Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting information

High-quality single-layer nanosheets of MS$_2$ (M= Mo, Nb, Ta, Ti) directly exfoliated from AMS$_2$ (A= Li, Na, K) Crystals

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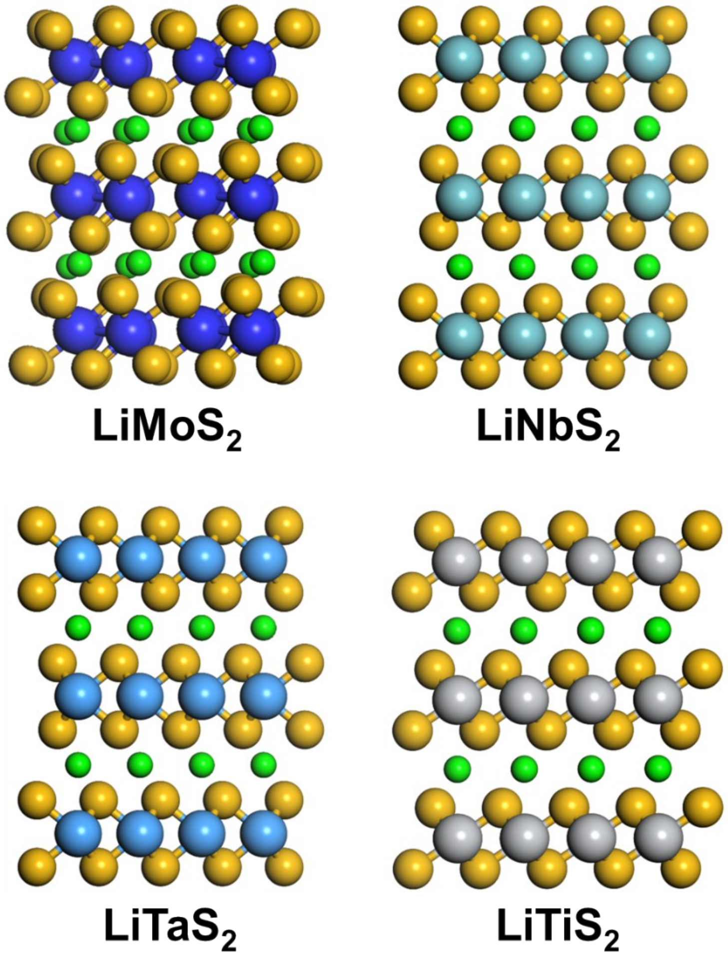
Supplementary Figures



$LiMoS_2$ $LiNbS_2$

$LiTaS_2$ $LiTiS_2$

Figure S1. Crystal structure of LiMS$_2$ (M=Mo, Nb, Ta, Ti)

