Supporting Information

Controlling the metal to semiconductor transition of MoS_2 and WS_2 in solution

Stanley S. Chou,[1,*] Yi-Kai Huang,[2] Jaemyung Kim,[2] Bryan Kaehr,[1] Brian M. Foley,[3] Ping Lu,[1] Conner Dykstra,[4] Patrick E. Hopkins,[3] C. Jeffrey Brinker,[1,4] Jiaxing Huang,[2,*] Vinayak P. Dravid [2,*]

[1] Advanced Materials Laboratory, Sandia National Laboratories, Albuquerque, NM 87185 (USA)

[2] Department of Materials Science and Engineering, International Institute of Nanotechnology, Northwestern University, Evanston, IL 60208 (USA)

[3] Department of Mechanical and Aerospace Engineering, University of Virginia, Charlottesville, VA 22904 (USA)

[4] Department of Chemical and Biomolecular Engineering Center for Micro-engineered Materials, University of New Mexico, Albuquerque, NM 87106 (USA)

Experimental Methods

Materials and Supplies. n-Butyl lithium in hexane (1.6 M), hexane, ODCB, octadescene, oleylamine and WS_2 powder were purchased from Sigma Aldrich, USA. MoS_2 powder (≈30 μm) was purchased from Rose Mill Materials Processing, USA.

MX_2 Exfoliation. Lithium intercalation of MoS_2 was carried out by stirring 1 g of MoS_2 in 10 ml of 0.8 M n-butyl lithium at room temperature, under Ar atmosphere. After 3 days, the mixture was filtered and washed with hexane. Immersing the Li intercalated compounds in water with sonication then induces exfoliation of individual sheets. First purifications were performed using two rounds of centrifugation at 25,000 g and redispersion of the soft pellets in water. Large aggregates were then removed by centrifugation at 500 g. The resulting mixture was then dialysed for three additional days against running water. A final round of centrifugation at 500 g removes aggregates. Intercalation and exfoliation of WS_2 was similarly performed, except intercalation was conducted at 100 ^oC.

Inductively coupled plasma mass spectrometry (ICP-MS). ICP-MS specimens were prepared by adding fixed aliquots (2.5 to 50 µl) of MoS_2 (or WS_2) to 100µl of HNO_3 (trace grade). Mixture digested at 75 ^oC for 6 hours. 25 µl of ICP-MS internal standard solution was added to each sample., Samples were diluted to 5 ml using di-H_2O. External standards were prepared using Mo standard solution from Sigma Aldrich. Accuracy of external standard preparation was checked by linear regression of ICP-MS signal ($R^2 > 99.999$). Mo concentration of undiluted specimen was then determined by using the dilution factor described above. Mass of MoS_2 in solution was estimated by taking formula weight ratios of MoS_2 versus Mo.

Transfer into Organic Solvents. A biphasic mixture was formed in a separation flask consisting of the organic solvent (e.g. ODCB) spiked with 2.5% oleylamine in one phase, and chemically exfoliated MX_2 sheets in water in the other. The mixture was vigorously shaken, and then allowed to separate for 2h. The process was repeated until the sufficient quantities are transferred. The organic portion was then collected, and residual water removed under vacuum.

Solution Annealing. MoS_2 and WS_2 sheets in organic solvent were transferred to a three-neck flask with a condenser column. While stirring at 150 rpm, the mixture was then purged of air using N_2 or Ar (> 30 m). Heating rate of ≈ 10^o C/min was used to reach the desired annealing temperature. Annealing temperature was held for 4 h, with stirring and under computer monitoring. After annealing, large aggregates were removed by low speed centrifugation at 50 rcf. Later, the remaining mixture was twice washed via centrifugation at 5000 rcf, and redispersed in hexane with 2.5% oleylamine or octadescene/ODCB-Hexane with 2.5% oleylamine.

Unsupported MoS_2 film preparation. MX_2 specimens were filtered over aluminum oxide (AO) membranes with 0.2 µm pores. The resulting film was then delaminated from the filter by gently flexing the AO membrane until the film lifts-off.

Characterization. Samples were prepared by diluting MoS_2 samples to the point of faint color (c.a. 0.05 mg/ml) and then dropping onto ultrathin carbon grids (3 nm carbon backing, Ted Pella). A FEI Titan G2 80-200 STEM with a Cs probe corrector was used for the STEM imaging. Raman and photoluminescent spectra were acquired using a Acton TriVista CRS Confocal Raman System (Princeton Instruments, USA) with λ = 514 nm laser excitation. SEM images were obtained using a LEO Gemini 1525. The XPS spectra were acquired using a Thermo Scientific ESCALAB 250 Xi.

XPS Analysis. Samples were prepared by filtering solution over anodisc filters (Whatman, 0.2 um pores), and washed with hexane. The sample was delaminated from the anodisc, and transferred onto freshly cleaned substrates (Si or SiO_2). Spectra were calibrated using C sp^2 at 284.6 eV. Symmetrical Gaussian peaks were used for fittings. 2H (semiconducting phase) peak positions were obtained from freshly cleaved single crystalline samples. 1T' positions were determined from the shifted peak positions observed with freshly exfoliated samples, with 2H peaks subtracted. Remaining spectra were fitted with positions determined from the aforementioned methods, which are also summarized in Table S1. In brief, Mo spectra were fitted by positioning 1T' Mo 3d5/2 at 228.1 eV and 2H Mo 3d 5/2 at 229.1 eV. Doublets in the form of Mo 3d 3/2 were positioned at 3.15 eV higher than the 5/2 peaks. Oxidized Mo peaks were fitted by positioning Mo 3d3/2 at 355.4 eV (the more clearly delineated peak), and Mo 3d5/2 at 3.15 eV lower than the 3d3/2 peak. Peak height of Mo 3d3/2 was constrained based on known height ratio, 0.69 of the 3d5/2 height, and the same FWHM. S spectra were fitted by assigning S 2P3/2 peaks at 161.9 and 160.9 eV for 2H and 1T' respectively. The doublet, S 2P1/2, was assigned at 1.16 eV higher than the 2P3/2, and constrained based on known height ratio, to 0.511 of 2P3/2, with the same FWHM. Reported phase compositions in the primary text were calculated using the Mo spectra (Mo 3d5/2), which is more defined. Phase compositions calculated from S spectra corroborates Mo calculations. Both are summarized in table S2.

	Peak Position	Comment
MoOx Mo 3d3/2	235.4 ± 0.4	N/A
MoOx Mo 3d5/2	232.3 ± 0.4	Constrained: Peak = 3d3 - 3.15 eV, Height = 3d3 ÷ 0.69, FWHM = 3d3
2H Mo 3d5/2	229.1 ± 0.1	N/A
2H Mo 3d3/2	Doublet	Peak = 3d5 + 3.15 eV (+0.2, -0.1), Height = 3d5*0.69, FWHM = 3d5
1T Mo 3d5/2	228.1 ± 0.1	N/A
1T Mo 3d3/2	Doublet	Peak = 3d5 + 3.15 eV (+0.2, -0.1), Height = 3d5*0.69, FWHM = 3d5
2H S2p3/2	161.9 ± 0.1	N/A
2H S2p1/2	Doublet	Peak = 2p3 + 1.16 eV (±0.1), Height = 2p3*0.511, FWHM = 2p3
1T S2p3/2	160.9 ± 0.1	N/A
1T S2p1/2	Doublet	Peak = 2p3 +1.16 eV (±0.1), Height = 2p3*0.511, FWHM = 2p3

Table S1. Summary of peak positions for XPS analysis

Quantification Method /	25 ^{o}C	75 ^{o}C	150 ^{o}C	300 ^{o}C
Mo 3d5/2	23.9 ± 7.8	32.3 ± 0.62	78.3 ± 6.2	89.2 ± 2.7
S 2P3/2	28.6 ± 9.2	51.5 ± 10.7	88.4 ± 9.5	96 ± 3.2

Table S2. 2H phase %, as calculated from Mo and S XPS spectra.

Processing	MoOx %
25 ^{o}C	7.2 ± 6.7
75 ^{o}C	10.9 ± 2.1
150 ^{o}C	10.7 ± 2.4
300 ^{o}C	7.4 ± 1.1
Single Crystal Reference	6.6 ± 1.2

Table S3. Oxidative content as calculated using Mo3d5 ratios for different specimens.

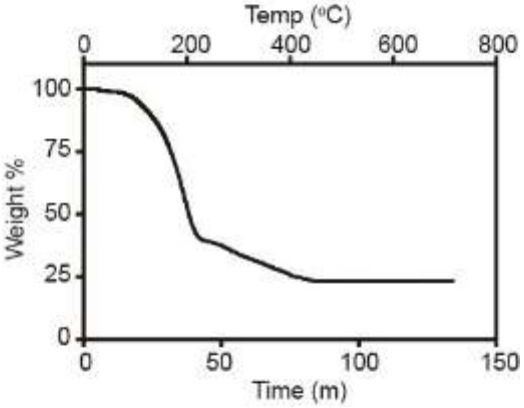

Figure S1. Thermogravimetric analysis (TGA) of MoS_2-ligand complex. Samples were prepared by transferred from water into chloroform using procedure described in the main text. Excess ligands were removed by two rounds of centrifugation and washing. After solvent evaporation, mixture were transferred into an alumina crucible and heated under Ar at a ramp rate of 5 ^{o}C/m. TGA results show 1:3 MoS_2 to ligand to mass ratio.

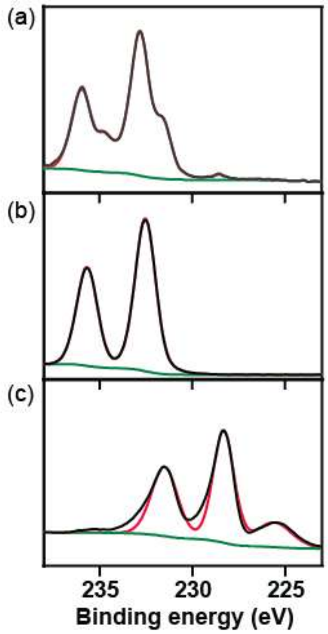

Figure S2 XPS spectra of Mo in (a) MoS_2 annealed in tetraethylene glycol at 150 ^oC. Annealing in other ethylene glycol solvents yielded similar results. (b) MoO_3 spectra as reference (c) As exfoliated MoS_2. Samples annealed in tetraethylene glycol and other glycols oxidize MoS_2 sheets at elevated temperatures. Resulting spectra thus resembles MoO_3 and other oxidized Mo species.

To facilitate optical characterization on individual sheets, a sheet of > 100 μm^2 was required due to optical probe size limitations. Large sheets such as these are atypical of chemically exfoliated materials. Nevertheless, retrieval of a large sheet was performed by dipping hydrophobic Si functionalized with octadecyltrichlorosilane into dilute solution of annealed sheets. The chips were then rinsed with hexane to remove ligands and loosely bound material. Figure S3 shows the characterization of a large sheets with a thickness of ~3.5 nm (3 – 5 monolayers)[19] with laterial dimensions that is compatible with the optical probe size. The Raman peaks characteristic of the 2H phase were again observed, suggests successful conversion metal to semiconductor transition.. Raman peak indicate 4 - 5 layers in thickness.[19] Photoluminescence characterization with 514 nm laser excitation demonstrated emission at λ ~ 680 nm, which is the band gap for thin-layered 2H MoS_2 (Eg ~ 1.8 eV).[7a, 20]

