Supplementary Information

Direct growth of molybdenum disulfide on arbitrary surfaces by chemical vapor deposition

Jiao Wang,[a] Linfeng Chen,[a] Wenjing Lu,[a] Mengqi Zeng,[a] Lifang Tan,[a] Feng Ren[b], Changzhong Jiang[b], and Lei Fu*[a]

[a] *College of Chemistry and Molecular Science, Wuhan University, Wuhan 430072, China.*
[b] *School of Physics and Technology, Wuhan University, Wuhan 430072, China.*

*To whom correspondence should be addressed: E-mail: leifu@whu.edu.cn

1. Detailed methods

CVD growth of MoS_2. Mo films were deposited on diverse insulating substrates using electron beam evaporator (ULVAC, ACS-4000-C4) under high vacuum conditions. The Mo target had a purity of > 99.95 wt.%. The deposited substrates (300-nm thick SiO_2/Si, quartz, cover glass, polyimide) were placed in a quartz tube furnace (HTF 55322C Lindberg/Blue M). Before the CVD growth, 1000 sccm Ar was introduced to exclude the remaining oxygen gas in the system. After the furnace temperature reached the desired temperature (250 ^oC–900 ^oC), a mix flow of Ar (400–900 sccm) and H_2S (4–20 sccm) was then supplied into the quartz tube for 1–10 minutes. The sample was cooled down to room temperature naturally.

Characterization. The systematical characterization of the samples was performed by optical microscopy (Olympus DX51, Olympus). AFM images were recorded by NT–MDT system. Raman spectroscopy and photoluminescence (PL) with an excitation wavelength 532 nm was carried out using Renishaw inVia, Renishaw. The power of the laser was 5 mW. The photoluminescence (PL) spectra of layered MoS_2 films were collected at room temperature. X-ray photoelectron spectroscopy (XPS, Thermo Scientific, ESCALAB 250Xi) was performed using monochromatic aluminum KR X-rays. Optical absorbance spectra were collected at room temperature using ZY (UV-3600) and VARIAN Cary-5000. The transmission electron microscopy (TEM) images were taken with a high-resolution TEM (HRTEM, JEOL JEM-2010) operating at 200 kV with MoS_2 samples directly transferred onto a copper grid.

2. CVD growth of MoS_2 flakes using MoO_3 along with sulfur on SiO_2/Si substrate (a controlled experiment)

MoO_3 is the most popular precursor for MoS_2 growth by CVD. However, it is difficult to obtain the uniform and continuous MoS_2 film using this method. As shown in Fig. S1a, the obtained MoS_2 samples are discontinuous flakes. Raman and XPS spectra are used to determine the composition of the resulting flakes. The Raman spectra reveal the peak positions of the E^1_{2g} and A^1_g modes corresponding to in-plane and out-of-plane vibrations (Fig. S1b). The two modes locate at 381 cm^{-1} and 406 cm^{-1}, respectively. The peaks at ~356 cm^{-1}, ~364 cm^{-1} and ~745 cm^{-1} are due to residual molybdenum oxide. We also detect Mo^{6+} at 234.5 eV in XPS (Fig. S1c) on the as-grown MoS_2. The peaks centered at 232.6 eV and 229.4 eV are corresponding to Mo $3d_{3/2}$ and $3d_{5/2}$, respectively. Fig. S1d shows the $2p_{1/2}$ and $2p_{3/2}$ core levels of sulfur at 162.5 eV and 161.3 eV, respectively. We conclude that both Raman and XPS results point to the present of unreacted molybdenum oxide and sulfur powder.

