure.[9a, 10] Compared with Fig. 1a, the TEM images (Fig. 1b-e) indicate that MoS_2 NSs prepared by ULI method reacted for 40 min, 1 h, 2 h, and 3 h, respectively, also have uniform morphology without obvious holes or cracks, which suggests that ULI method has no obvious harm to the structure of MoS_2 NSs (Electronic Supplementary Information, ESI, Fig. S1a). The HRTEM images (Fig. 1g-j) show that the MoS_2 NSs prepared by ULI method with different times have nearly identical lattice spacing and crystalinity compared with those prepared by CLI, which indicates no significant crystal structure change occurs. The thickness of MoS_2 NSs is estimated to be about 1.1 nm from HRTEM images (ESI, Fig. S1b) of the folded edges, which is similar to the thickness of single-layer MoS_2 NSs measured by AFM.[9a, 10] Moreover, the SAED patterns (Fig. 1l-o) of MoS_2 NSs prepared by ULI method also remain the same with CLI-MoS_2 NSs. The TEM and SAED results demonstrate that ULI method can produce MoS_2 NSs with the same quality and morphology of CLI method.
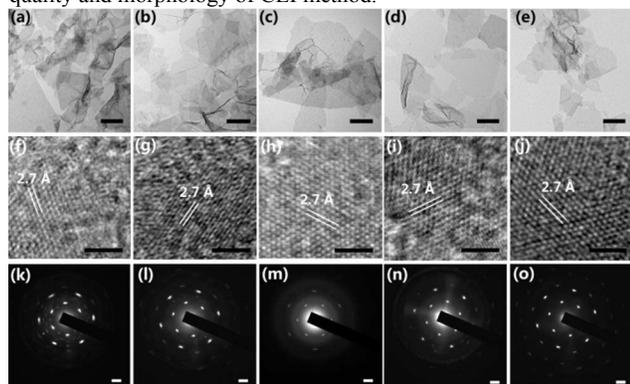

Fig. 1 TEM (a-e), HRTEM (f-i), and SAED (k-o) images of MoS_2 NSs prepared by different methods and under different times: CLI for 48 h (a, f, k); ULI for 40 min (b, g, l), 1 h (c, h, m), 2 h (d, i, n), and 3 h (e, j, o). Scale bars: 200 nm for Fig.1a-e, 2 nm for Fig. 1f-j, and 2 1/nm for Fig. 1k-o.

Atomic force microscopy (AFM) was used to determine the thickness of the MoS_2 NSs. As shown in Fig. 2a, the average thickness of the MoS_2 NSs prepared by ULI method is about 1.3 nm, which is similar to the reported values for single-layer MoS_2 NSs prepared by

CLI method.[9a, 9b, 10] Large-scale AFM images (Fig. 2b) further confirms that most of the as-prepared MoS_2 NSs are uniform single-layers, which suggests that ULI is a reliable method to prepare high quality single-layer MoS_2 NSs. As illustrated in X-ray diffraction (XRD) patterns (Fig. 2c), the diffraction lines of restacked films of MoS_2 NSs match well with the standard diffraction data of MoS_2 (JCPDS, 87-2416). While the absence of (002) line for aqueous dispersion of MoS_2 NSs is an evidence of the presence of single-layers.[8, 10] The broadening peaks located at about 29° and 42° of MoS_2 NSs in water can be ascribed to (100) and (110) lines, which was also reported for the aqueous suspension of single-layer MoS_2 due to the existence of water.[16] There are five distinct Raman scattering peaks for MoS_2 NSs prepared by ULI method (Fig. 2d). Among them, the peaks at 379.1 cm^{-1} and 401.0 cm^{-1} belong to the in-plane E^1_{2g} and out-of-plane A_{1g} modes, respectively.[10, 17] Compared with MoS_2 powder, A_{1g} vibration softens, which indicates the MoS_2 NSs has small thickness.[9a] Moreover, three relative weak peaks located at 151.3 cm^{-1} (J_1), 224.4 cm^{-1} (J_2), and 325.0 cm^{-1} (J_3) are not seen in bulk MoS_2, corresponding to the vibrations at the M points of the Brillouin zone.[17] The presence of J_1, J_2, and J_3 suggests that 1T-MoS_2 exists in as-prepared MoS_2 NSs, because these vibrational modes are not Raman active in 2H-MoS_2.[17]
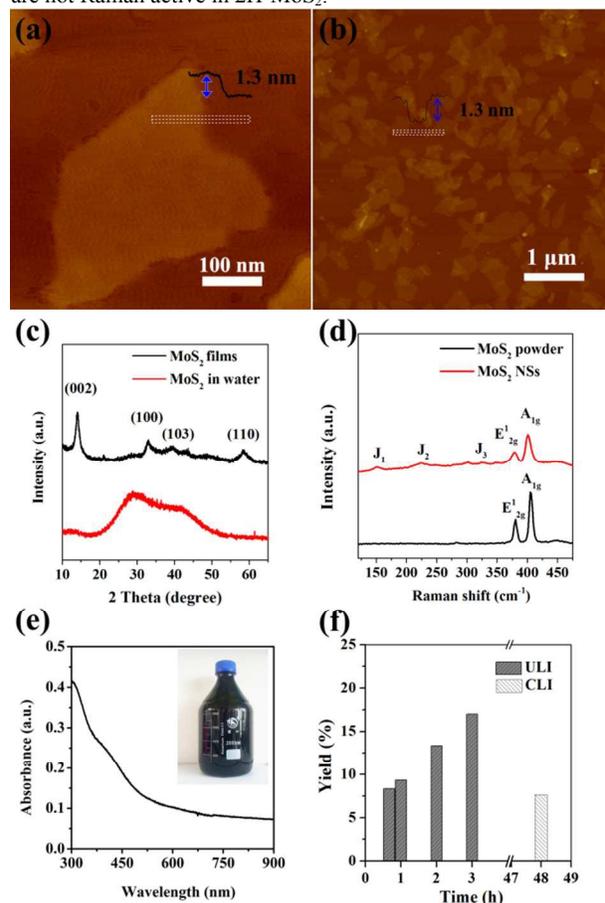