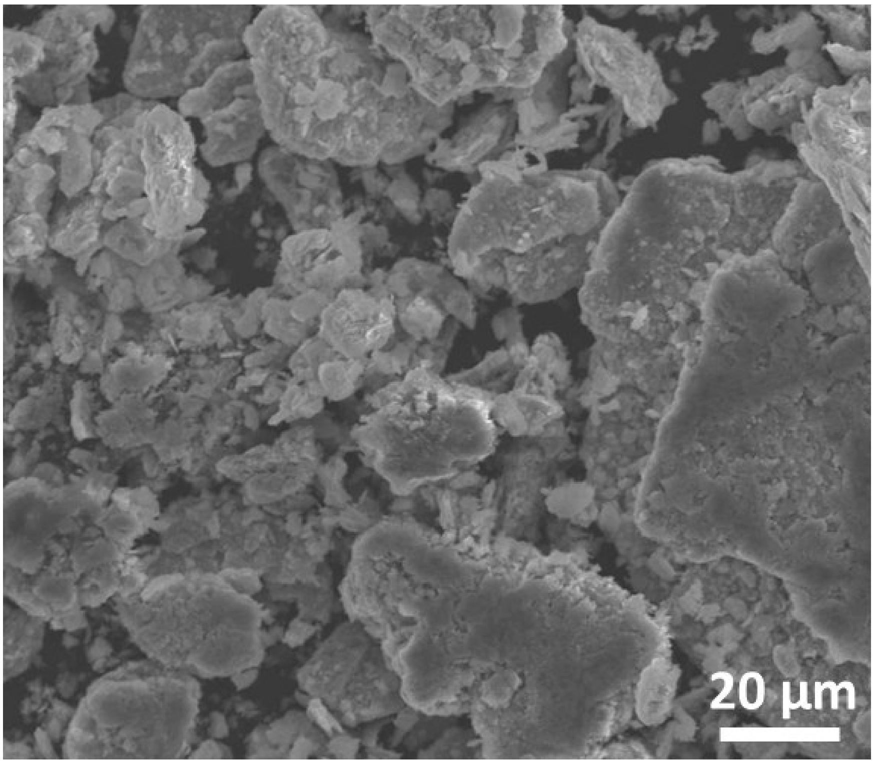


Figure S2. The ref-Li_xMoS_2 prepared by the n-butyl lithium method

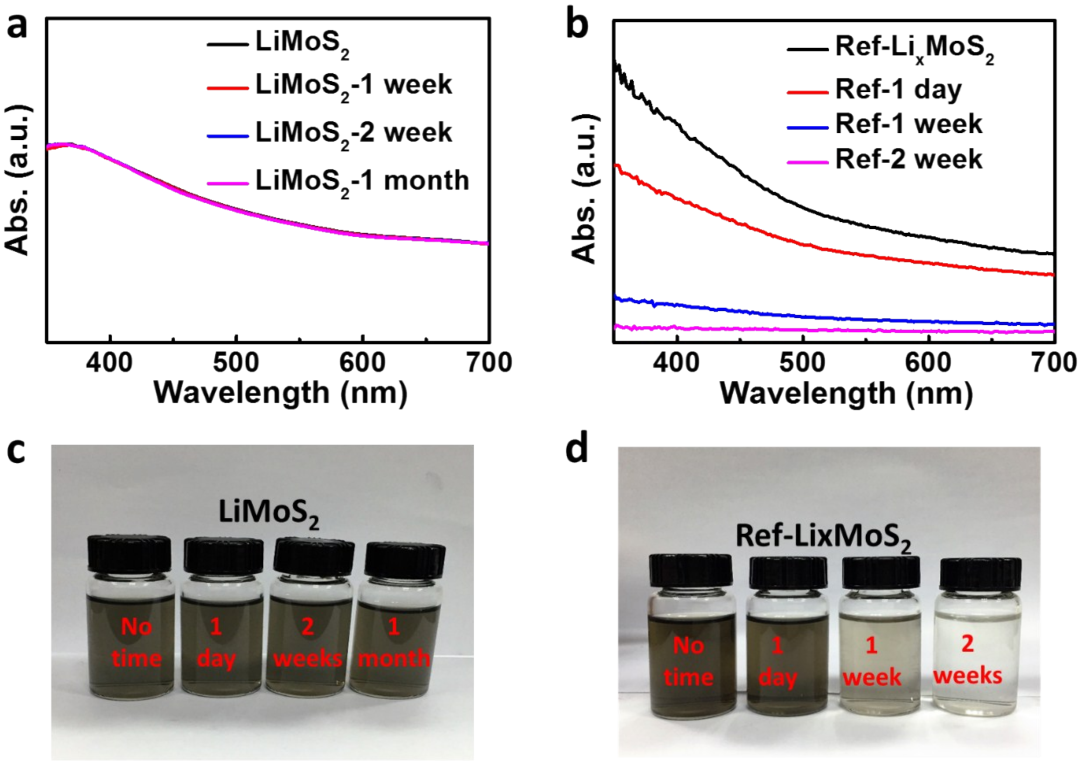


Figure S3. Absorption spectra of the MoS_2 nanosheets colloids prepared by $LiMoS_2$ crystals (a) and ref-Li_xMoS_2 (b) stored for different time; the photograph of colloids produced by the $LiMoS_2$ (c) and ref-LixMoS_2 (d) stored for different time.