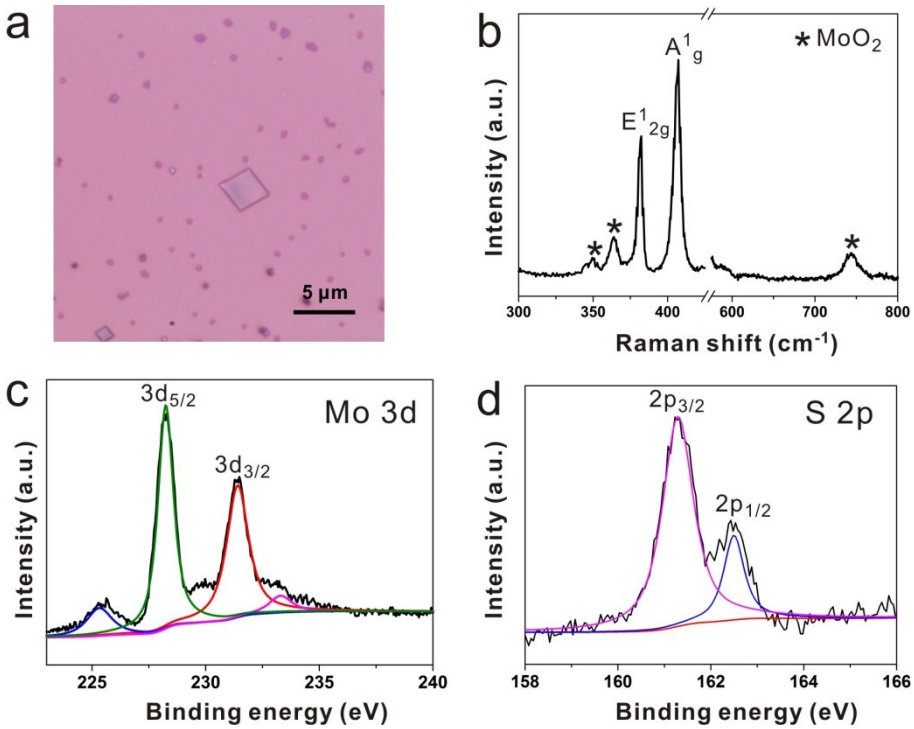

Fig. S1. (a) The optical image of as-made MoS_2/MoO_2 flake on SiO_2/Si substrate at 650–850 ^oC. (b) The Raman spectra of MoS_2 /MoO_2 flake corresponding to (a). (c) and (d) show the XPS characterization of the as-made flakes.

3. Surface roughness of direct-growth and transferred MoS_2 films on SiO_2/Si substrate

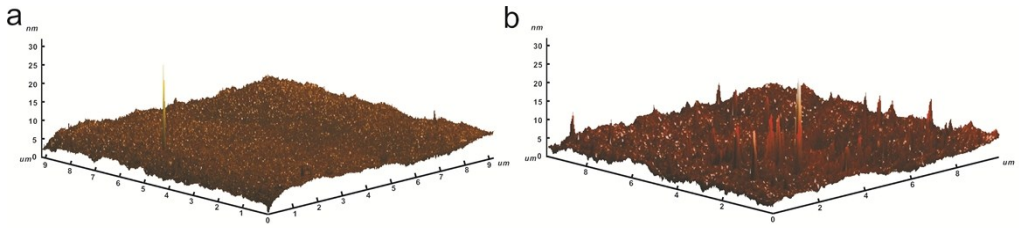

Fig. S2. The 3D surface roughness image of (a) the direct-growth MoS_2, in which there is no obvious wrinkles and residual impurities; (b) the transferred MoS_2, which shows obvious wrinkles and impurity.

4. Optical images and Raman spectra of direct-growth MoS_2 films varied from 2 to 9 layers on SiO_2/Si substrate

The directly grown MoS_2 films are basically uniform without visible cracks and wrinkles under optical microscope. And the 2~9 layers MoS_2 films on SiO_2/Si substrates exhibit a uniform color distribution.