Fig. 2 (a) and (b) AFM images of MoS_2 NSs prepared by ULI with different scales; (c) XRD patterns of MoS_2 NSs prepared by ULI in the forms of restacked film and water dispersion; (d) Raman spectra of MoS_2 NSs prepared by ULI and the bulk MoS_2 powder; (e) UV-Vis absorption spectrum of MoS_2 NSs prepared by ULI, inset: photo of MoS_2 NSs aqueous dispersion; (f) Yield of single-layer MoS_2 NSs

prepared by ULI at different times and MoS_2 NSs prepared by CLI for 48 h.

Fig. 2e shows the UV-Vis absorption spectrum of MoS_2 NSs prepared by ULI. Compared to $2H-MoS_2$, the weak shoulder peak located near 600 nm shows little excitonic feature due to the formation of $1T-MoS_2$ NSs.[9a] Since ULI method is very efficient and doesn't need complicated equipments, MoS_2 NSs can be prepared in large quantities. The inset in Fig. 2e is a photograph of 2 liter aqueous dispersion of MoS_2 NSs prepared by ULI. X-ray photoelectron spectroscopy (XPS) was used to investigate the composition of the MoS_2 NSs prepared by ULI method and the results confirm that Mo exists as +4 oxidation state and no obvious Mo (VI) can be found (ESI, Fig. S2).

Inductively coupled plasma optical emission spectrometer (ICP-OES) was used to determine the yield of single-layer MoS_2 NSs after exfoliation. As shown in Fig. 2f, the yield (8.4%) of single-layer MoS_2 NSs using ULI for 40 min is higher than the yield of CLI method (7.6%) for 48 h, which is a decrease of reaction time by more than 70 times.[8-9] Prolonging ultrasonication time to 3 h, the yield of single-layer MoS_2 NSs reaches about 17.2%. As shown in Fig. S3 (ESI), when the molar ratio (n-BuLi to MoS_2) increases from 0.4 to 2 by using ULI method for 1h, the yield of MoS_2 NSs increases from 0.3% to 9.2%; while further increases the molar ratio from 2 to 18, the yield slightly increases from 9.2% to 10.3%. These results indicate that there is a upper limit for lithium intercalation into MoS_2 and over intercalation of lithium may cause decomposition of MoS_2, which has been reported for the electrochemical intercalation method.[10] The greatly reduced reaction time suggests that the lithium intercalation has been greatly enhanced during ultrasonication. As we know, acoustic cavitation and associated nonlinear physical effects are the main origins for the unique sonochemistry.[11, 18] Shockwave generated by acoustic cavitation can fragment the fragile solid material to smaller pieces, which may have the possibility to increase the surface area of MoS_2 powder and increase the reactivity.[19] In order to study the origin of the enhanced lithium intercalation reaction, we first performed control experiments by sonicating MoS_2 powder in hexane. As can be seen from the TEM images for different ultrasonication times (ESI, Fig. S4), the morphology of MoS_2 has no obvious change. The average size of MoS_2 particles decreases from the initial 2.0 μm to about 1.8 μm, and keep nearly constant for even longer ultrasonication time (ESI, Fig. S5). However, only 10% decrease of the MoS_2 particle size can't sufficiently explain the greatly enhanced lithium intercalation of MoS_2.