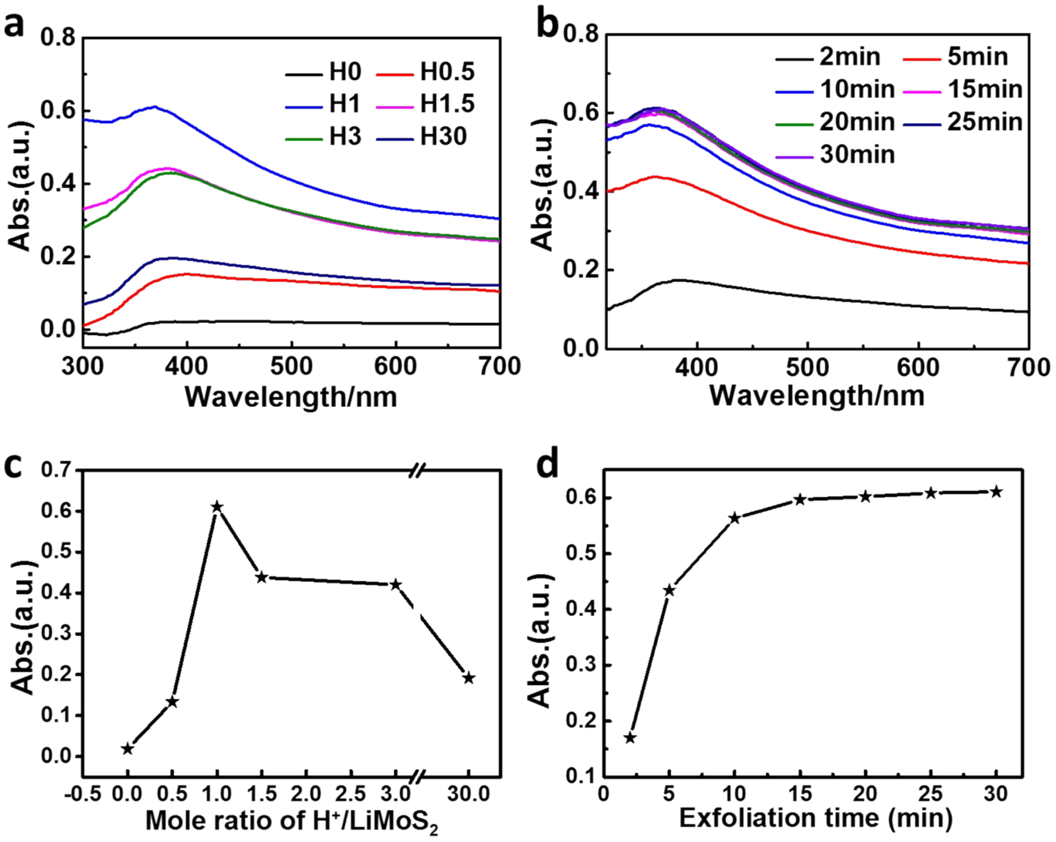


Figure S4. UV-Vis spectra (a) and corresponding absorption intensities (b) of nanosheets colloids prepared by various concentration of hydrochloric acid for 30 min (mole ratio of $H^+/LiMoS_2$ = 0, 0.5, 1, 1.5, 3, 30, respectively; wavelength of 370 nm); UV-Vis spectra (c) and corresponding absorption intensities (d) of colloids exfoliated for different time under condition of $H^+/LiMoS_2$=1 (the optimal acid concentration).

In a typical process, 5 mg $LiMoS_2$ powders were added into 200 ml deionized water with precisely controlled contents of hydrochloric acid. Then, the solution was stirred and sonicated for 30 min for exfoliation. The exfoliation effect of different ratios of $H^+/LiMoS_2$ was investigated. Along with the exfoliation of MoS_2 nanosheets, the color of the dispersion solution became darker, which was characterized by the UV-Vis spectra. As is shown in Figure S2a&c, the amount of hydrogen ion is a very significant factor in this process, and the optimal concentration is achieved when the mole ratio of hydrogen ions and $LiMoS_2$ is equal to 1:1. Without the addition of hydrogen ions, the $LiMoS_2$ crystals could almost not be exfoliated. This can be explained by the following equations:

$$LiMoS_2 + H^+ \rightarrow (MoS_2)_{\text{monolayers}} + Li^+ + H_2\uparrow$$

$$r(H_2)=k[Li_{\text{active}}]^x[H^+]^y$$

As we all know, one of the most significant driving force of exfoliation is from the generated hydrogen, which could separate the adjacent layers. Therefore, accelerating the hydrogen evolution reaction rate will boost the exfoliation. On the basis of chemical reaction kinetics, in order to increase the reaction rate, either $[Li_{\text{active}}]$ or $[H^+]$ should be increased. For ref-Li_xMoS_2, though the $[H^+]$ is very low (10^{-7}mol/L) in pure water, the $[Li_{\text{active}}]$ is large enough to drive the reaction to a high level. Hence the ref-Li_xMoS_2 can be exfoliated in deionized water without any additive agents, which is similar to results in other reports[1, 2]. However, the $[Li_{\text{active}}]$ for $LiMoS_2$ crystals is very low due to the exceptional stability of the material, so the reaction rate is too slow to boost the exfoliation in pure water. When hydrochloric acid is added, the rate of hydrogen evolution reaction is increased, thus benefiting the exfoliation. However, when the mole ratio of $H^+/LiMoS_2$ is more than 1:1, the exfoliation results turn worse. This may be because excessive hydrogen ions cause the agglomeration of the exfoliated edges of $LiMoS_2$ particles, thus inhibiting further exfoliation of the material.

