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Supplementary Information

Solution synthesis of few-layer 2H MX_2 (M=Mo,W; X= S,Se)

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Supplementary Figures

Figure S1 shows the O 1s, C 1s, and S 2p region of the XPS spectra for MoS_2 containing no HDD, 150 mM, and 500mM HDD in the precursor solution. Deconvolution of the O 1s XPS spectra of MoS_2 flakes synthesized without HDD reveals the presence of peaks attributed to oxides at 530.5 eV, and a second peak at 532.3 eV attributed to adsorbed oxygen species (OH^- or H_2O).[1] The 530.5 eV peak associated with oxide species decreased drastically when 150 mM HDD was used in the synthesis of the MoS_2 flakes and remained the same for 500 mM HDD. The peak attributed to chemisorbed oxygen remained constant for all synthesis conditions. The MoS_2 exhibited a strong peak at 284.8 eV from C- C and C-H bonds, likely due to hydrocarbon contamination from air exposure. Also, a small contribution from the carbon-oxygen bond at ~ 286 eV.[1] Since the C 1s XPS spectra stayed the same regardless of the HDD concentration, increasing HDD concentration did not increase the carbon content of the MoS_2, suggesting that the excess HDD was removed during the washing. The S 2p region of the spectra can be fitted to doublet peaks at 161.9 eV and 163.3 eV corresponding to S $2p_{3/2}$ and S $2p_{1/2}$ [2] and remained the same for all synthesis conditions.

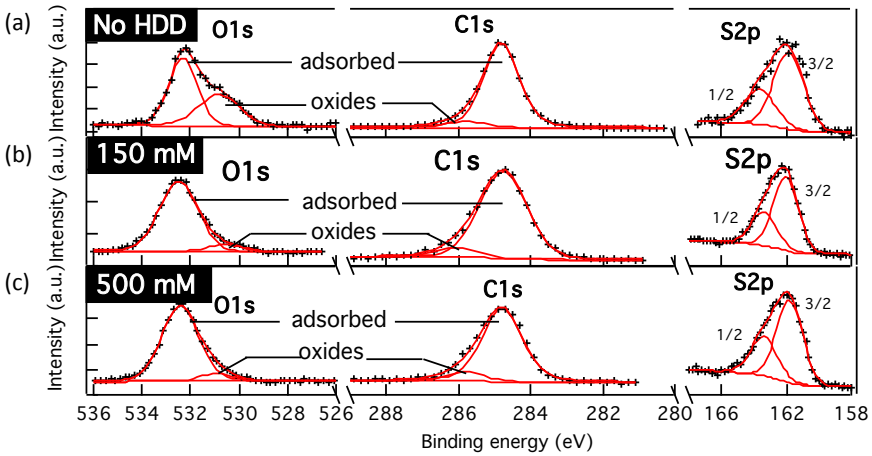

Fig. S1 O 1s, C 1s, and S 2p of XPS spectra for synthetized MoS_2 at different HDD concentrations: (a) No HDD, (b) 150 mM, and (c) 500 mM.

The O 1s and C 1s region of the XPS spectra for MoS_2, $MoSe_2$, WS_2, and WSe_2 synthetized using 150 mM HDD in the precursor solution are shown in Figure S2. The O 1s XPS spectra for all synthetized TMDs are similar, showing the prominent peak attributed to chemisorbed oxygen at 532.3 eV and a much weaker contribution of a peak associated with oxides at 530.5 eV. In the C 1s region, all TMDs exhibit a strong peak associated with hydrocarbon absorption. A small contribution from the carbon-oxygen bond can also be seen in MoS_2, $MoSe_2$, and WSe_2. In addition, $MoSe_2$ and WSe_2 showed a third peak at lower binding energies (~282 eV) assigned to a selenium Auger band.[3]