On the other hand, shockwave produced in sonicated liquid can generate high-speed microscopic turbulence within the liquid-solid interfacial films, which has been proved to significantly increase the mass transfer and accelerate the reaction rate of the liquid-solid reaction.[20] The lithium intercalation is a heterogeous reaction and n-BuLi in solution reacts with solid MoS_2 at the limited liquid-solid interface. Therefore, the turbulence of the solution may substantially accelerate the transport of n-BuLi molecules to the surface of MoS_2, which will contribute to the lithium intercalation. Moreover, in conventional lithium intercalation reaction of TMDCs, n-BuLi molecules in hexane solution usually form hexamer aggregates with relatively low reactivity, which significantly hinder the reaction and limit the yield of the nanosheets.[21] To overcome this rate-limiting factor, the aggregates of n-BuLi should further dissociate to more active species, such as monomers or other low extent aggregates.[21] Although

long time heating at high temperature (100℃) has been used to solve this problem, the reaction condition is dangerous to operate and may lead extra damage to the crystal structure of TMDCs.[9a, 9b] As we know, acoustic cavitation effect can create localized hot spots with extremely high temperature (~5000 K) in very short time,[11] which may provide high energy to activate the n-BuLi aggregates and accelerate the lithium intercalation.[22] Therefore, we assume that ultrasonication not only directly enhances the mass transfer of n-BuLi, but may also activate the low reactive aggregates of n-BuLi, which may have synergetic enhancement to accelerate lithium intercalation reaction.

Using ULI method we also prepared other TMDCs NSs. As shown in TEM images (Fig. 3a and b), exfoliated WS_2 and TiS_2 NSs have relative uniform morphology with lateral size of 200-1000 nm. HRTEM image (Fig. 3c) indicates that WS_2 NSs have hexagonal lattice structure with lattice spacing of 2.7 Å, which can be assigned to (100) plane.[10] HRTEM image (Fig. 3d) reveals that TiS_2 has interplanar distance of 3.0 Å, which matches with the (100) plane[23]. Thickness of the WS_2 and TiS_2 NSs was determined by AFM to be about 1.3 nm and 1.0 nm, respectively, which shows that the as-prepared nanosheets are single-layers.[10] XPS and Raman spectroscopy were used to investigate the composition and structure of WS_2 and TiS_2 NSs and results also confirm the successful preparation of single-layer WS_2 and TiS_2 NSs by ULI (ESI, Fig. S7 and Fig. S8).
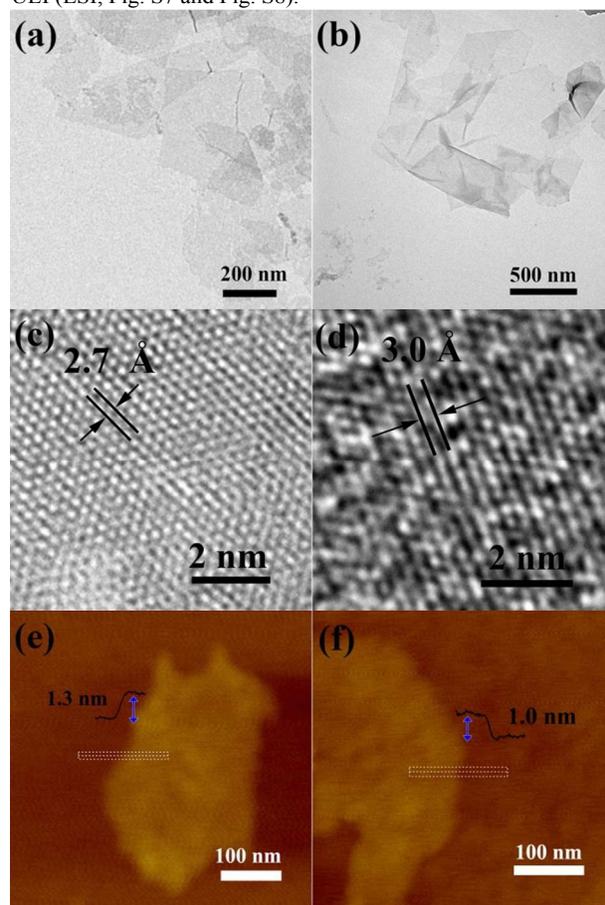

Fig. 3 (a) TEM, (c) HRTEM, and (e) AFM images of WS_2 NSs prepared by ULI；(b) TEM, (d) HRTEM, and (f) AFM images of TiS_2 NSs prepared by ULI.

In summary, due to the long reaction time and low efficiency of conventional lithium intercalation of TMDCs by n-BuLi, we explored

ultrasonication to enhance the mass transport and reactivity of n-BuLi by utilizing the unique acoustic cavitation and related effects. By ultrasonication in a common ultrasonic cleaner, efficiency of lithium intercalation into MoS_2 by n-BuLi can be greatly enhanced. Compared with the CLI method, ULI method can reduce the reaction time from 2 days to 1-3 h and give even higher yields of MoS_2 NSs. Moreover, this approach is very general and can also be used to produce single-layer nanosheets of other TMDCs, such as WS_2 and TiS_2.

Notes and references

During the revision of this communication, we became aware of a similar study[24].

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†Electronic Supplementary Information (ESI) available: Experimental details, characterization methods, XPS spectra of MoS_2 NSs, TEM images of MoS_2 powder sonicated for different times; UV-Vis, XPS, and Raman spectra of WS_2 and TiS_2 NSs. See DOI: 10.1039/c000000x/

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