Sonication time is also an important factor in the exfoliation process. As is shown in Figure 2b&d, the absorption spectra of the dispersion solution is enhanced as the exfoliation time prolongs. When the sonication time reaches 15 minutes, the solution has nearly turned into the darkest color, which means the exfoliation effect has reached the best point. With an excess of exfoliation time, the color of the solution changes little. After sonication, no obvious sediments were found in the dispersion solution. Hence, this acid-assisted method can exfoliate bulk materials into MoS_2 nanosheets in just 15 minutes.

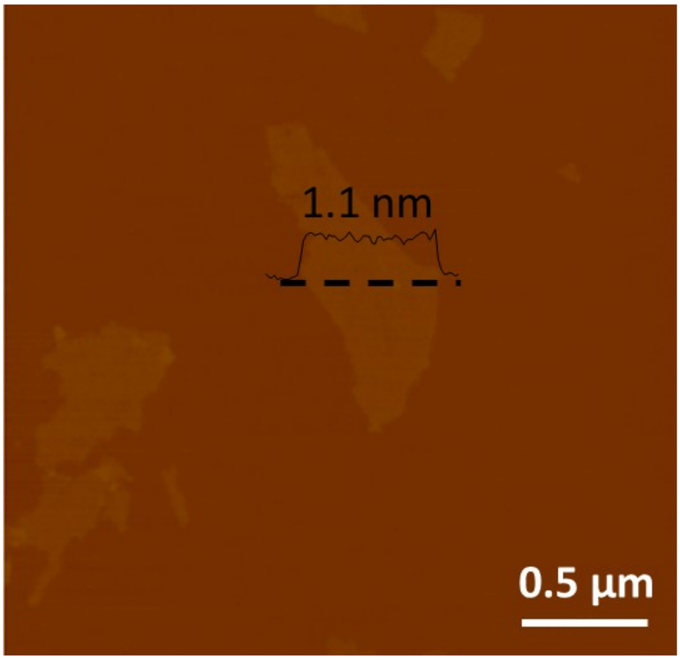


Figure S5. MoS_2 nanosheets prepared by n-butyl lithium method.

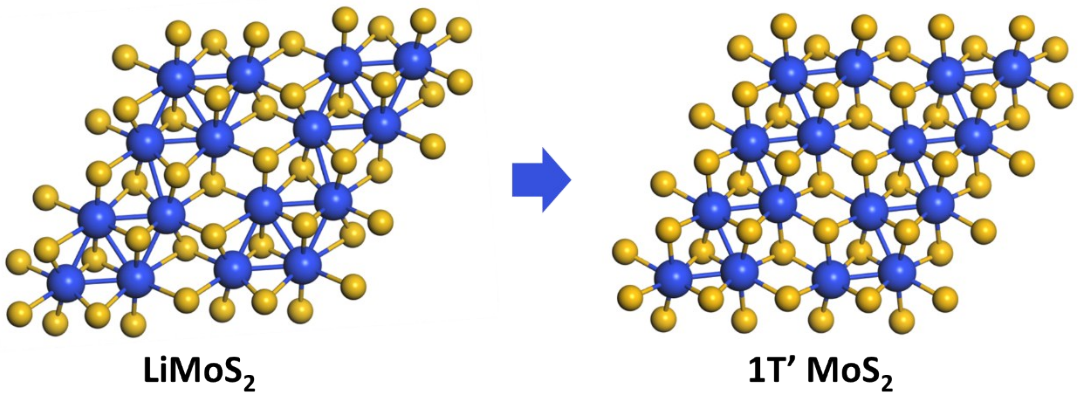


Figure S6. S–Mo–S unit layer in $LiMoS_2$ crystals and 1T’ MoS_2.

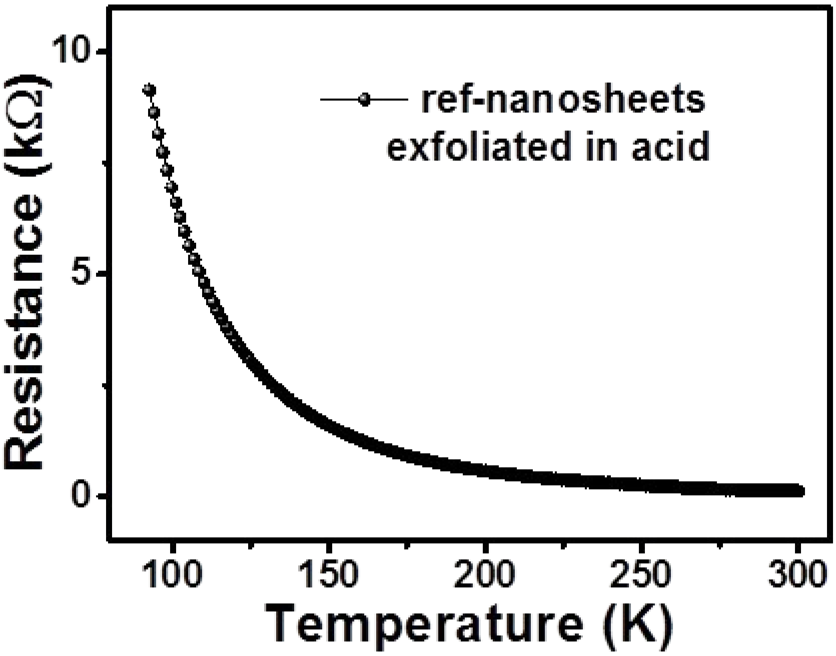


Figure S7. The temperature-dependence resistance of ref-nanosheets exfoliated in acid solution ($H^+/Li_xMoS_2=1$).

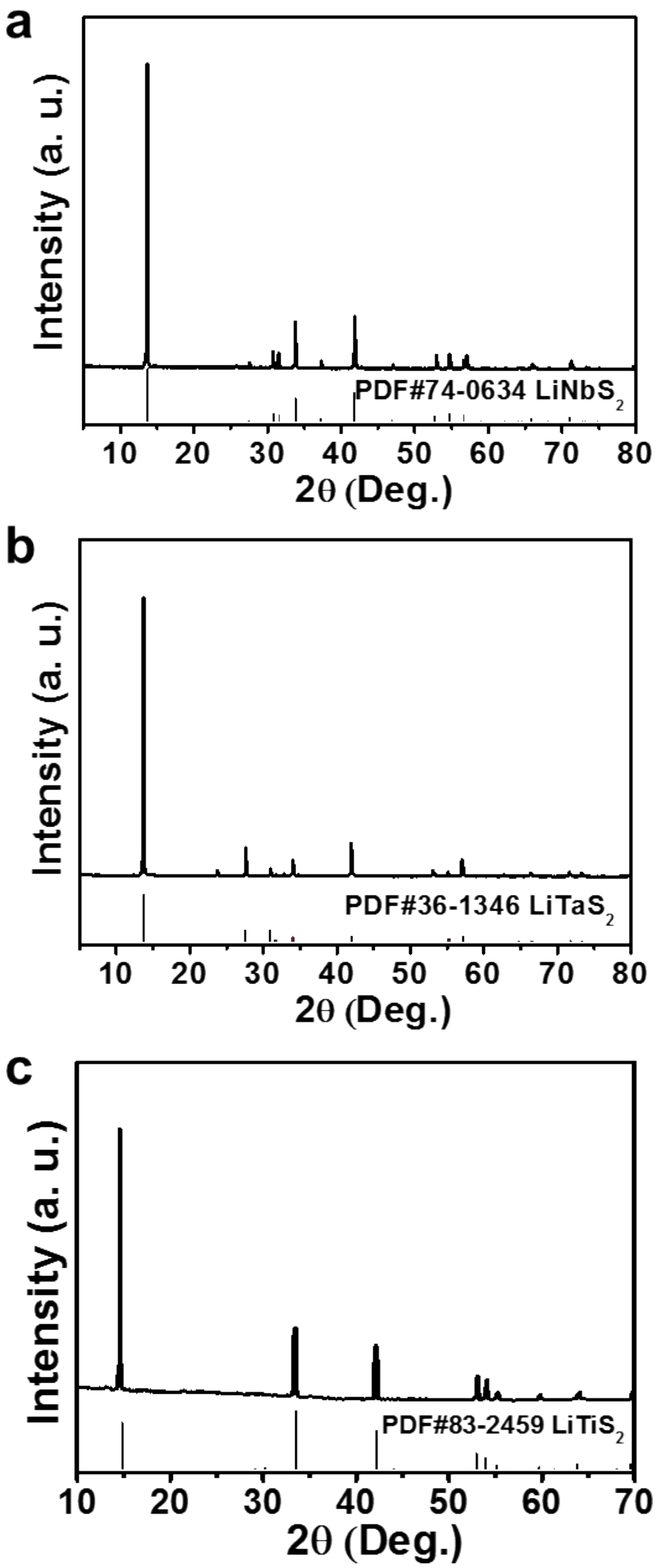


Figure S8. XRD of (a) $LiNbS_2$; (b) $LiTaS_2$; (c) $LiTiS_2$.

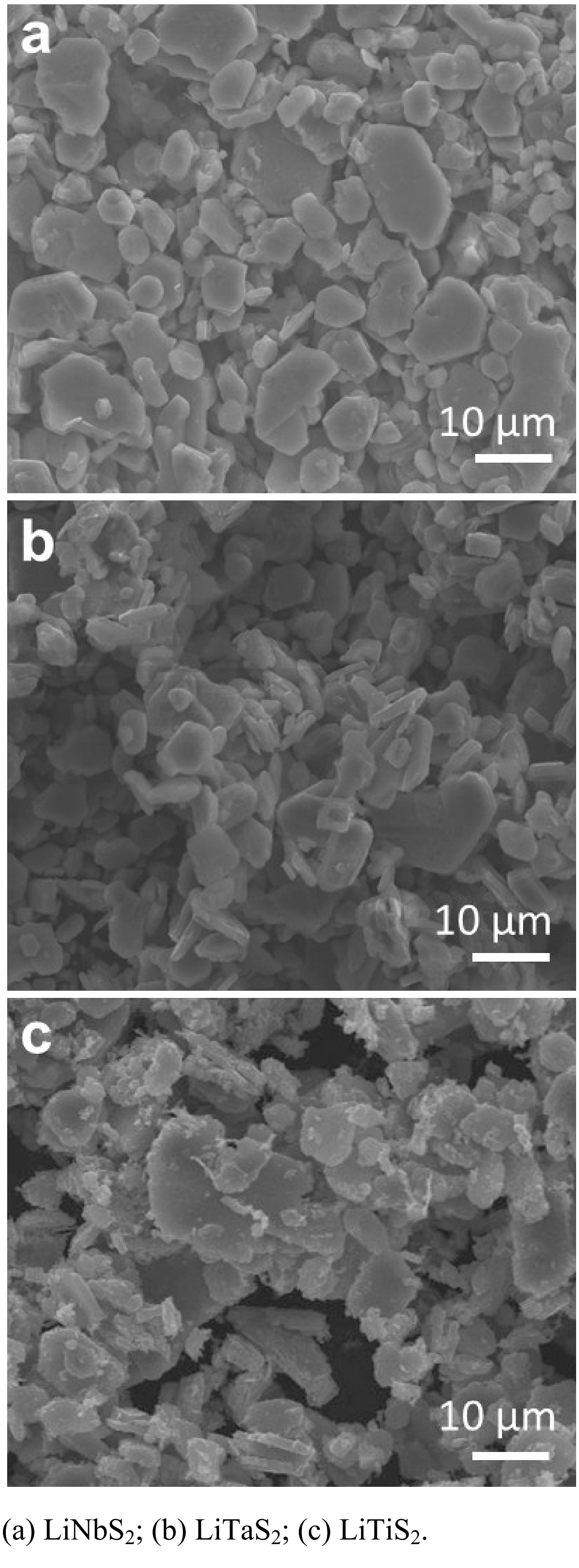


Figure S9. SEM of (a) $LiNbS_2$; (b) $LiTaS_2$; (c) $LiTiS_2$.