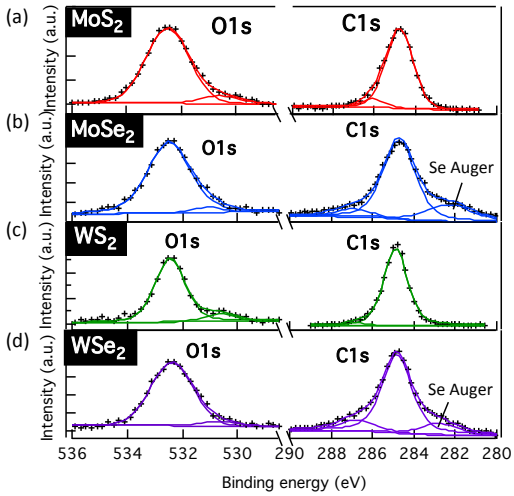

Fig. S2 O 1s and C 1s XPS spectra of synthetized TMDs using 150 mM HDD: (a) MoS_2, (b) $MoSe_2$, (c) WS_2, and (d) WSe_2.

Reaction yields were determined using thermogravimetric analysis (TGA). After synthesis, the suspensions were washed with 20 mL of anhydrous ethanol and the TMD flakes were precipitated by centrifugation at 10,000 rpm for 10 minutes. The solid product was redispersed in dichloromethane, vacuum filtered through a filter paper on a Büchner funnel, dried in an oven at 80 °C for 2 hours, and weighed. TGA in air yields a stable weight fraction at 600 – 700 °C corresponding to the metal oxide (MoO_3 or WO_3).[4] Thus, the equivalent mass of metal oxide in the dried solid product was calculated by multiplying the dried solid product mass with the oxide weight fraction from TGA. The quantity of metal in the product, which is equal to the quantity of TMD, was calculated by dividing the equivalent mass of metal oxide by the molecular weight of the metal oxide. Similarly, the quantity of metal in the precursor was determined by dividing the precursor mass by the precursor molecular weight. The yield was then calculated using the ratio of the two quantities multiplied by the M4+ fraction from XPS. We found a yield between 57-65% for the four TMD studied.

TGA of our TMD samples showed two transitions over the temperature range examined. Figure S3 shows the TGA data taken in air for MoS_2 as an example. The first transition begins at 270 °C, accompanied by mass loss of about 16%, and corresponds to evaporation of oleylamine solvent form the TMD surface. The second evident transition begins at ~450 °C, with a mass loss of 34 %, and corresponds to the complete thermal decomposition of the oleylamine molecules as well as the oxidation of MoS_2 to MoO_3. Similar TGA profiles have been reported for MoS_2 synthesized in oleylamine.[4] The weight loss at ~ 800 °C is due to evaporation of MoO_3.

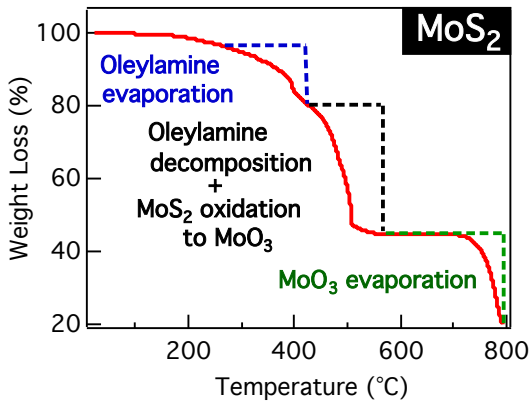

Fig. S3 TGA profile showing the weight loss of the synthesized MoS_2 flakes by heating in air. The temperature increasing rate is 8 °C/min.

The mass of TMD was calculated by multiplying the mass of the dried solid product times the weight fraction remaining at 600-800 °C, which is metal oxide (MoO_3 or WO_3), from TGA. The moles of metal in the TMD were determined by dividing the oxide mass by the oxide molecular weight. Similarly, the moles of metal in the precursor were determined by dividing the

precursor mass by the precursor molecular weight. The yield is then calculated using the ratio of the two numbers multiplied by the M^{4+} fraction from XPS.

