

Supporting Information

Seed Crystal Homogeneity Controls Lateral and Vertical Heteroepitaxy of Monolayer MoS₂ and WS₂

*Youngdong Yoo, Zachary P. Degregorio, James E. Johns**

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, United States.

* Please address correspondence to jjohns@umn.edu.

Synthesis of ultraclean and particle-decorated MoS₂ monolayers

Synthetic details of in-plane and vertical WS₂/MoS₂ heterostructures

Transfer of WS₂/MoS₂ heterostructures onto a TEM grid

Characterization (STEM, TEM, AFM, KPFM, Raman, PL, and SEM measurements)

Figure S1: High-resolution AFM height image of monolayer MoS₂ grown with hydrogen

Figure S2: Raman spectra and Lorentz fitting results for monolayer MoS₂

Figure S3: SEM images of monolayer MoS₂ grown with and without hydrogen

Figure S4: PL spectra of in-plane heterostructures taken under a laser excitation of 514.5 nm

Figure S5: Raman peak position mapping of in-plane heterostructures.

Figure S6: AFM friction image of the same flake shown in Figure 2g

Figure S7: KPFM data of in-plane heterostructures.

Figure S8: HAADF-STEM images of vertical heterostructures

Figure S9: Vertical heterostructures synthesized under low flux conditions.

Synthesis of ultraclean and particle-decorated MoS₂ monolayers

Ultraclean MoS₂ monolayers were synthesized in a horizontal hot-wall single-zone tube furnace, equipped with a vacuum pump and mass flow controllers. An alumina crucible (50 x 20 x 20 mm, MTI Corporation) containing 400 mg of MoO₃ powder (99.999 %, Acros Organics) was placed at the center of the furnace in a 3-inch diameter quartz tube. A c-cut sapphire substrate (MTI Corporation) was placed polished-face-up on an upside-down alumina crucible, which was placed directly next to the crucible containing MoO₃ powder. 800 mg of sulfur powder (99.999%, Alfa Aesar) was located upstream. After the tube was evacuated to less than 100 mTorr, Ar and H₂ gas were supplied at rates of 20 and 4 sccm (standard cubic centimeters per minute), respectively. The reaction was carried out under atmospheric pressure. The MoO₃ was heated to 710 °C at a rate of 22 °C/min and kept at 710 °C for 5 min. The temperature of sulfur powder was measured to be approximately 280 °C. After the reaction, Ar gas was supplied at a rate of 200 sccm to purge any sulfur vapors and the furnace was rapidly cooled down by opening the lid of the furnace. The experimental conditions for the synthesis of the MoS₂ monolayers decorated with particles are the same as those for the synthesis of ultraclean MoS₂ monolayers except that no H₂ gas is used.

Synthetic details of in-plane and vertical WS₂/MoS₂ heterostructures

To synthesize WS₂/MoS₂ heterostructures, monolayer MoS₂ grown on c-cut sapphire was used as a substrate. 500 mg of WO₃ powder (99.998 %, Alfa Aesar) was placed at the center of the furnace in a 2-inch diameter quartz tube. The substrate was placed a few centimeters downstream from the center, and sulfur powder was located upstream. Ar and H₂ gas were introduced at rates of 60 and 5 sccm, respectively, maintaining a chamber pressure of 350 mTorr during the growth.

The WO_3 powder was heated to 1050 °C at a rate of 11 °C/min and kept at 1050 °C for 5 min. The temperatures of the substrate and sulfur powder were measured to be about 940 °C and 160 °C, respectively. The furnace was rapidly cooled down after the reaction. In-plane WS_2/MoS_2 heterostructures were synthesized when ultraclean monolayer MoS_2 was used as a substrate, while vertical WS_2/MoS_2 heterostructures were synthesized when the monolayer MoS_2 decorated with particles was used as a substrate.

Transfer of WS_2/MoS_2 heterostructures onto a TEM grid.