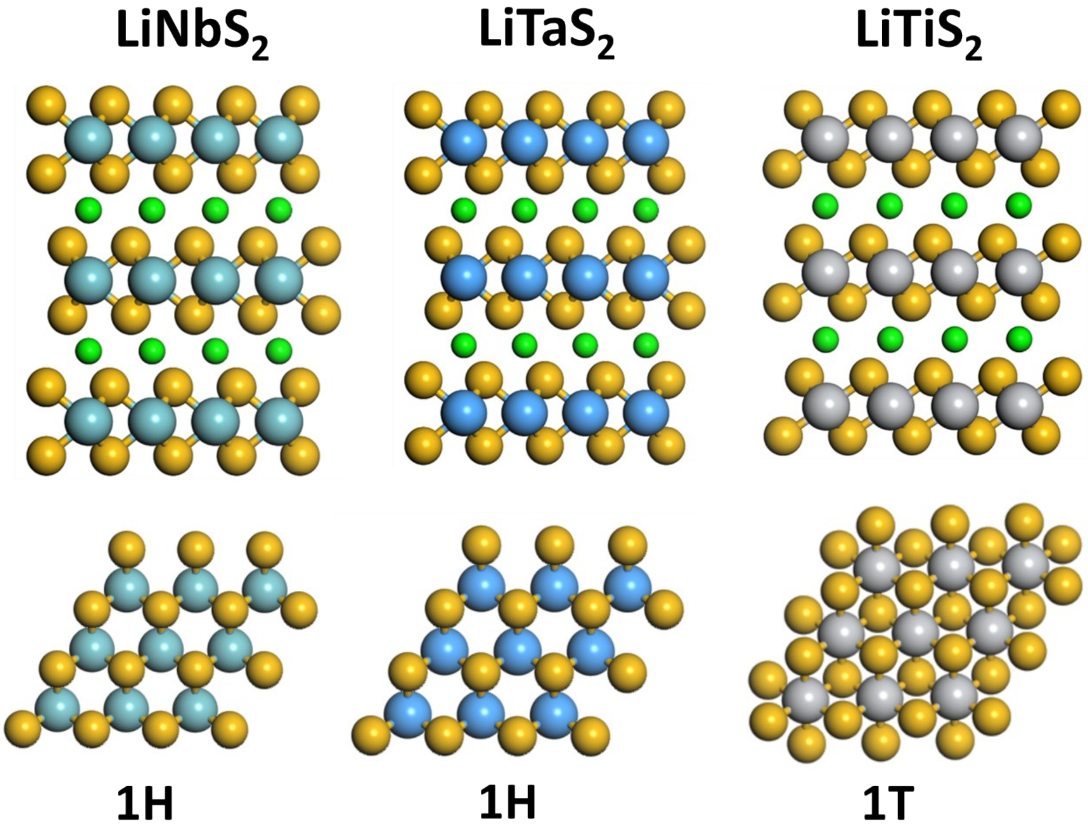


Figure S10. The structures of $LiNbS_2$, $LiTaS_2$ and $LiTiS_2$ crystals and their single layers.

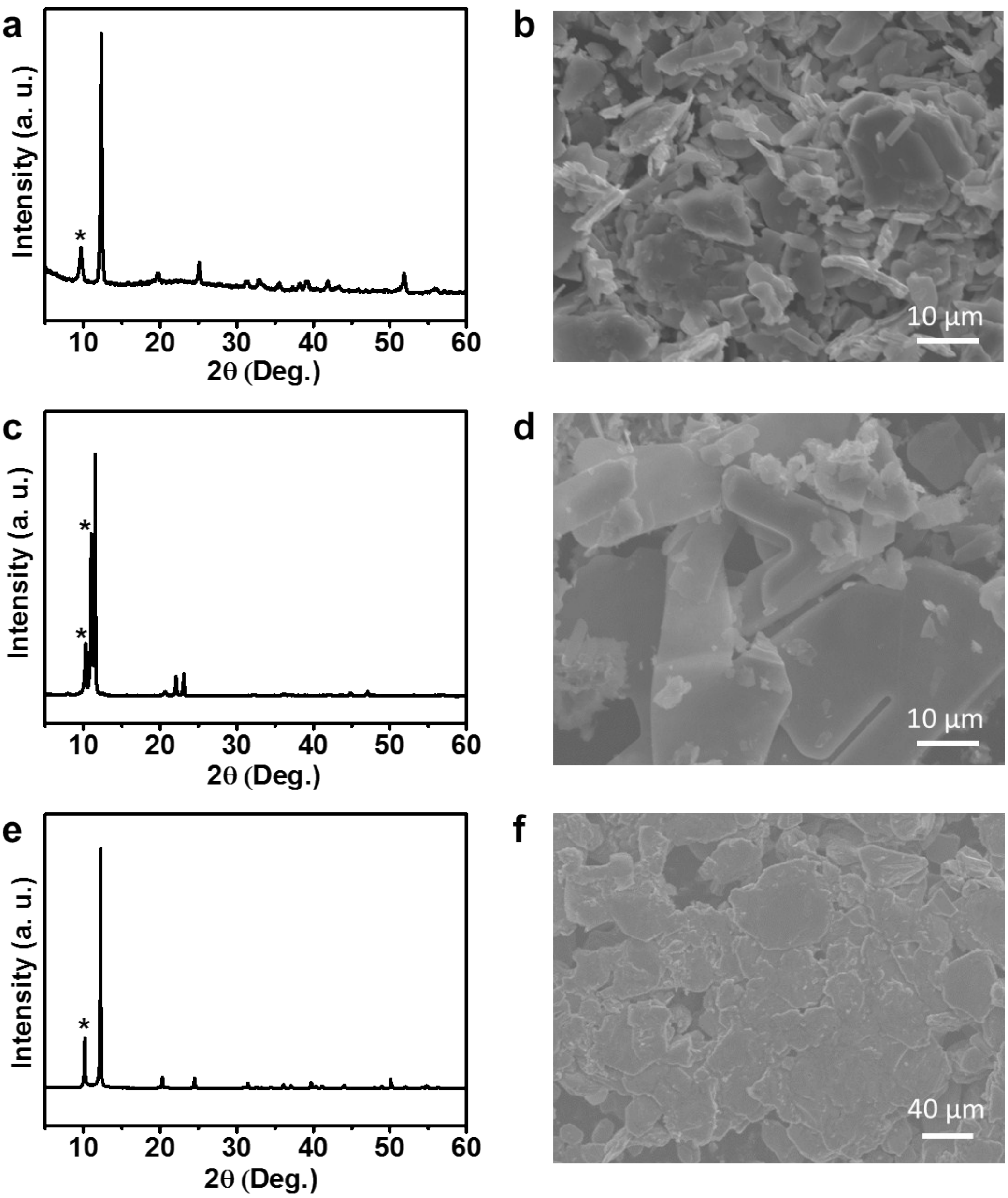


Figure S11. XRD of (a) $NaMoS_2$; (c) $KMoS_2$; (e) $NaNbS_2$; SEM of (b) $NaMoS_2$; (d) $KMoS_2$; (f) $NaNbS_2$; the peaks labeled with "*" are formed by the intercalation of H_2O into the interlayers of these layered compounds, which are very sensitive to moisture[3].

