Electronic Supplementary Information

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

Lihui Yuwen,a Huan Yu,a Xiangrong Yang,a Jiajia Zhou,a Qi Zhang,a Yuqian Zhang,a Zhimin Luo,a Shao Su,a and Lianhui Wang*,a

a Key Laboratory for Organic Electronics and Information Displays & Institute of Advanced Materials(IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing University of Posts & Telecommunications, 9 Wenyuan Road, Nanjing 210023, China.
Tel.: +86 25 85866333; Fax: +86 25 85866396.
E-mail: iamlhwang@njupt.edu.cn;

S1. Experimental Section

S2. Characterization

S3. TEM image of MoS₂ NSs and HRTEM image for folded edges

S4. XPS spectra of MoS₂ NSs

S5. Yields of MoS₂ NSs at different molar ratios of n-BuLi to MoS₂

S6. TEM images of MoS₂ powder sonicated at different times

S7. UV-Vis absorption spectra of WS₂ and TiS₂ NSs

S8. XPS spectra of WS₂ and TiS₂ NSs

S9. Raman spectra of WS₂ and TiS₂ NSs
S1. Experimental Section

1. Chemicals

Three different transition metal dichalcogenides (TMDCs) compounds were used in powder form: MoS$_2$ (<2 μm, 99%, Sigma-Aldrich), WS$_2$ (<6 μm, 99.99%, Aladdin), and TiS$_2$ (<50 μm, 99.5%, Cerametek Materials). The n-butyllithium (n-BuLi, 2.4 M hexane solution) was purchased from Amethyst. All aqueous solutions in this study were prepared by using ultrapure water (Millipore, 18.2 MΩ).

2. Preparation of TMDCs NSs by ULI

In a typical reaction, MoS$_2$ powder (0.2 g, 1.25 mmol) was first added into a 25 mL Schlenk tube. Air in this tube was evacuated and then backfilled with pure Ar. After repeating the vacuum-Ar cycle for three times, the tube was sealed and protected with Ar. n-BuLi in hexane solution (1.04 mL, 2.50 mmol) was introduced into the Schlenk tube by a syringe. Ultrasonication enhanced lithium intercalation of MoS$_2$ was performed in a ultrasonic cleaner (53 kHz, 180W, SK3310HP, KUDOS) for different times (Caution: It is strongly recommended that the rubber plug of the Schlenk tube should be tightly sealed by Parafilm in order to avoid the overflow of n-BuLi and keep safe). Before exfoliation of the Li-intercalated MoS$_2$, the Schlenk tube was left to stand for 30 min and the residual n-BuLi in supernatant was removed. Under Ar flow, deaerated ultrapure water (10 mL) was carefully introduced into the tube drop by drop to avoid violent H$_2$ evolution.

The aqueous suspension of MoS$_2$ NSs was sonicated for 30 min to complete the exfoliation (as for TiS$_2$, the tube should be immersed in iced water). Equal volume of ethanol was added into the MoS$_2$ NSs suspension and centrifuged at 12000 rpm for 20 min. The precipitate was dispersed in ethanol and repeated the centrifugation procedure. Then, the sediment was separated and dispersed in ultrapure water. After centrifuged at 5000 rpm for 30 min, the large aggregates of MoS$_2$ in the bottom of the tube were discarded. The supernatant was collected and centrifuged at 12000 rpm for 1 h. The black sediment was dispersed in ultrapure water and the centrifugation was repeated for another two times. At last, the precipitate was dispersed in water and stored at 4 °C.

The preparation of WS$_2$ and TiS$_2$ NSs used similar procedures, except that the molar ratios of n-BuLi to TMDCs were 60:1 and 10:1 for WS$_2$ and TiS$_2$, respectively.

3. Preparation of MoS$_2$ NSs by CLI

The reaction conditions and purification procedures for CLI method is the same to that of ULI, except that during the lithium intercalation step by n-BuLi no ultrasonication was used.

S2. Characterization

TEM images were taken on HT7700 (Hitachi, Japan) with acceleration voltage of 100 kV. HRTEM and SAED were performed on JEM-2100F (JEOL, Japan) with acceleration voltage of 200 kV. X-ray diffraction patterns were obtained by using a D8 ADVANCE X-ray diffractometer (Bruker, Germany) with Cu Kα radiation (λ=1.54178 Å). Atomic force microscopy (AFM) characterization was performed on bruker Nanoscope IIIa. X-ray photoelectron spectroscopy (XPS) was performed on a PHI 5000 VersaProbe with Al Kα (hv = 1486.6 eV) as the excitation source. The UV-Vis absorption spectra were recorded on a UV-Vis-NIR spectrophotometer (UV-
3600, Shimadzu, Japan). MoS$_2$ concentration was determined by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Optima 5300DV, Perkin Elmer) according to the reported procedure$^1$.