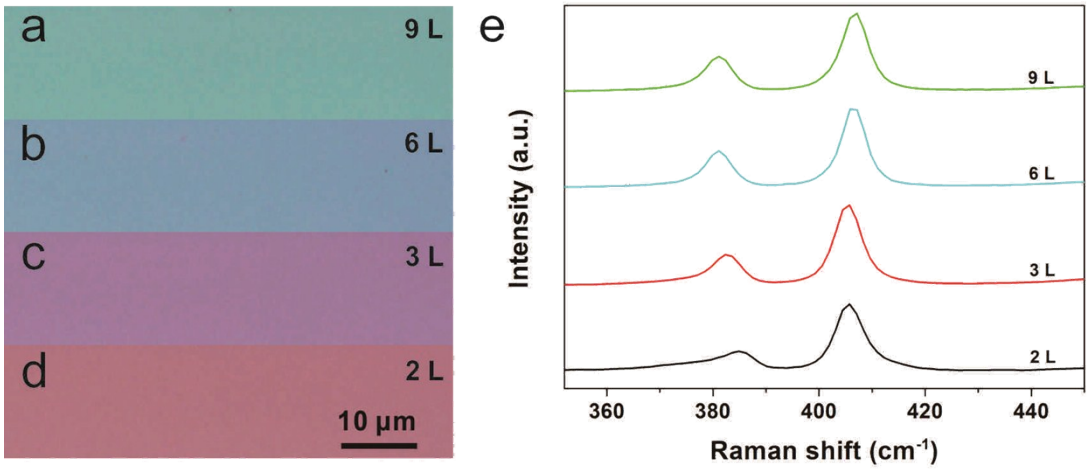

Fig. S3. With increasing the thickness of deposited Mo films, the direct-growth MoS_2 of layer increasing can be obtained. (a–d) display the optical images, showing good continuity and uniformity. (e) The Raman spectra of the MoS_2 films prepared with the layer increasing.

5. Step measurements and Raman spectra (statistical analysis of frequency difference of E^1_{2g} and A^1_g) of direct-growth MoS_2 films varied from 2 to 9 layers on SiO_2/Si substrate

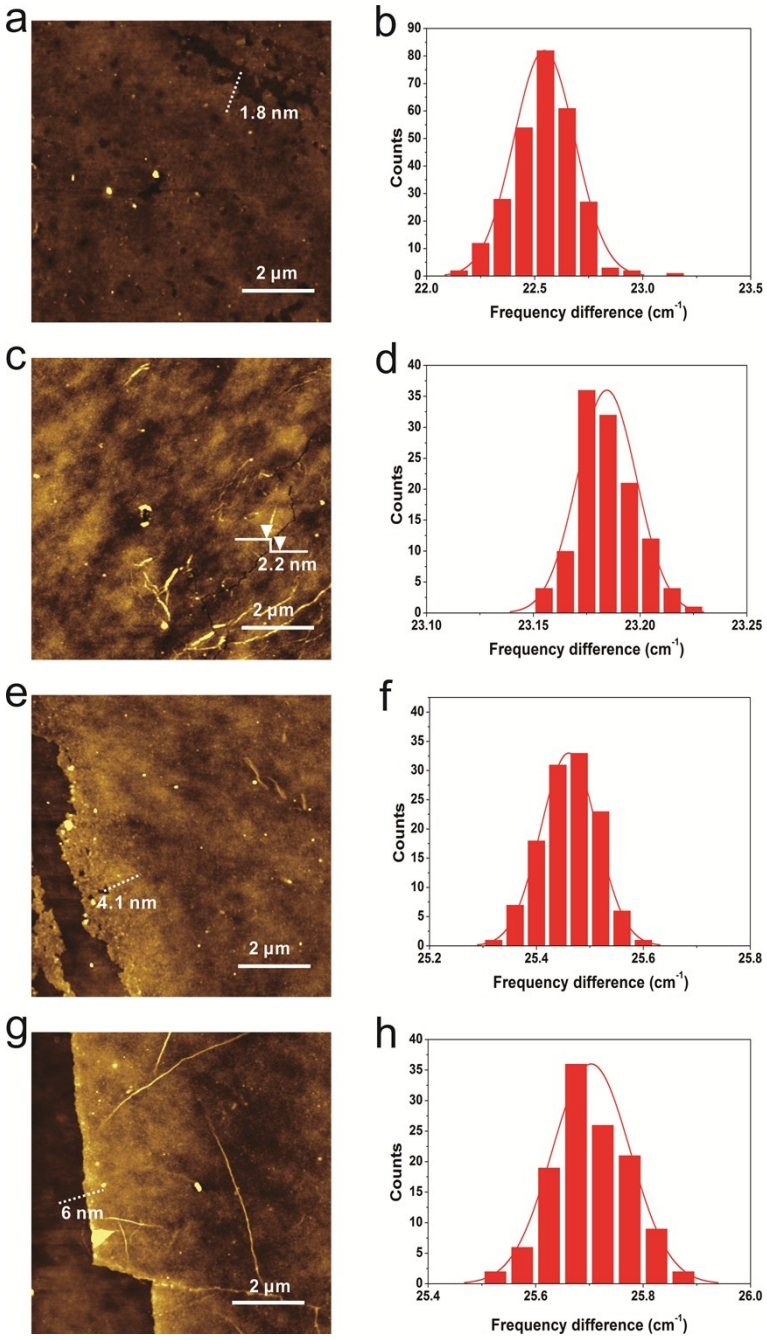

Fig. S4. (a), (c), (e) and (g) show the step measurements of MoS_2 films transferred on SiO_2/Si from directly grown samples with variation of the deposited Mo layer; (b), (d), (f) and (h) show the statistical analysis of Raman spectra on the frequency difference of $E^1_{2g}$and A^1_gon few layer direct-growth MoS_2; all the measured frequency difference is collected from an area of 10 × 10 μm in the MoS_2 film; mapping step: 1 μm; the frequency difference fall into the range of 22~26 cm^{-1} corresponding to different thickness of MoS_2.

6. Raman mapping images of peak position differences between A_g^1 and E_{2g}^1 modes on direct growth samples

Raman mapping images of the peak position differences between the A_g^1 and E_{2g}^1 modes over an area of 10×10 μm show nearly uniform color distribution (Fig. S5), revealing the thickness variation is negligible. The relative frequency differences between the modes varied from 22 cm^{-1} to 26 cm^{-1}, which corresponded to 2 to 9 layered MoS_2 films.

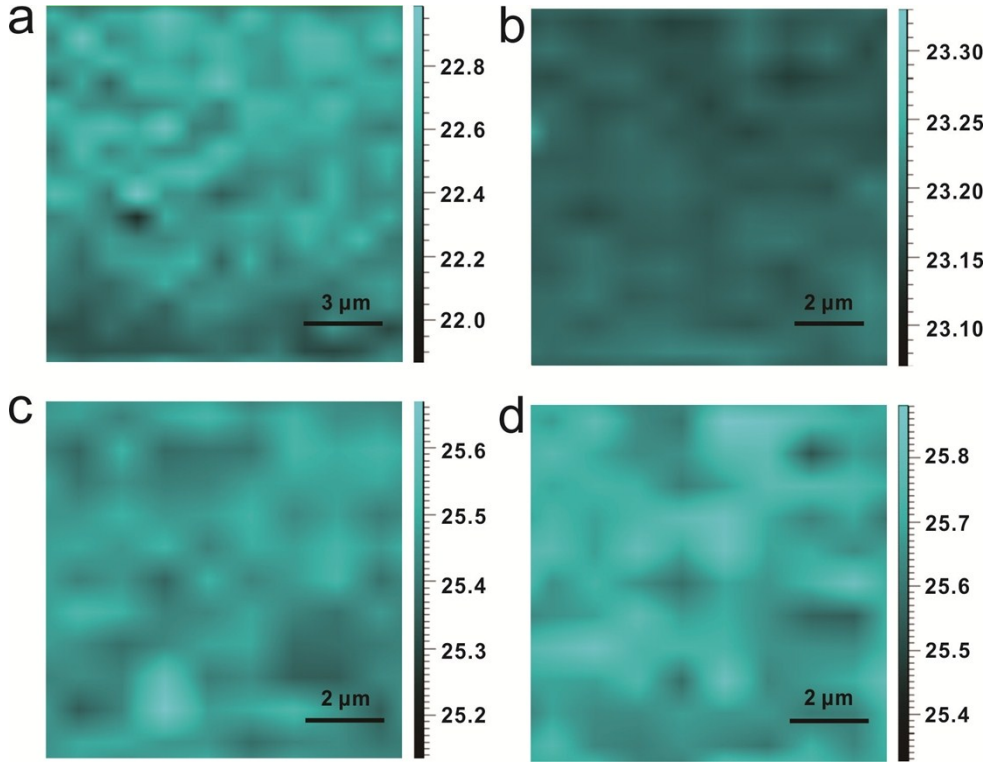

Fig. S5. Raman mapping images of the peak position differences between the A_g^1 and E_{2g}^1 modes from the 2-, 3-, 6-, 9-layered MoS_2 films on SiO_2/Si substrates, showing uniform surfaces.

7. Optical images of direct-growth MoS_2 ribbons array on SiO_2/Si substrate

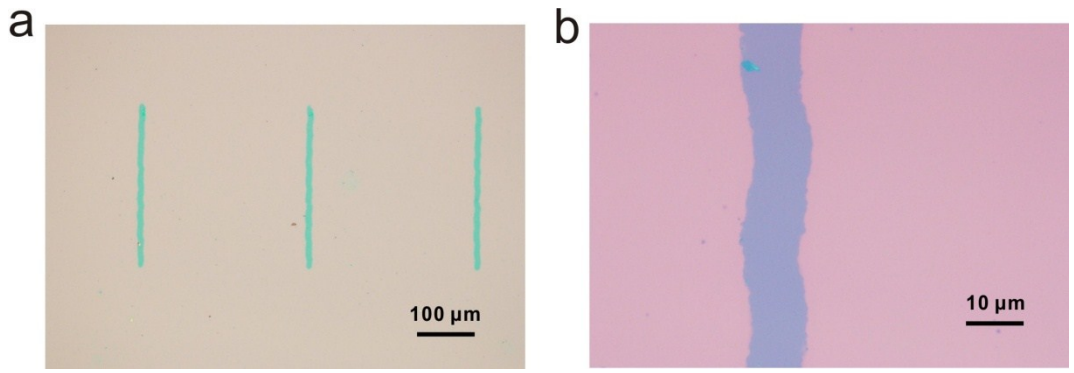

Figure S6. Optical images of direct-growth MoS_2 ribbons arrays on SiO_2/Si substrate at the growth temperature of 900 ^oC.

8. UV-vis-IR spectra, transmittance and XPS spectra of direct-growth MoS_2 on quartz

Three layers MoS_2 with 100% surface coverage with the growth temperature varied from 500 °C to 900 °C is prepared for spectroscopic characterization. The excitonic absorption of MoS_2 on quartz has no obvious changes with the variation of growth temperature.

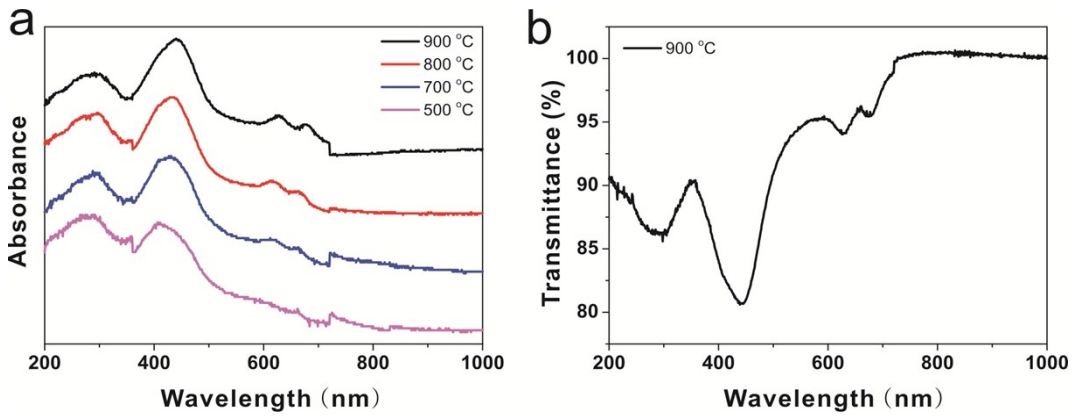

Figure S7. (**a**) UV-vis-IR of few layers MoS_2 grown on quartz with the same deposited Mo layer at 900 °C, 800 °C, 700 °C, 500 °C, respectively. (**b**) The transmittance of MoS_2 grown at 900 °C.

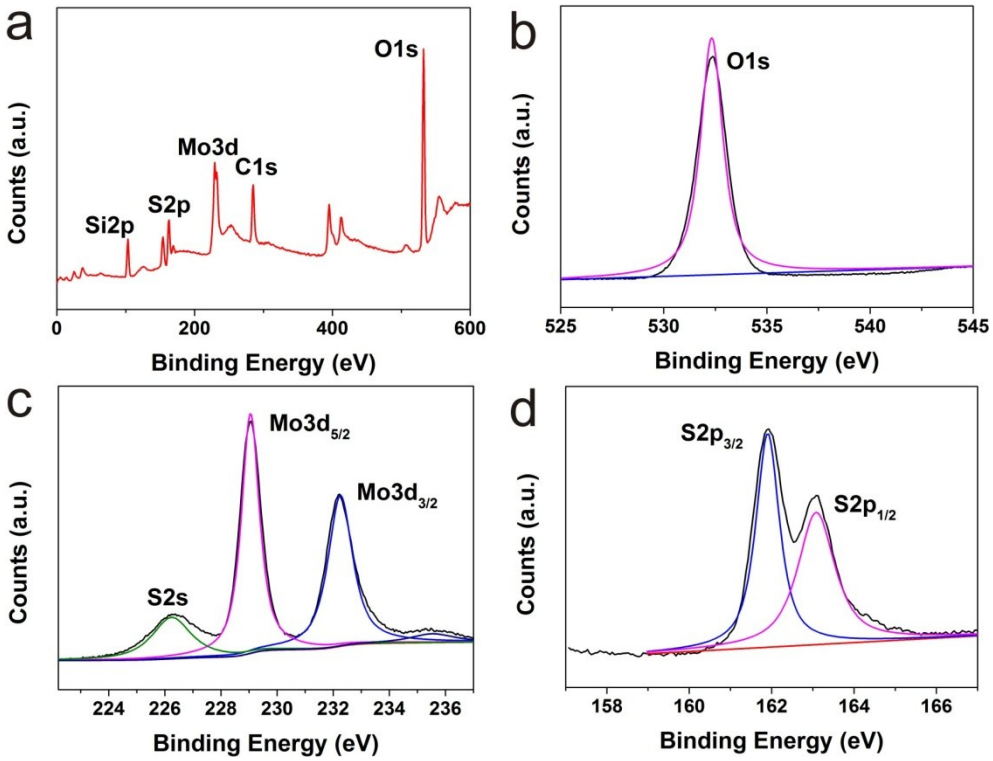

Figure S8. XPS spectrum of MoS_2 film directly grown on quartz substrate at 300 °C. The survey of XPS spectrum shows in (a). (b) The O1s spectrum only shows the peak position of Si–O bond centered at 532.3 eV, indicating the surface oxide originated from the underlying SiO_2 substrate, and there is no metal oxide in the film. (c) The peaks of Mo $3d_{5/2}$ and Mo $3d_{3/2}$ are centered at 229 eV and 232.3 eV, respectively. And the presence of peak centered at 226.2 eV indicates the oxidation of S with –2. (d) S $2p_{3/2}$ and S $2p_{1/2}$ peaks are centered at 161.9 eV and 163.1 eV, respectively. The peak position values of Mo3d and S2p are quite consistent with previous studies.

9. Raman spectra of direct-growth MoS_2 on SiO_2/Si and cover glass at low temperature

We explored the low temperature growth of MoS_2 using our strategy. The growth temperature was as low as 250 ^oC under the condition of 400 sccm Ar and 4–20 sccm H_2S.

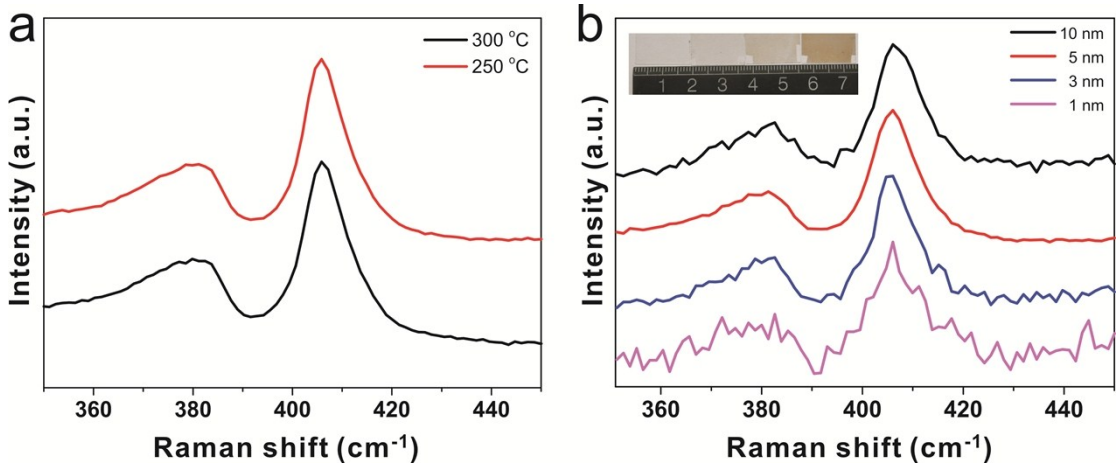

Figure S9. Raman spectra of MoS_2 synthesized at low temperature on SiO_2/Si (Fig. S9a) and cover glass (Fig. S9b) substrates.

10. XPS characterization of direct-growth MoS_2 at low temperature

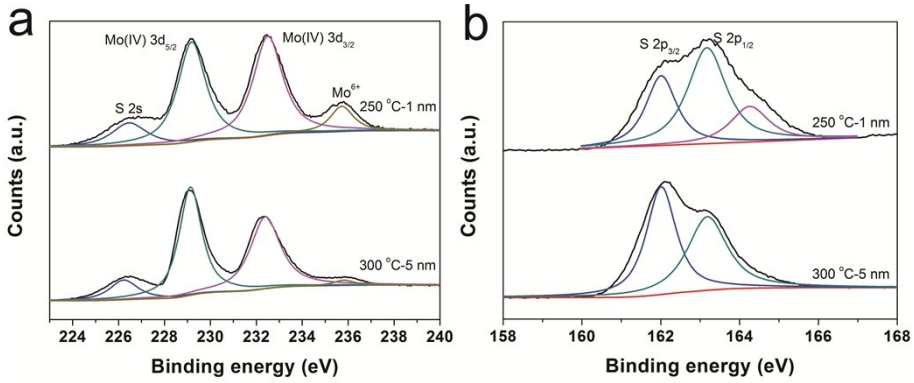

Figure S10. The characterization of XPS is performed on the direct-growth samples on polyimide substrate.

11. XPS spectra of the deposited Mo film treated with the same growth process with the absence of H_2S at 300 ^oC (a controlled experiment)

We performed the controlled experiments to discover the origin of the trace Mo^{6+} in Fig. 4a. The deposited Mo film was placed in the tube furnace and was processed under the same growth conditions but without H_2S. Fig. S11a reveals the 6+ oxidation state of Mo, and Fig. S11c shows the oxide peak position at 531.2 eV, indicating the existence of MoO_3. During the CVD process, slight oxygen leak is unavoidable, which will lead to the oxidation of Mo. When H_2S gas was introduced into the growth chamber, the deposited Mo films were suffered sufficient sulfurization. In the O1s spectra, none of the peaks originated from Mo–O bond was detected (Fig. S8b). The only peak centered at 532.3 eV belongs to Si–O bond, indicating the surface oxygen is originated from underlying SiO_2 substrate.

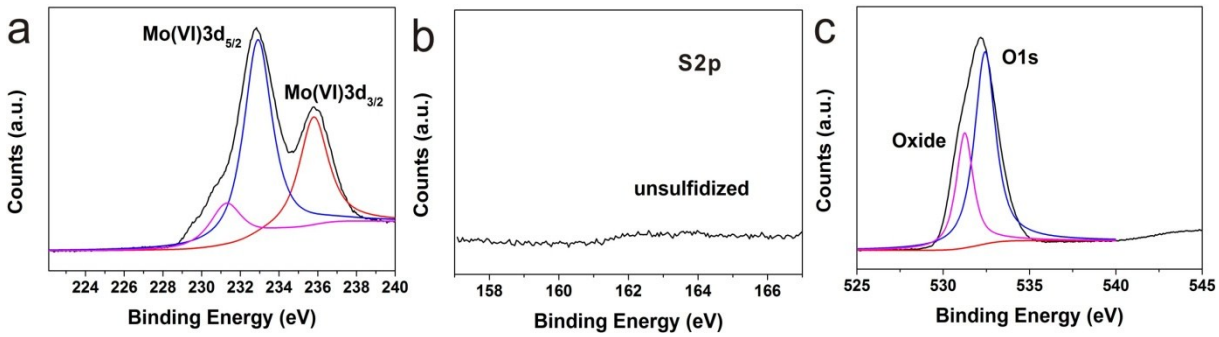

Figure S11. XPS spectrum of the deposited Mo film on SiO_2/Si substrate under the same growth condition with the absence of H_2S at 300 ^oC. (a) The binding energy of the unsulfidized Mo $3d_{5/2}$ and $3d_{3/2}$ are at the central of 232.9 eV and 235.8 eV. (b) There are no signals of $S2p_{3/2}$ and $S2p_{1/2}$. (c) The oxide peak position is central at 531.2 eV, showing the presence of metal oxide.