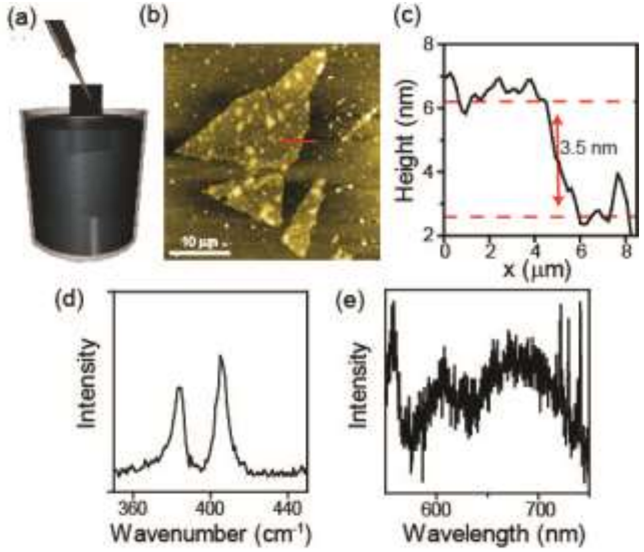

Figure S3 Characterization of individual sheets after annealing. (a) Illustration of dip coating process to capture sheets. (b) A large sheet from the dip coating process. (c) AFM profile, (d) Raman spectra and (e) photoluminescence spectra from the sheet.

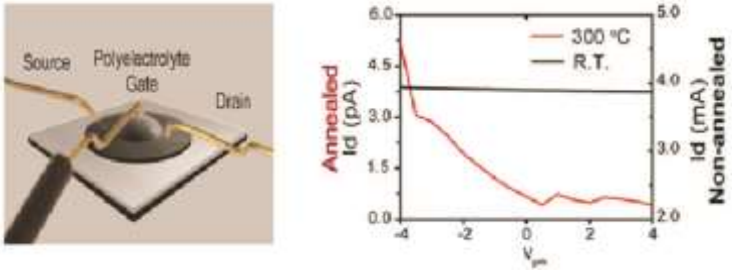

Figure S4 Transistor response: Annealed (left y-axis, pA) and non-annealed (right y-axis, mA).

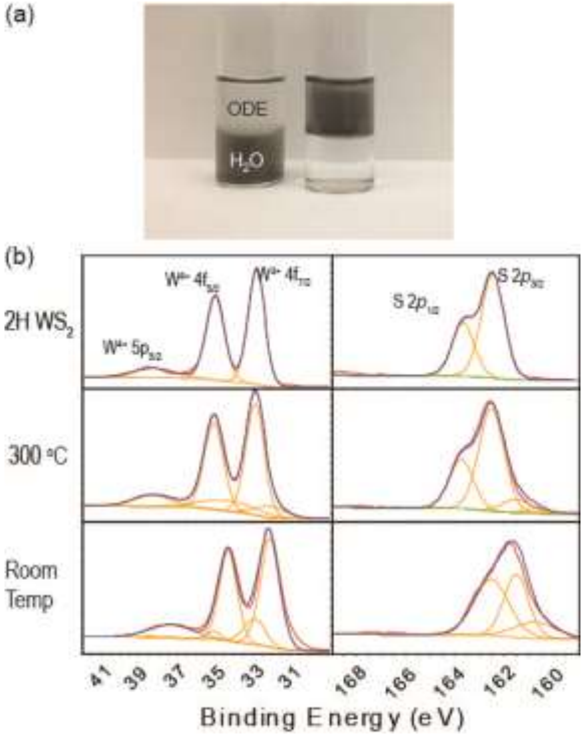

Figure S5 (a) Phase transfer of chemically exfoliated WS_2 from water in to octadecene (b) XPS spectra of different WS_2 samples with and without annealing. Similar to MoS_2, chemical exfoliation signatures indicative of the metallic phase were converted to the semiconducting phase using elevated solution temperatures.