

Chemical Vapor Deposition of High-Quality Large-Sized MoS₂ Crystals on Silicon Dioxide Substrates

Jianyi Chen, Wei Tang, Bingbing Tian, Bo Liu, Xiaoxu Zhao, Yanpeng Liu, Tianhua Ren, Wei Liu, Dechao Geng, Hu Young Jeong, Hyeon Suk Shin, Wu Zhou, and Kian Ping Loh*

Post-graphene, there is intense interest in transition metal dichalcogenide (TMD) owing to its unique properties of large spin-orbit coupling and a bandgap, which offer new possibilities in electronics and valleytronics.^[1–3] MoS₂ is one of the most widely studied TMDs. It is a layered 2D material in which the transition metal Mo atoms are sandwiched between two planes of S atoms.^[4,5] Bulk MoS₂ crystals have an indirect bandgap of ≈ 1.29 eV, however its monolayer exhibits a direct bandgap of ≈ 1.8 eV.^[6] Monolayer MoS₂ gives rise to strong photo- and electro-luminescence due to the direct bandgap.^[7,8] According to previous reports,^[9,10] the room temperature mobility of MoS₂ can reach ≈ 410 cm² V⁻¹ s⁻¹ with a high on/off ratio of 10⁸. The excellent optical and electrical properties render MoS₂ an attractive candidate for applications as transistor, photodetectors, photovoltaic cells, piezoelectricity, and spintronic devices.^[9–14]

To date, many efforts have been developed to prepare monolayer MoS₂, including micromechanical exfoliation, chemical

exfoliation, hydrothermal synthesis, and physical vapor deposition.^[2,15,16] Among these methods, chemical vapor deposition (CVD) is most promising in terms of scalability, simple operation and low cost, and has been used to grow various 2D materials directly on dielectric substrates.^[17–26] However, similar to other TMDs,^[19–21] CVD-grown continuous MoS₂ film suffer from a high density of rotational domain boundaries.^[27,28] There is increasing evidence that defects inherent in polycrystalline films prevent the full potential of 2D materials to be realized.^[29,30] Therefore it is very important to grow large MoS₂ single crystals to minimize the presence of defects arising from boundaries.

Recently Chen. et al. studied the role of oxygen on the growth of MoS₂, and obtained large-sized crystals by a low-pressure CVD method.^[31] However the introduction of oxygen into reaction system is dangerous, and is not an essential prerequisite to the growth of large-sized crystals. Here, we found that, by controlling the growth process under ambient pressure using a two-stage CVD method, the nucleation density of MoS₂ can be significantly reduced, thus also forming large-sized crystals. Unlike expensive sapphire, the direct growth of MoS₂ crystals on low-cost SiO₂/Si substrates is more compatible with current Si processing techniques for fabrication of electronic devices. The as-made MoS₂ grains are monolayer crystals. Their maximum size can reach up to ≈ 305 μ m, comparable to that of previous reports.^[27–30] Raman spectroscopy, transmission electron microscopy (TEM) and field effect transistor (FET) measurements indicate that these crystals have excellent crystallinity and electronic properties. The electron mobility can reach about 30 cm² V⁻¹ s⁻¹ with an on/off ratio above 10⁶. The growth method can also be used to grow other TMD crystals such as MoSe₂ and WS₂. We further use the method for epitaxial growth of lateral MoS₂/WS₂ heterojunctions. The atomically sharp in-plane junctions have excellent current rectification behavior, which is important for potential applications in electronics and optoelectronics.