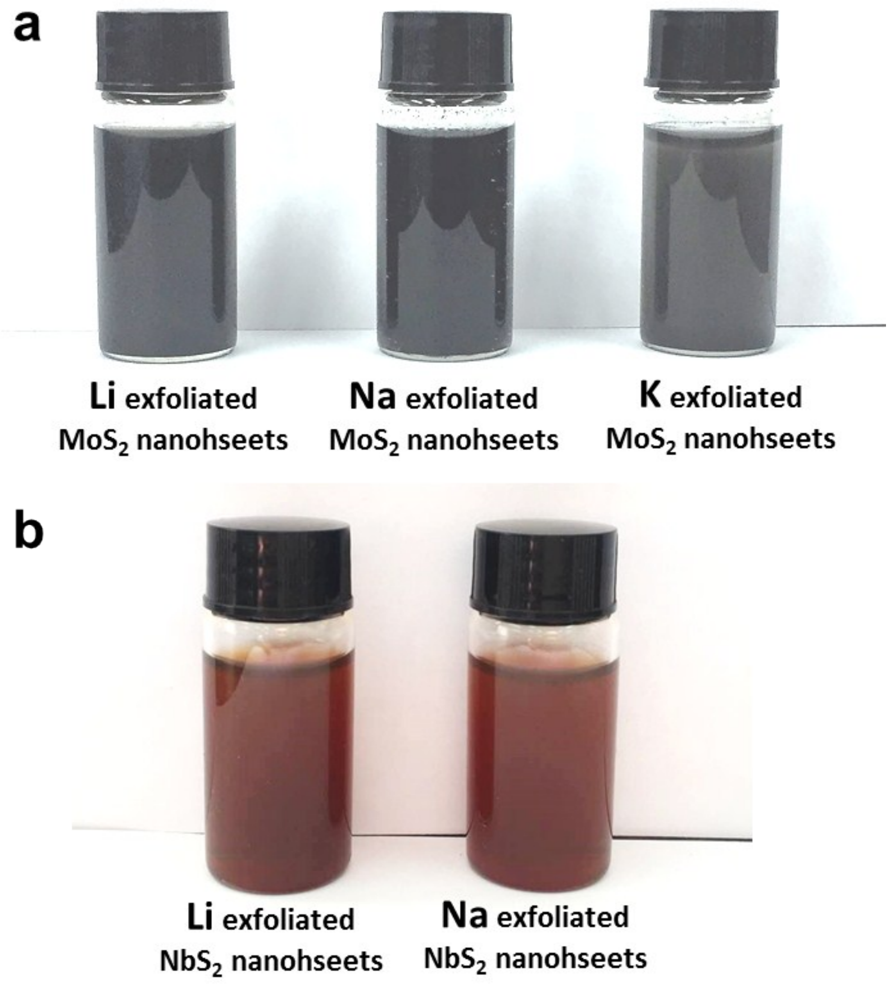


Figure S12. a. MoS_2 nanosheets obtained by $LiMoS_2$, $NaMoS_2$ and $KMoS_2$, respectively; b. NbS_2 nanosheets obtained by $LiNbS_2$ and $NaNbS_2$.

Among the three precursors, $LiMS_2$ is the best for exfoliation, while KMS_2 is the worst. The reason may be attributed to the biggest radius of the hydrated lithium ions, which are formed in the exfoliation process and separate the adjacent layers. This is different from the preparation of the transition metal oxide nanosheets, which are usually achieved by the intercalation of big ions, such as $Cs_{0.7}Ti_{1.825}O_4$[4], $K_4Nb_6O_{17}$[5], $RbTaO_3$[6] and so on.

Supplementary Tables

Table S1. Electrical conductivities of the anealed samples (S/cm)

Samples	**25 °C**	**100 °C**	**200 °C**	**300 °C**
MoS_2 nanosheets	**618**	**367**	**0.181**	**0.0562**
Ref-nanosheets	**35.4**	**0.551**	**0.00279**	**0.00302**

References

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