A 5 % solution of poly(methyl methacrylate) (PMMA) (MW ~996000, Sigma-Aldrich) in anisole was spin coated onto WS_2/MoS_2 heterostructures grown on a c-cut sapphire substrate at 3000 rpm for 1 min. After coating, the sample was baked at 50 °C for 10 min. The underlying sapphire substrate was etched in a 30 % aqueous solution of KOH (Fisher Scientific) for several hours, and then the WS_2/MoS_2 heterostructures/PMMA film was rinsed in deionized water and transferred onto a TEM grid. To remove PMMA residue, the TEM specimen was cleaned with dozens of drops of acetone and then annealed at 350 °C with 100 sccm of H_2 gas and 100 sccm of Ar gas at atmospheric pressure.

Characterization (STEM, TEM, AFM, KPFM, Raman, PL, and SEM measurements)

Scanning transmission electron microscopy (STEM) imaging was carried out using an aberration-corrected FEI Titan G2 TEM operated at an accelerating voltage of 60 kV. Before STEM imaging, TEM specimens were annealed at 160 °C for 4 hours under vacuum to avoid hydrocarbon contamination. TEM, HRTEM, and SAED patterns were taken on FEI Tecnai G2 F30 TEM operated at an accelerating voltage of 300 kV. AFM data were taken in contact mode

on a Bruker Nanoscope V Multimode 8 SPM using silicon tips having nominal force constant of 0.60 N/m. KPFM measurements were performed using a Bruker SCM-PIT probe possessing a Platinum-Iridium coated, electrically conductive tip which has a tip radius of about 20 nm. Raman and PL spectra and the mapping were acquired using a 632.8 nm laser excitation focused through a 100x objective lens with a power of 30 μ W at room temperature. SEM images were taken on a JEOL JSM-6500F SEM operated at an accelerating voltage of 5 kV.

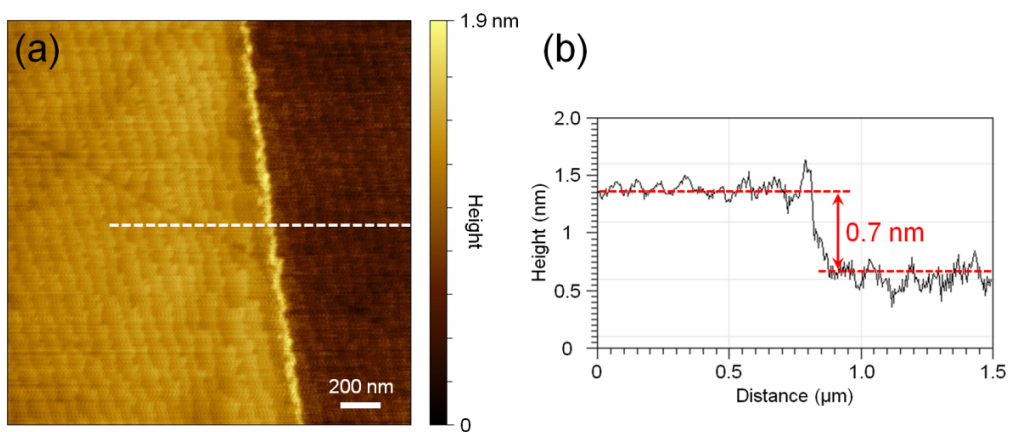


Figure S1. (a) High-resolution AFM height image of monolayer MoS₂ grown with hydrogen. (b) Height line profiles along the dotted white line in (a).

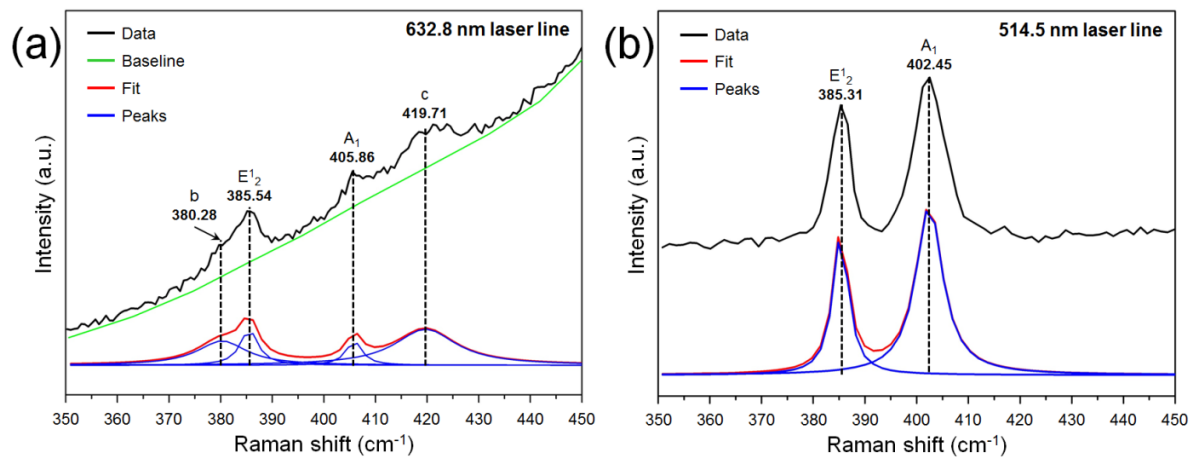


Figure S2. Raman spectra and Lorentz fitting results for monolayer MoS₂. (a) Raman spectrum of a monolayer MoS₂ flake excited by a HeNe laser at 632.8 nm. (b) Raman spectrum of a monolayer MoS₂ flake excited by an Ar⁺ ion laser at 514.5 nm.

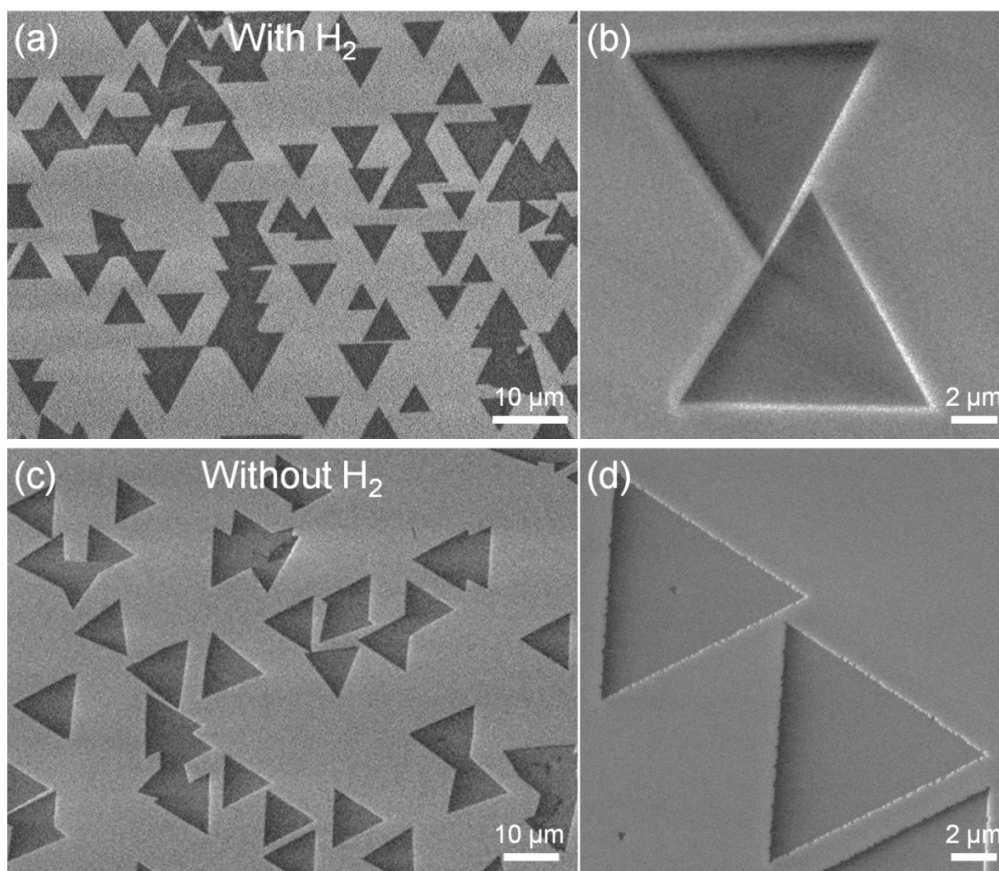


Figure S3. SEM images of monolayer MoS₂ grown (a,b) with and (c,d) without hydrogen, respectively.

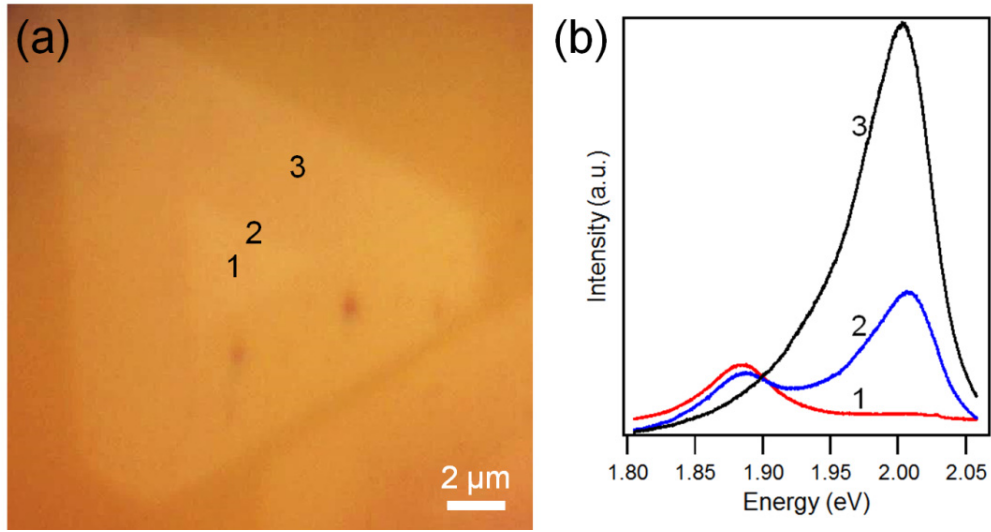


Figure S4. (a) Optical microscope image of in-plane WS₂/MoS₂ heterostructures. (b) PL spectra excited by an Ar⁺ ion laser at 514.5 nm taken from the points marked by 1-3 in (a). Both values of the full width at half maximum (FWHM) for PL peaks of MoS₂ and WS₂ obtained from the in-plane heterostructure are calculated to be in the range of 0.06 to 0.07 eV, consistent with previous reports of high-quality monolayer MoS₂ and WS₂ [*Nano Lett.* 2013, 13, 3447-3454].

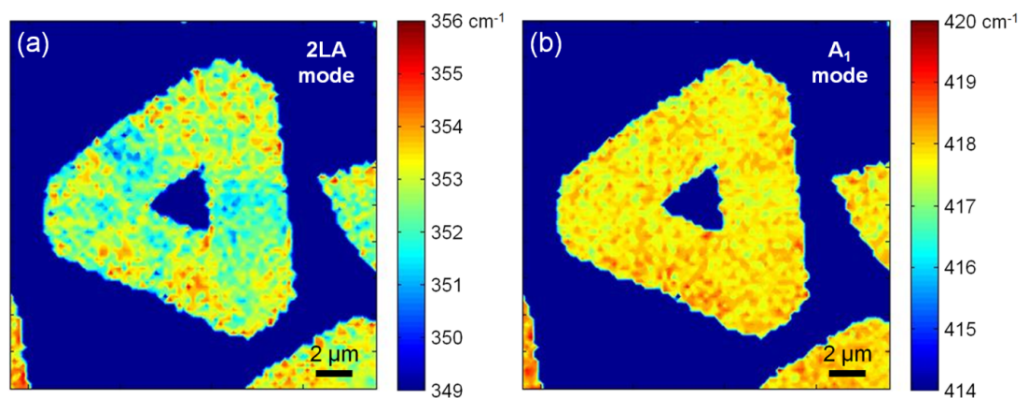


Figure S5. (a, b) Raman peak position mapping at the 2LA and A₁ modes of WS₂ from in-plane heterostructures, respectively.

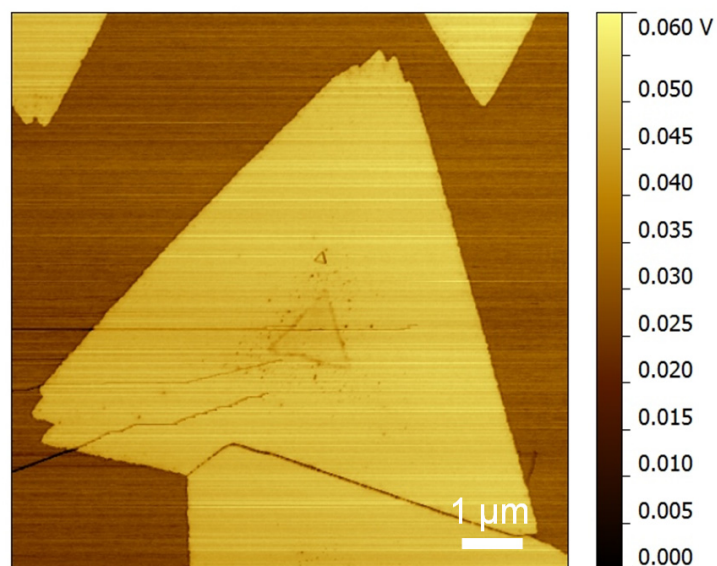


Figure S6. AFM friction image of the same WS₂/MoS₂ flake shown in Figure 2h. The height and friction images were acquired simultaneously. The boundary of the interior MoS₂ is clearly visible.

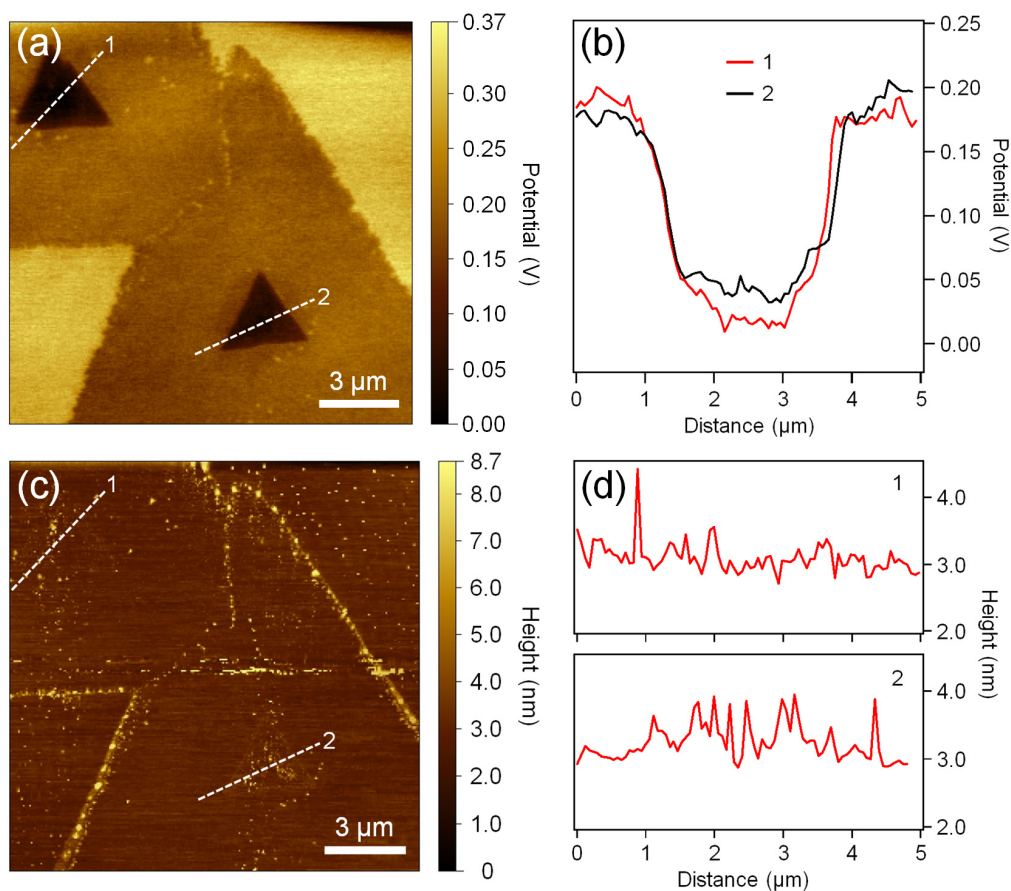


Figure S7. (a) KPFM surface potential image of in-plane heteroepitaxial WS₂-MoS₂ monolayers. The distinct contrast between the inner triangles of MoS₂ and the outer ribbons of WS₂ indicates that clear surface potential differences exist across the lateral junction, confirming as-synthesized heterostructures have high-quality lateral junctions. (b) Surface potential line profiles along the dotted white lines in (a). (c) Height image of the same flakes, which was acquired simultaneously. (d) Height line profiles along the dotted white lines in (a).

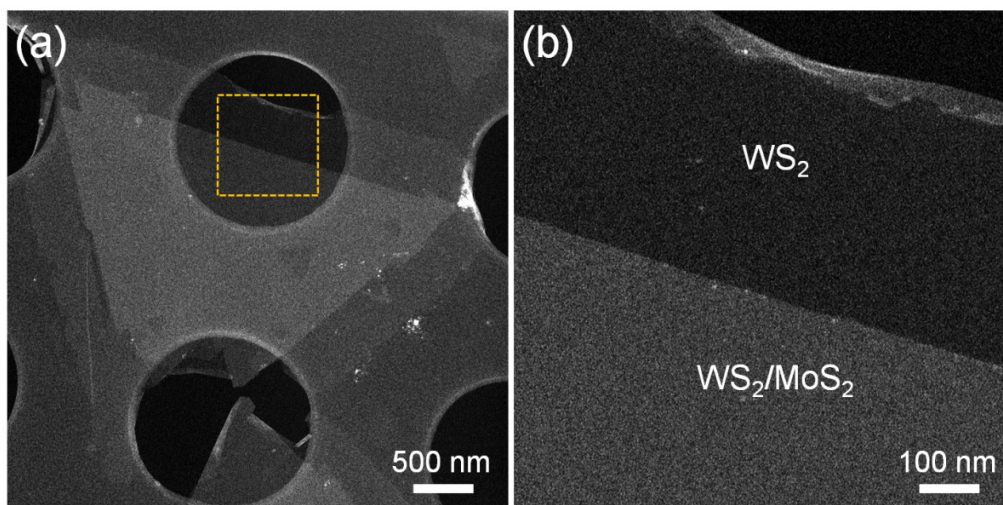


Figure S8. (a) HAADF-STEM image of vertical WS_2/MoS_2 heterostructures. (b) Magnified image of the orange dotted square of (a).

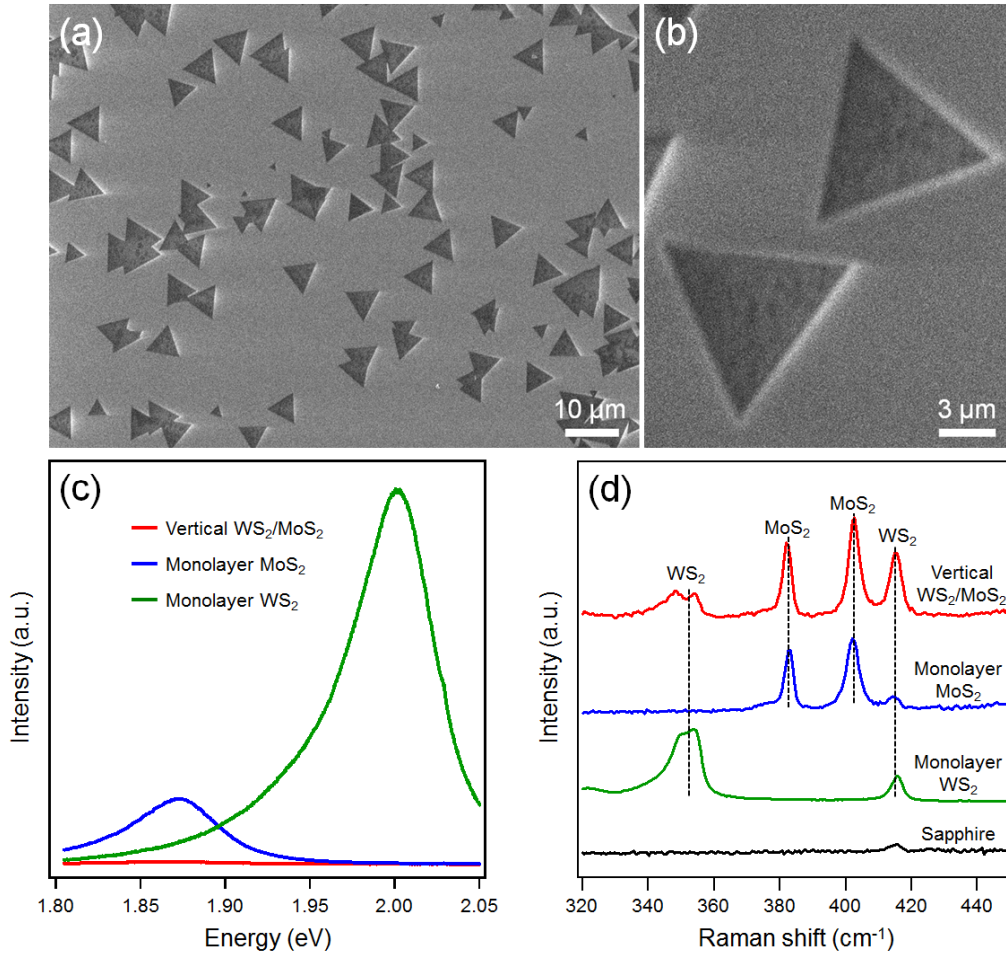


Figure S9. (a, b) SEM images of vertical WS_2/MoS_2 heterostructures possessing no WS_2 ribbons synthesized from monolayer MoS_2 grown without hydrogen under low flux conditions. The temperatures of WO_3 powder and MoS_2 seed crystals were about $960\ ^\circ\text{C}$ and $940\ ^\circ\text{C}$, respectively. (c) PL spectra of the vertical heterostructure (red curve), monolayer MoS_2 (blue curve), and monolayer WS_2 (green curve). (d) Raman spectra of the vertical heterostructure (red curve), monolayer MoS_2 (blue curve), monolayer WS_2 (green curve), and the sapphire substrate (black curve).