The CVD process was performed under ambient pressure and the detailed growth procedures are described in Figure 1a and Figure S1 in the Supporting Information. According to previous reports,^[32,33] to realize the growth of large-sized 2D materials, it is important to decrease the nucleation density and increase the growth rate of the nuclei. To achieve that, our strategy is to compartmentalize the growth process: separating the induction stage from the growth stage. The induction stage is needed to isolate the growth substrate before the targeted high temperature and equilibrium evaporation rate is reached, since the nucleation and growth can occur during heating stage (Figure S2, Supporting Information), resulting in the formation

Dr. J. Chen, W. Tang, Dr. B. Tian, Dr. B. Liu, X. Zhao, Y. Liu, T. Ren, W. Liu, Dr. D. Geng, Prof. K. P. Loh
Centre for Advanced 2D Materials
National University of Singapore
6 Science Drive 2, Singapore 117546, Singapore
E-mail: chmlohkp@nus.edu.sg



Dr. J. Chen, W. Tang, Dr. B. Tian, Dr. B. Liu, X. Zhao, Y. Liu, T. Ren, W. Liu, Dr. D. Geng, Prof. K. P. Loh
Department of Chemistry
National University of Singapore
3 Science Drive 3, Singapore 117546, Singapore

Prof. H. S. Shin
Department of Chemistry
Ulsan National Institute of Science and Technology (UNIST)
UNIST-gil 50, Ulsan 689-798, Republic of Korea

Prof. H. S. Shin
Department of Energy Engineering
Ulsan National Institute of Science and Technology (UNIST)
UNIST-gil 50, Ulsan 689-798, Republic of Korea

Prof. H. Y. Jeong, Prof. H. S. Shin
UNIST Central Research Facilities (UCRF)
Institute of Basic Science
Ulsan National Institute of Science and Technology (UNIST)
UNIST-gil 50, Ulsan 689-798, Republic of Korea

Prof. W. Zhou
Materials Science and Technology Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831, USA

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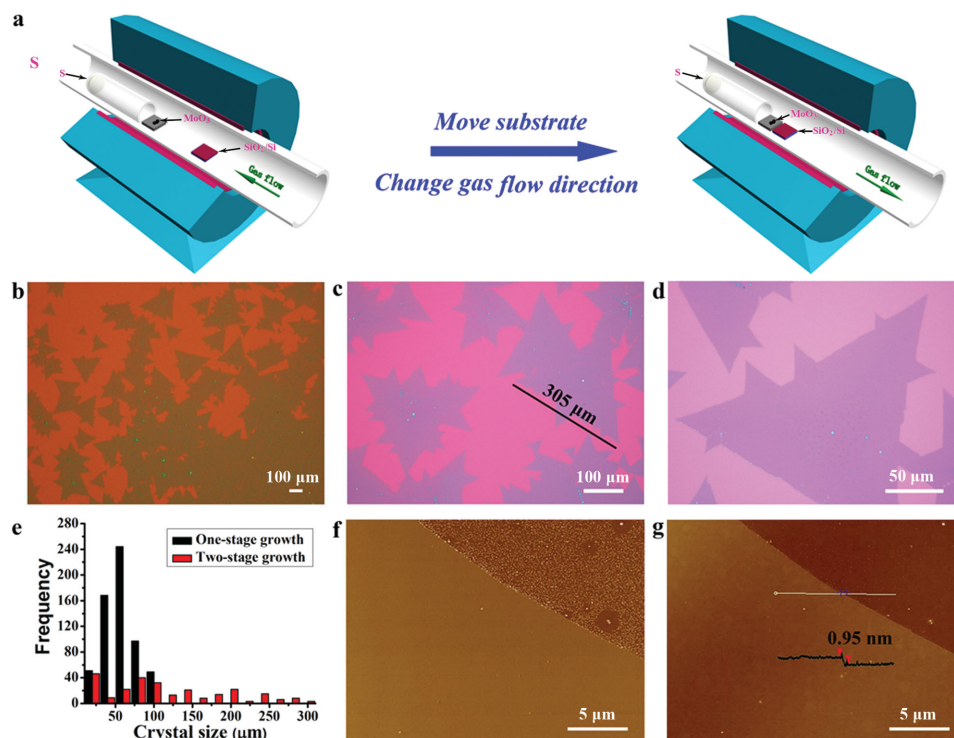


Figure 1. a) Schematics for the CVD synthesis of large-sized MoS₂ crystals. b–d) Typical optical images of triangular MoS₂ crystals. e) Size distribution of MoS₂ crystals obtained by different methods. f) AFM phase and g) height images of MoS₂ monolayer.

of a high density of smaller crystals. Briefly, MoS₂ crystals were grown on SiO₂/Si substrates with sulfur (S) and molybdenum trioxide (MoO₃) as the precursors using a modified CVD system (Figure 1a). MoO₃ powder (about 1.0 mg) was placed on a quartz slide, which were located in the heating zone center of the furnace. A smaller quartz test tube, containing 0.8 g of S, was located upstream, and the open end exposed to the center of the furnace. Unlike the widely used method in which substrates are put face-down above the MoO₃ source, our SiO₂/Si substrate was put at the downstream side (the left picture in Figure 1a). During the induction phase, the furnace temperature was raised to 850 °C and 200 sccm Ar was introduced in a direction flowing away from the substrate to prevent any unintentional nucleation and growth of MoS₂ crystals. When the targeted growth temperature and equilibrium vapor pressure in the growth zone was reached, the SiO₂/Si substrate was rapidly introduced into the growth zone where MoO₃ sources were located by using a homemade setup. Meanwhile, the direction of gas flow was reversed and flow rate set to 20 sccm to allow reactants to flow to the substrate (the right picture in Figure 1a). The growth time was about 10 min (Figure S3, Supporting Information). Compared with the general one-stage growth process, the physical segregation of the CVD process into induction and growth stages allows the substrate to be exposed to the targeted high temperature and vapor pressure quickly, thus avoiding undesired nucleation during the ramp up period (Figure S4, Supporting Information).

Figure 1b show the optical image of the as-grown MoS₂ crystals. For comparison, we also show the optical image of MoS₂ crystals grown by a one-stage method (Figure S5, Supporting

Information). Due to the optical contrast, it is straightforward to identify MoS₂ domains from the SiO₂ substrate. Similar to previous reports,^[27–30] adjacent MoS₂ crystals have coalesced to form a film. The crystal size of MoS₂ crystals ranges from several tens to hundreds of micrometers. Discrete smaller crystals show a regular triangular morphology, while larger crystals easily form twin crystals with smaller crystals (Figure 1c). An enlarged image of MoS₂ crystals, shown in Figure 1d, displays a uniform color contrast on the SiO₂/Si substrate, indicating that the crystals are of uniform thickness. Figure 1e shows a size histogram of MoS₂ crystals observed using optical microscopy. The majority of the MoS₂ crystals are one order of magnitude in area than those produced using one-stage method.

To identify the number of layers for our MoS₂ sample, the edges of crystals are measured using atomic force microscopy (AFM). Figure 1f,g are typical tapping mode AFM images of a MoS₂ crystal. The sharper, straighter edge may indicate the formation of molybdenum zigzag (Mo-zz) edge structure.^[29] The homogeneity of film thickness is evidenced by color homogeneity. Height profiles across MoS₂ edge samples (Figure 1g) show that thickness of our sample is about 0.95 nm, corresponding to monolayer MoS₂.

MoS₂ crystals were further characterized by using TEM, selected area electron diffraction (SAED), scanning transmission electron microscope (STEM). These techniques provide important information about the structure and quality of MoS₂ crystals as detailed below. After the MoS₂ crystals were transferred to a copper grid, the layer count on the edge of the image (Figure 2a) indicated that the crystal is monolayer MoS₂. The high-magnification TEM image in Figure 2b shows

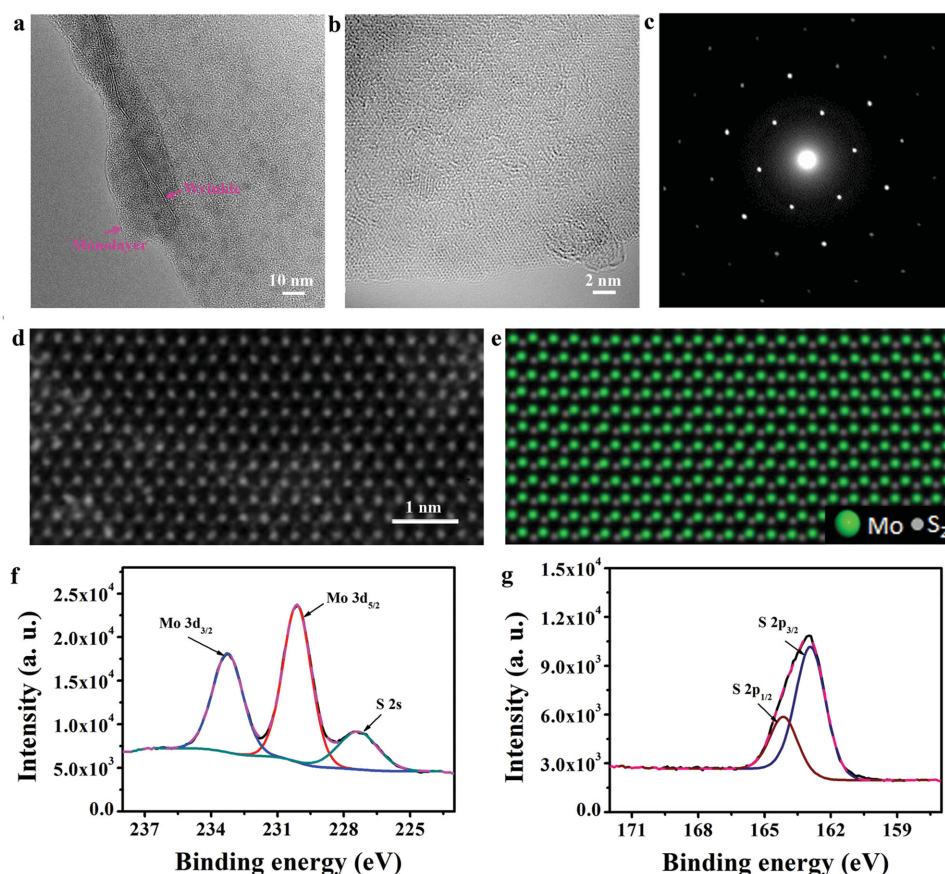


Figure 2. a,b) High-resolution TEM images of MoS₂ crystals. c) SAED pattern of MoS₂ crystals. d) High-magnification STEM ADF image of MoS₂ crystals. e) The atomic models correspond to the structure in (e). f,g) XPS spectra of MoS₂ crystals showing f) Mo 3d and g) S 2p peaks.

a honeycomb arrangement of atoms, and the selected SAED pattern in Figure 2c displays one set of hexagonal symmetrical patterns, indicating the hexagonal lattice structure of MoS₂ crystals.^[34] The atomic structure of MoS₂ crystals was studied by annular dark field (ADF) imaging (Figure 2d). The corresponding atomic model is shown in Figure 2e. Because the signal intensity in the STEM–ADF image is directly related to the average atomic number (*Z*), STEM–ADF image can thus be used to visualize the spatial distribution of Mo and S due to their different image contrast levels.^[35] The sharp atomic images indicate that our samples have a high crystalline quality, in accordance with previous reports.

X-ray photoelectron spectroscopy (XPS) was used to examine the elemental composition and bonding of MoS₂ samples. Only four elements (Mo, S, O, and Si) are observed in the spectra (Figure S6, Supporting Information), confirming that MoS₂ was directly synthesized on SiO₂/Si substrates. The Mo 3d and S 2p peaks provide important information about the stoichiometry and bonding of the MoS₂ crystals (Figure 2f,g). The Mo 3d_{5/2} and 3d_{3/2} peaks are located at ≈230.0 and ≈233.2 eV, respectively, while the S 2p_{1/2} and S 2p_{3/2} peaks are located at ≈164.0 and ≈162.9 eV, respectively. These peak positions are consistent with the reported values for 2H-MoS₂ crystals.^[34] The positions of the Mo peaks indicate the reduction of Mo from Mo⁶⁺ (MoO₃) to Mo⁴⁺ (MoS₂). The Mo/S ratio obtained from Mo 3d and S 2p XPS is about 1:1.97, suggesting that the CVD MoS₂

film is stoichiometric with some S vacancies,^[36] which were reported as the dominant point defect in CVD-grown MoS₂.^[37]

Raman and photoluminescence (PL) microscopy are powerful methods for the characterization of crystal quality and bandgap in TMD materials. Typical monolayer MoS₂ crystals were characterized with Raman and PL using a laser wavelength of 532 nm. Figure 3a shows the Raman spectrum of the MoS₂ sample. The monolayer sheet exhibits two characteristic Raman bands at 400.2 and 383.4 cm^{−1}, corresponding to the A_{1g} and E_{2g} modes of monolayer MoS₂ crystals,^[28,34] and their full-width-half-maximum (FWHM) values are about 6.8 and 3.8 cm^{−1}, respectively. The PL spectrum (Figure 3b) shows highly distinct photoluminescence peaks at ≈623 and 673 nm, corresponding to the A1 and B1 direct excitonic transitions of MoS₂ monolayer, respectively.^[8,28] To probe the micro-scale structure of the crystal, we also conducted Raman and PL mapping centered at ≈400.1 cm^{−1} (the A_{1g} mode), ≈383.4 cm^{−1} (the E_{2g} mode) and ≈673 nm (the PL mode), as shown in Figure 3c–e. The uniform color intensity observed suggests that the MoS₂ crystal is uniform in thickness.

To assess the generality of the method for growing other TMDs crystals, we also tried to synthesize MoSe₂ and WS₂ crystals using a similar strategy. MoSe₂ and WS₂ were grown using MoO₃, Se and WO₃, S powders as the source precursors respectively. The difference is that a small quantity of H₂ (1.5 sccm) is required to enhance the selenization reaction of

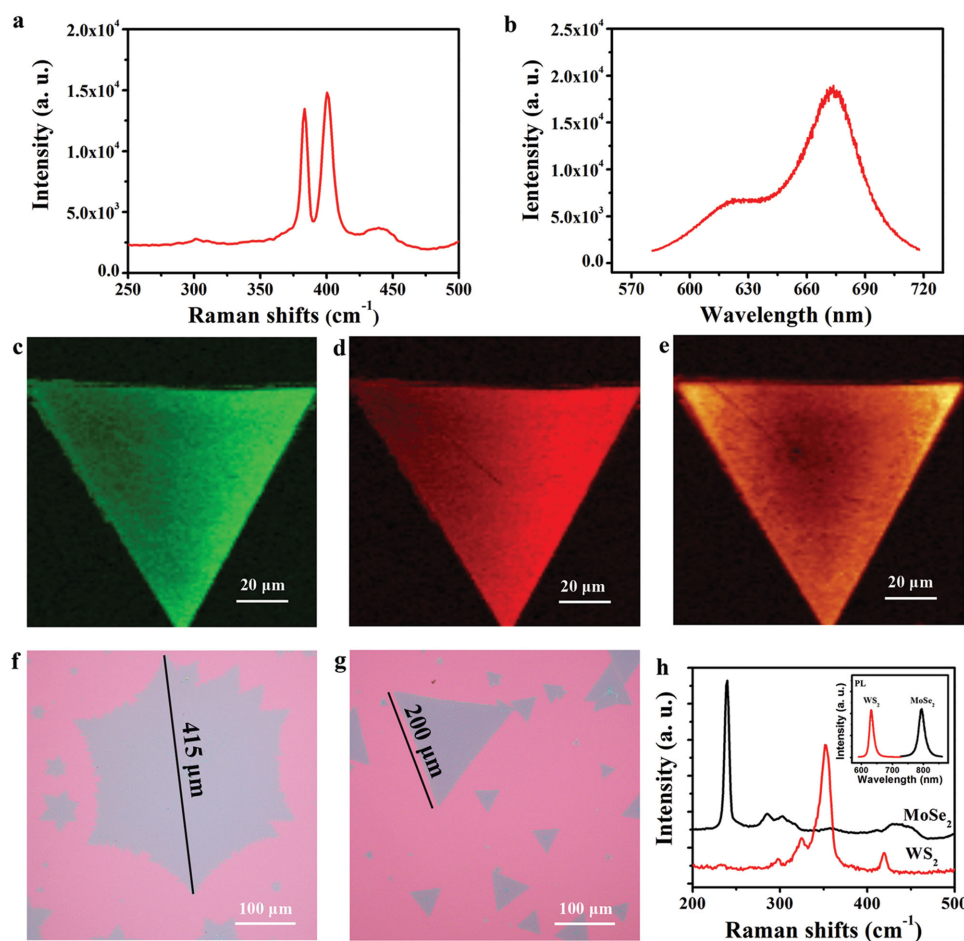


Figure 3. a) Raman and b) PL spectra of MoSe₂ monolayer. c–e) Raman and PL mapping centered at f) ≈ 400.1 cm⁻¹, g) ≈ 383.4 cm⁻¹, and h) ≈ 673 nm. Optical images of f) large-sized hexagonal MoSe₂ and g) triangular WS₂ crystals. h) Raman spectra of MoSe₂ and WS₂ monolayer. The inset shows PL spectra of MoSe₂ and WS₂ monolayer.

MoO₃ during the growth of MoSe₂ crystals. The introduction of H₂ also changes the relative edge free energy of Se edges and Mo edges, thus forming hexagonal crystals under suitable conditions.^[38,39] Nevertheless, we have obtained large-sized MoSe₂ and WS₂ crystals on SiO₂/Si substrates. (Figure 3f,g). Figure 3h shows the Raman spectra of these MoSe₂ and WS₂ crystals. The A_{1g} and E_{2g} modes of MoSe₂ single-layer are located at ≈ 239.7 cm⁻¹ (A_{1g}), 286.2 cm⁻¹ (E_{2g}) respectively, while the A_{1g} and E_{2g} modes of WS₂ single-layer are located at 418.8 and 352.3 cm⁻¹ respectively.^[40,41] The PL spectra (inset) shows the characteristic emission peaks corresponding to the emission of MoSe₂ (≈ 794 nm) and WS₂ (≈ 632 nm) monolayer.^[42,43] These results indicate that these crystals are monolayer crystals with perfect optical properties.

To investigate the electronic quality of the CVD-grown MoS₂ crystals, we measured the electrical transport properties. **Figure 4a** shows a schematic diagram of MoS₂ FETs fabricated on SiO₂/Si substrates using Ti/Au as the source–drain (S–D) electrodes and a doped silicon substrate as the back gate. The typical *I*–*V* characteristics for a MoS₂ FET measured in nitrogen atmosphere is shown in Figure 4b. A linear *I*_{DS}–*V*_{DS} relationship is clearly observed, indicating that ohmic contacts were formed at the source and drain electrodes. The transfer

characteristics (drain current *I*_{DS} vs gate voltage *V*_G) of the MoS₂ device are shown in Figure 4c. The *I*_{DS} value increases monotonically with increasing *V*_G, which is indicative of n-type semiconducting behavior. The field-effect mobility of this MoS₂ FET was estimated to be ≈ 28 cm² V⁻¹ s⁻¹ with an on/off ratio above 10⁶. The mobilities of all the 20 devices we measured are in the range of 1–30 cm² V⁻¹ s⁻¹, comparable to previous reports.^[28–30] The mobility could be improved by high-*k* top gate dielectrics and interface engineering.^[10,31,44]

Beyond the growth of single crystals, we have also realized the growth of WS₂ crystals along the edges of MoS₂ crystals, and formed MoS₂/WS₂ lateral heterojunctions by our method (**Figure 5a** and **Figure S7**, Supporting Information). Observation under STEM indicates that the lateral interface is atomically sharp (**Figure 5b**), without extensive (WMo)₂ alloying region.^[45–48] The chemical modulation across the lateral heterostructure is confirmed by elemental mapping using electron energy-loss spectroscopy (EELS) imaging (**Figure 5c–e**). The Raman and PL mapping of the characteristic peaks and peaks of WS₂ and MoS₂ also revealed the structural modulation between MoS₂ and WS₂ (**Figure 5f,g** and **Figure S8**, Supporting Information). The lateral stitching of MoS₂ monolayer and WS₂ monolayer has formed an in-plane heterojunction. The electrical

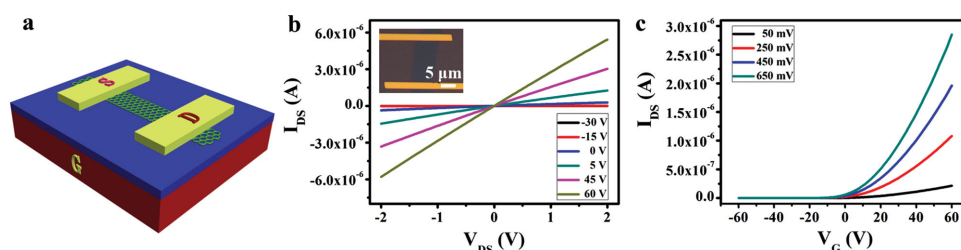


Figure 4. a) Schematic diagram of MoS₂-based device. MoS₂ ribbon is obtained by EBL and vapor-phase etching techniques. b) Current (I_{SD})/voltage (V_{SD}) output characteristics of a MoS₂ FET device at various back gate voltages. The inset shows the optical image of the device. c) Transfer curves ($I_{\text{DS}}-V_{\text{G}}$) of a back-gated MoS₂ device at various source–drain voltages.

transport across the interface of monolayer MoS₂/WS₂ in-plane heterojunctions was measured (Figure S9, Supporting Information). The forward bias current is higher than the reverse current, suggesting reasonably good rectification across this in-plane heterojunction.

In summary, we have successfully realized the growth of large-sized, high-quality MoS₂ crystals. The nucleation density of crystals can be decreased by separating the induction

stage from the growth stage, and the maximum size of MoS₂ crystals can reach about 305 μm . Electrical transport measurements indicate that the MoS₂ crystals have electron mobility up to about 30 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, comparable to those of exfoliated flakes and CVD synthetic crystals. The growth method can also be used to grow other TMD crystals such as MoSe₂ and WS₂, suggesting the universality of the method. In addition, we have also demonstrated the lateral

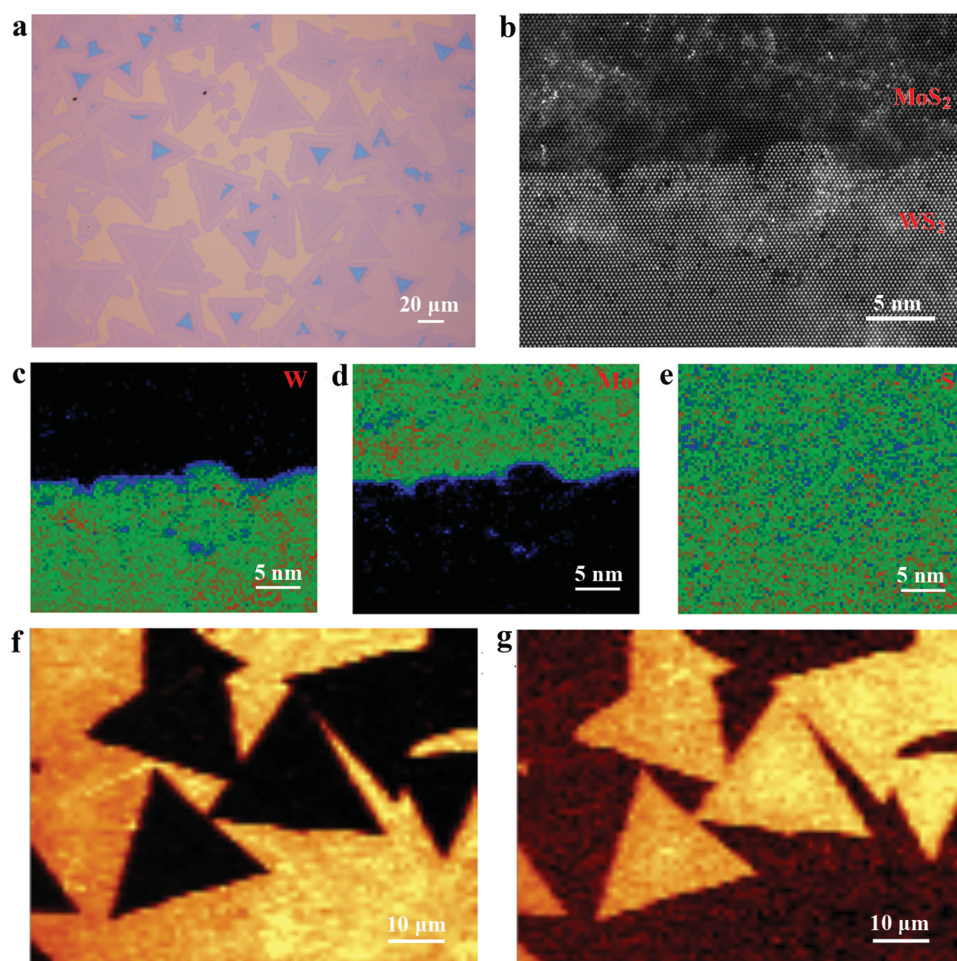


Figure 5. a) Optical image of MoS₂/WS₂ in-plane heterojunctions. b) High-magnification STEM ADF image of the lateral MoS₂/WS₂ heterojunction. Elemental mapping images of c) Mo, d) W, and e) S atoms. Raman mapping of the characteristic E_{12g}^1 peaks of WS₂ centered at f) $\approx 352.3 \text{ cm}^{-1}$ and g) MoS₂ centered at $\approx 383.4 \text{ cm}^{-1}$.

epitaxy growth of MoS₂/WS₂ in-plane heterojunctions. These junctions have atomically sharp interface with a good rectification characteristic.

Experimental Section

Preparation of MoS₂ Crystals: MoS₂ crystals were grown on dielectric substrates by using a modified ambient pressure CVD method. A little MoO₃ powder (about 1.0 mg) was placed on growth substrate which was introduced into the heating zone center of the 2 in. furnace. A smaller quartz tube with one end sealed containing 0.8 g of sulfur powder was located upstream, and the open end extended to the center of the furnace. The SiO₂/Si growth substrate was put at the downstream side. The furnace temperature was raised to 850 °C and 200 sccm Ar was introduced in a direction flowing away from the substrate. The SiO₂/Si substrate was moved and made close to MoO₃ sources. Meanwhile, the direction of flowing gas was changed and the gas flow at 20 sccm was controlled. After stabilizing the system for 10 min, the furnace was cooled to room temperature.

Characterization: Optical images were obtained using a Nikon ECLIPSE LV100D microscopy. AFM images were performed using a Bruker Dimension FastScan Atomic Force Microscope in the tapping mode. Raman spectra were recorded at room temperature using a WITec Raman Microscope with laser excitation at 532 nm. TEM was performed with FEI Titan transmission electron microscope operated at 80 kV. STEM imaging and EELS analysis were performed on an aberration-corrected Nion UltraSTEM-100 operating at 60 kV. XPS analysis was carried out on an Omicron EAC2000-125 analyzer. Base pressure during analysis was 10⁻⁹ Torr. An Al K α monochromatized radiation (h ν = 1486.6 eV) was employed as the X-ray source.

Device and Electrical Measurements: Triangular MoS₂ crystals were etched into ribbons by electron beam lithography (EBL) and oxygen plasma. FETs were fabricated on SiO₂/Si wafers with Ti/Au (5/50 nm) as source-drain electrodes and the doped silicon substrate as the back gate. The FET characteristics were measured in N₂ at room temperature. A Keithley 4200SC semiconductor parameter analyzer was used to measure the electrical characteristics of the devices.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

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