Figure S4 shows an AFM topography image of small MoS_2 flakes. The thickness of these small particles was found to be three times higher than the large lateral size flakes. We believe that these thick flakes are small pieces of TMDs detached during the sonication for the sample preparation due to TMDs low tensile strengths.[5]

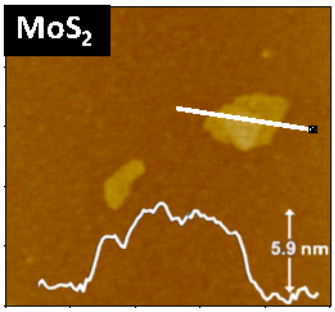

Fig. S4 1 x 1 µm AFM image of thick MoS_2 nanoflakes with small lateral size. Inset: Height profile taken along the white line in the AFM image.

Raman spectroscopy is used to probe the phase of few-layer TMDs. The peak positions for all materials are consistent with trigonal prismatic (2H) phase. The Raman spectra in Figure S5a depicts the in-plane E^1_{2g} and out-of-plane A_{1g} vibration modes of MoS_2 at 376 cm^{-1} and 402 cm^{-1}, respectively.[6] Fig. S5b confirms the typical out-of-plane A_{1g} vibration mode for $MoSe_2$ at 249 cm^{-1}.[7] Figure S5c shows E^1_{2g} and A_{1g} modes of WS_2 at 360 cm^{-1} and 424 cm^{-1}, respectively.[8] The E^1_{2g} and A_{1g} modes of WSe_2 cannot be distinguished and only a broad peak is observed at 255 cm^{-1} (Figure S5d).[7]

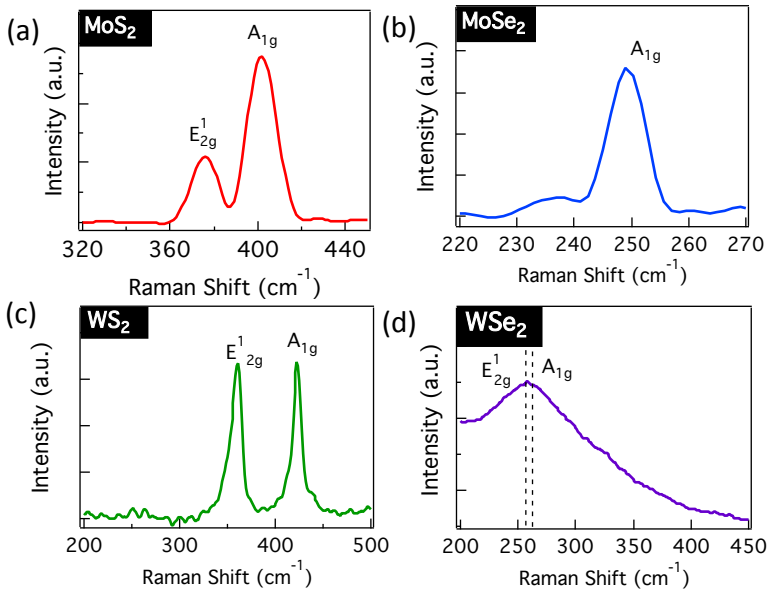

Fig. S5 Raman spectra of TMD films deposited on silicon substrates. (a) MoS_2, (b) $MoSe_2$, (c) WS_2 and (d) WSe_2.

To obtain insight of the electronic properties of these TMDs, work function (Φ) and ionization energy (IE) measurements were performed on TMD films drop casted on silicon. Table S1 summarizes Φ and IE values found on MoS_2, $MoSe_2$, WS_2, and WSe_2. The difference between Φ and IE for all synthesized TMDs was relatively small (< 0.2 eV), suggesting that these materials are p-type semiconductors.

Table S1 Work function and ionization energy of synthesized TMDs using 150 mM HDD

	Φ (eV)	**IE (eV)**
MoS_2	4.65 ± 0.03	4.74 ± 0.05
$MoSe_2$	4.63 ± 0.06	4.72 ± 0.05
WS_2	4.35 ± 0.08	4.53 ± 0.05
WSe_2	4.48 ± 0.03	4.66 ± 0.10

References

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