**S3. TEM image of MoS$_2$ NSs and HRTEM image for folded edges**

![TEM and HRTEM images](image)

Fig. S1 (a) TEM image of MoS$_2$ NSs prepared by ULI for 3 h. (b) HRTEM image for folded edges of single-layer MoS$_2$ NSs prepared by ULI for 3 h.

**S4. XPS spectra of MoS$_2$ NSs**

![XPS spectra](image)

Fig. S2 (a) XPS spectra of Mo 3d and (b) S 2p core level peak regions of MoS$_2$ NSs prepared by ULI.

**S5. Yields of MoS2 NSs at different molar ratios of n-BuLi to MoS2**
Fig. S3 Yield of MoS$_2$ NSs obtained at different molar ratios of n-BuLi to MoS$_2$ by ULI method for 1h.

**S6. TEM images of MoS$_2$ powder sonicated at different times**

Fig. S4 TEM images of MoS$_2$ powder under ultrasonication with different times in hexane. From a to d, the ultrasonication time is 0 h, 1 h, 2 h, and 3 h, respectively. The ultrasonication condition is identical to the ULI method, except without n-BuLi. The scale bar is 10 μm.
Fig. S5 The average size of MoS$_2$ powder after different ultrasonication times for 0 h, 1 h, 2 h, and 3 h. Size statistics is based on more than 150 MoS$_2$ particles.

S7. UV-Vis absorption spectra of WS$_2$ and TiS$_2$ NSs

Fig. S6 UV-Vis absorption spectra of WS$_2$ (a) and TiS$_2$ (b) NSs prepared by ULI method. The insets show the photos of WS$_2$ (a) and TiS$_2$ (b) NSs aqueous dispersions in a sample bottle.

As shown in Fig. S6a, the excitonic peaks of bulk WS$_2$ located at about 520 nm and 640 nm have almost vanished, which is a sign of formation of single-layer 1T-WS$_2$ NSs and suggests successful exfoliation of WS$_2$. Absorption peak near 600 nm in Fig. S6b is similar to the reported value of TiS$_2$ NSs$^3$.

S8. XPS spectra of WS$_2$ and TiS$_2$ NSs
**Fig. S7** (a) XPS spectra of W 4f core level energy regions for WS\(_2\) NSs prepared by ULI; (b) XPS spectra of Ti 2p core level energy regions for TiS\(_2\) NSs prepared by ULI.

XPS spectra of W 4f core level peak regions in Fig. S7a can be deconvoluted into three groups of peaks with binding energy ranging from 40 eV to 30 eV: (1) The doublet peaks located at 32.1 eV and 34.3 eV can be assigned to W 4f\(_{7/2}\) and W 4f\(_{5/2}\) of 1T-WS\(_2\), respectively; (2) The doublet peaks located at 33.2 eV and 35.3 eV originate from W 4f\(_{7/2}\) and W 4f\(_{5/2}\) of 2H-WS\(_2\), respectively; (3) The peak around 37.7 eV belongs to W 5p, according to the reported literature\(^4\). The results show that W atoms in as-prepared WS\(_2\) NSs have +4 oxidation state. Fig. S7b shows the XPS spectra of Ti 2p core level energy regions of TiS\(_2\) NSs. The peaks near 458.0 eV and 463.8 eV can be assigned to Ti 2p\(_{3/2}\) and Ti 2p\(_{1/2}\), respectively\(^5\).

**S9. Raman spectra of WS\(_2\) and TiS\(_2\) NSs**

**Fig. S8** Raman spectra of (a) WS\(_2\) NSs films and (b) TiS\(_2\) NSs films prepared by ULI.

There are two distinct Raman scattering peaks (351.6 cm\(^{-1}\) and 415.9 cm\(^{-1}\)) for WS\(_2\) NSs prepared by ULI method (Fig. S8a), which belong to the in-plane \(E_{1g}^{1}\) and out-of-plane \(A_{1g}\) modes, respectively. Compared with WS\(_2\) powder, \(E_{1g}^{2}\) vibration stiffens slightly, which indicates that the
as-prepared WS$_2$ NSs has small thickness$^6$. The Raman peaks located at 331 cm$^{-1}$ and 229 cm$^{-1}$ of TiS$_2$ NSs can be ascribed to E$_{1g}$ and A$_{1g}$ vibrational modes, respectively (Fig. S8b)$^7$. There is a bout 2 cm$^{-1}$ shift of E$_{1g}$ peak compared with bulk TiS$_2$, suggesting a decrease of the layer numbers$^5$.

References: