Supplementary Information

Large-Area High Quality MoS_2 Monolayers Grown by Sulfur Vapor Counter Flow Diffusion

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1. Experimental setup and results of MoS_2 growth when sulfur powder located upstream

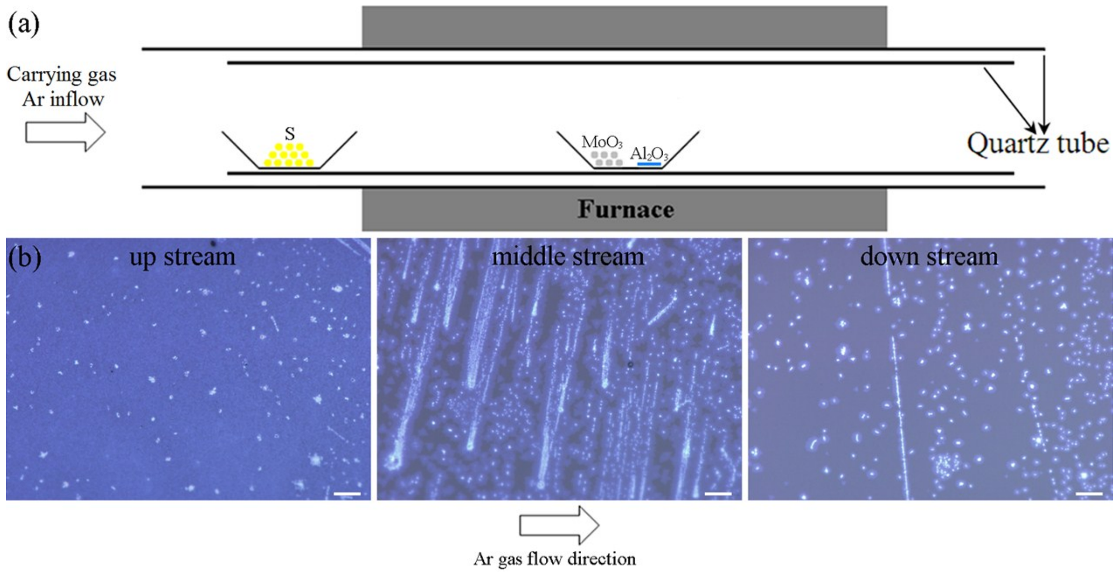

Figure S1. (a) Schematic illustration for MoS_2 growth on Al_2O_3 (0001) substrate with sulfur powder placed upstream. (b) Optical microscope images of synthesized MoS_2 on sapphire taken along the Ar gas flow direction. The scale bars are 10 μm.

MoS_2 has been grown by chemical vapor deposition (CVD) method on sapphire c-plane. Two crucibles, one containing 200 mg of sublimated sulfur was located at the upstream entry of the furnace and another containing 6 mg of MoO_3 powder was placed at the center of the furnace, respectively, as shown in Figure S1a. A well cleaned Al_2O_3 (0001) single crystal substrate was placed near the MoO_3 powder. MoS_2 samples were fabricated by maintaining at 700 °C for 10 min with a heating rate of 15 °C min^{-1} and 50 sccm Ar flow at ambient.

The change of as-deposited MoS_2 morphology along the carrier gas flow direction is shown in Figure S1b. Because of the high sulfur vapor concentration, MoO_3 sulfurization is violent and partial pressure of gaseous MoS_2 is elevated, resulting in thicker layers and bulk MoS_2 particles grown on the up stream side of substrate and irregular shaped monolayers interspersed with bulk MoS_2 particles formed on the middle-down stream side. No space is suitable for monolayer MoS_2 growth. So how to moderate sulfurization reaction to lower the partial pressure of gaseous MoS_2 is the key problem needed to be solved in monolayer MoS_2 growth.

2. Optical microscope observation and atomic force microscope measurement of the exfoliated monolayer MoS_2 sample

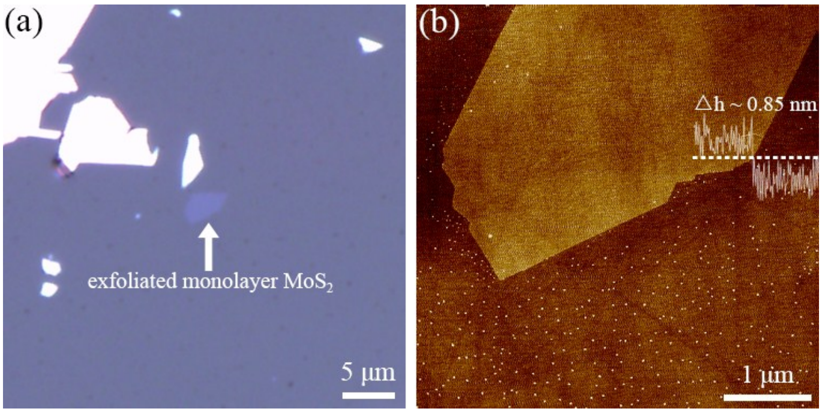

Figure S2. (a) Optical microscope image and (b) atomic force microscope image of the exfoliated monolayer MoS_2 sample. Section-view along the white dash line shows that the sample thickness is about 0.85 nm, which confirms the monolayer nature of the exfoliated MoS_2 sample.

3. Raman measurements of the intermediate oxides and initially formed monolayer MoS_2

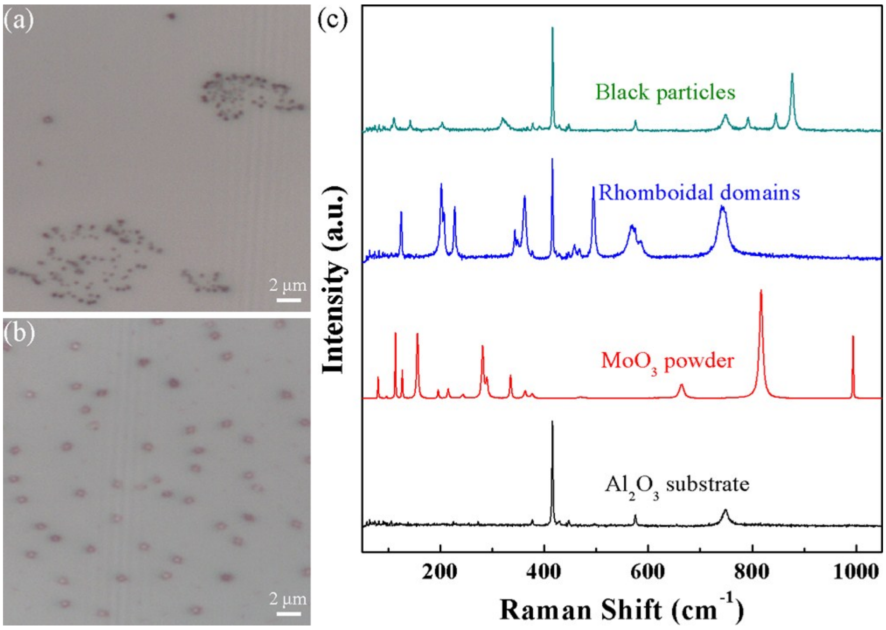

Figure S3. Optical microscope images of (a) the small black particles and (b) rhomboidal shaped domains. (c) Raman spectra of the small black particles, rhomboidal shaped domains, MoO_3 powder, and the bare sapphire substrate, respectively.

The small black particles nucleated when $D_{dist} \leq 10.0$ cm (D_{dist} is the distance between MoO_3 precursor and sapphire substrate) show six Raman peaks assigned to Mo_4O_{11} (~ 877, 845, 792, 390, 323 and 205 cm^{-1}).[1] Similarly, Raman signature of the rhomboidal shaped domains corresponds to MoO_2 with Raman bands at 743, 585, 571, 495, 459, 363, 345, 227 and 207 cm^{-1}.[1]

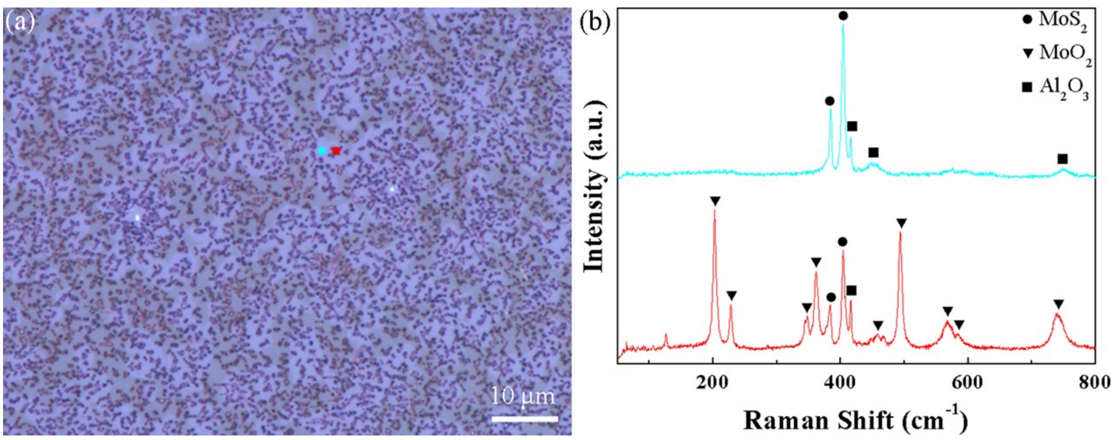

Figure S4. (a) Larger version of the image taken at D_{dist} = 15.0 cm. (b) Raman spectra acquired from different regions highlighted in (a). These results illustrate that the initially formed monolayer MoS_2 grows around MoO_2 domains.

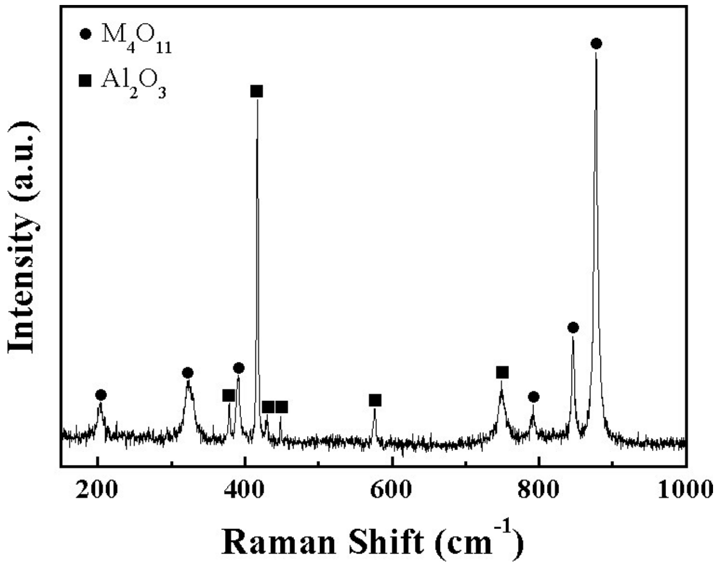

Figure S5. Raman spectrum of the small black particles shown in Figure 6c of the main text. Peaks marked with ● and ■ correspond to Mo_4O_{11} and Al_2O_3, respectively.

4. The influence of Ar flow rate on the resultant MoS_2/MoO_2 microplates

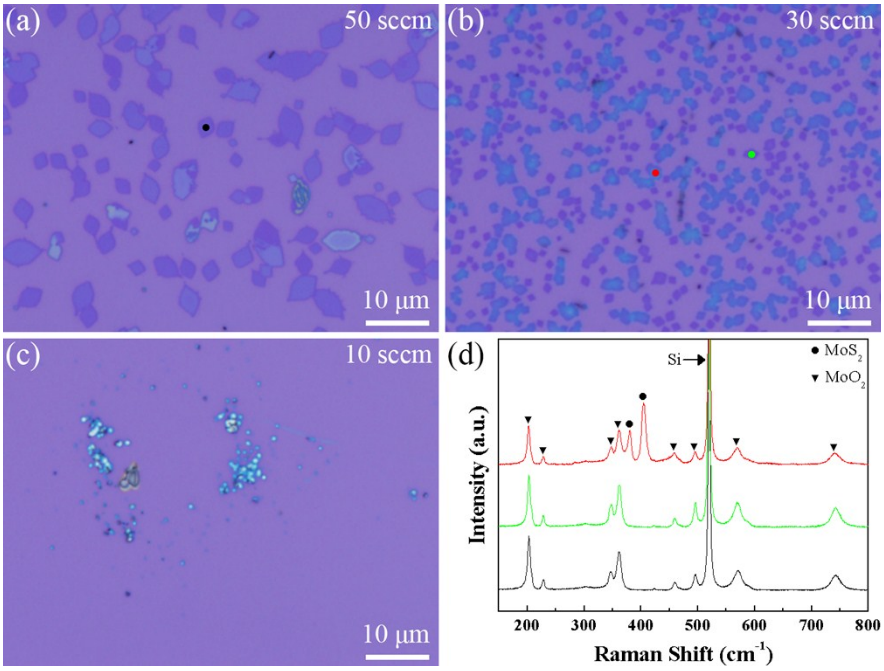

Figure S6. (a-c) Optical microscope images of the products synthesized with different Ar flow rate of 50, 30, and 10 sccm, respectively, SiO_2/Si substrates are located at the center of furnace. (d) Raman spectra acquired from different samples and different regions highlighted in (a) and (b).

The Ar flow rate also has an influence on the resultant MoS_2/MoO_2 microplates, as shown in Figure S6. When Ar flow rate is 50 sccm, sulfur vapor concentration is low in the growth zone, only MoO_2 microplates are formed. With the decrease of Ar flow rate to 30 sccm, sulfur vapor concentration increases, the surface of parts of MoO_2 microplates is sulfurized to give rise to the formation of MoS_2/MoO_2. Further decrease of Ar flow rate to 10 sccm leads to very high sulfur vapor concentration in the growth zone, which in turn causes the formation of MoS_2 particles on the SiO_2/Si substrates. So, like the growth of MoS_2 monolayers, a proper Ar flow rate is needed for the synthesis of MoS_2/MoO_2 microplates. In our experiment, 20 sccm Ar is appropriate to grow MoS_2/MoO_2 microplates.

Reference

1 M. Dieterle and G. Mestl, *Phys. Chem. Chem. Phys.* 2002, **4**, 822-826.