Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

Atomic MoS_2 Monolayers Synthesized from Metal-Organic Complex by Chemical Vapor Deposition

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1. Experimental Details

(1) Synthesis of Mo-DMDTC

Molybdenum dimethyldithiocarbamate complex (Mo-DMDTC) was synthesized by the coprecipitation between $MoCl_5$ (Alfa Aesar, 99.6%) and sodium dimethyldithiocarbamate (Na-DMDTC) (Sigma Aldrich, 98%) in aqueous solution. A solution of Na-DMDTC (6 mmol in 10 mL DI water) was added to the aqueous solution of $MoCl_5$ (1 mmol in 80 mL DI water) under magnetic stirring for 6 h at room temperature. Dropwise addition of Na-DMDTC solution resulted in purple-colored precipitate (Mo-DMDTC), which was separated by centrifuging at 5,000 rpm for 10 min and dried at ~70 ^{o}C in air.

(2) Growth of monolayer MoS_2 flakes

The growth of monolayer MoS_2 flakes was carried out in a home-built CVD furnace with 1 inch quartz tube under atmospheric pressure (Figure S1). Mo-DMDTC (40 μL, 4 mg·mL^{-1} dispersed in ethanol) was drop-dried onto a sapphire substrate and placed in the center of the furnace. Another sapphire substrate with a size of ~3 cm×1.5 cm covered on the substrate supporting Mo-DMDTC (facing down as grown substrate). Sulfur powder was placed in a ceramic boat upstream. After purging the system with Ar for 5 min, the furnace was heated up to 650 ^{o}C in 12 min with 150 sccm Ar. When the temperature of furnace reached 650 ^{o}C, sulfur was heated by a heating belt at ~170 ^{o}C. After 40 min, the furnace was heated up to 800 ^{o}C and stayed at this temperature for 10 min. Then the furnace was naturally cooled down to room temperature and the heating belt was removed at ~400 ^{o}C.

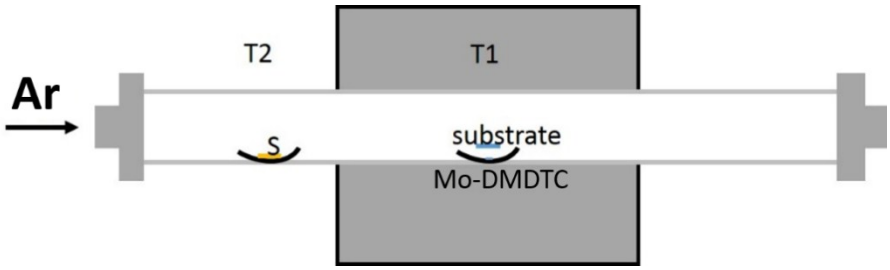

Figure S1 Schematic for the set-up used for the growth of MoS_2 flakes

(3) Transfer of MoS_2 flakes

After the growth, the sapphire substrate with MoS_2 flakes was coated with PMMA thin film (Allresist GmbH, AR-P 679.04) by spin-coating at 2,000 rpm for 1 min, followed by baking at 170

°C for 2 h. Then the baked sample was soaked in hot KOH solution (5 wt %). After the PMMA film detached from the substrate, the PMMA film was taken out of the KOH solution and rinsed thoroughly with DI water. The cleaned PMMA film was attached to a 300 nm thick SiO_2/Si substrate and baked at ~80 °C to promote the interaction of MoS_2 flakes with the substrate. Finally, the PMMA film was removed by acetone vapor to leave MoS_2 flakes on the substrate.

(4) Device fabrication and measurement

Source and drain electrodes (10 nm Ti/50 nm Au) were fabricated on MoS_2 flakes by electron-beam lithography followed by electron-beam evaporation on 300 nm SiO_2/Si substrates. The channel length of FETs we made was ~1.0 μm. The obtained MoS_2 FETs were measured with probe station in vacuum at a base pressure of ~10^{-5} mbar at room temperature using Agilent B1500A. The mobility of FETs was estimated using the method according to previous report[1].

(5) Characterizations

The FTIR spectra were collected with Bruker VERTEX 70 and the UV-vis spectra were taken with Hitachi Limited U-3900. XPS and TG-MS curves were taken with Thermo Scientific Escalab 250Xi and NETZSCH X70, respectively. AES was collected with ULVAC-PHI 700. TOF-SIMS was taken with TOF.SIMS 5. The optical images were taken with Olympus BX 51M microscope. AFM images were captured with Bruker Dimension Icon in scanasyst mode. Raman and PL spectra were collected with Horiba-Jobin-Yvon Raman system using a 514 nm laser. TEM images, SAED patterns and high resolution TEM images were taken with JEOL 2100 at 200 KV.

2. More charaterizations on Mo-DMDTC

According to the TG-MS analysis, the thermal-decomposition of Mo-DMDTC displayed a two-step weight loss and four major products were detected during the decomposition process (Figure S2(b), (c) and (d)). The existence of H_2O (m/z = 18) indicated that hydrated water was contained in Mo-DMDTC. The other two products were assigned to CO (m/z = 28) and CO_2 (m/z = 44) which could be possibly attributed to the mild oxidation of some organic products by trace oxygen in the system. The product with a m/z of 76 should be CS_2. Due to the limitation of this test, only gas with boiling point lower than 200 °C could be detected. We can infer that the DMDTC ligand should mainly change to CS_2 and $(CH_3)_2NCSN(CH_3)_2$ based on previous studies

on the thermal-decomposition of other metal-DMDTC complexes[2].

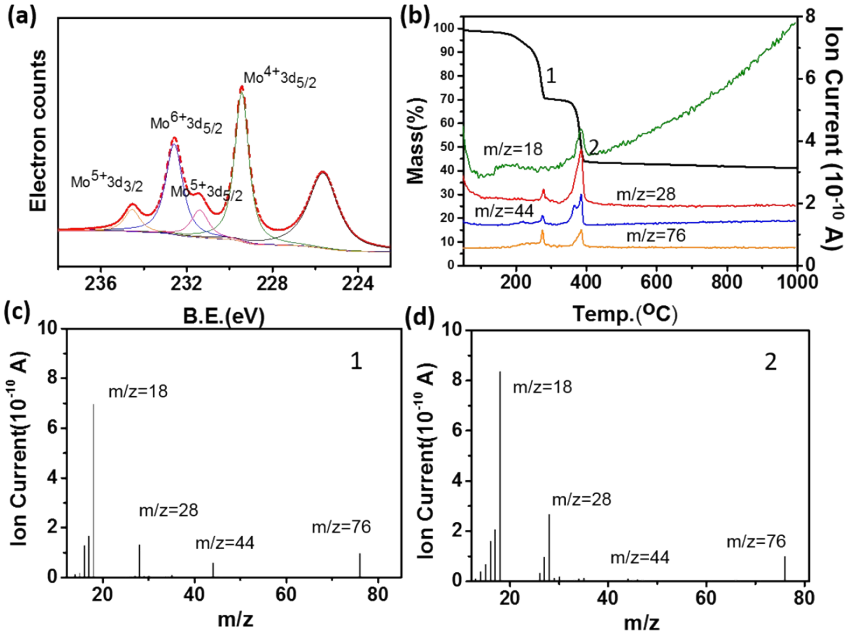

Figure S2 (a) XPS of Mo-DMDTC. (b) TG curve and MS ion currents of characteristic fragments for the decomposition of Mo-DMDTC. (c, d) Two typical mass spectra for the products produced at the steps marked with 1 and 2 in (b), respectively.

3. Thermal decomposition of Mo-DMDTC

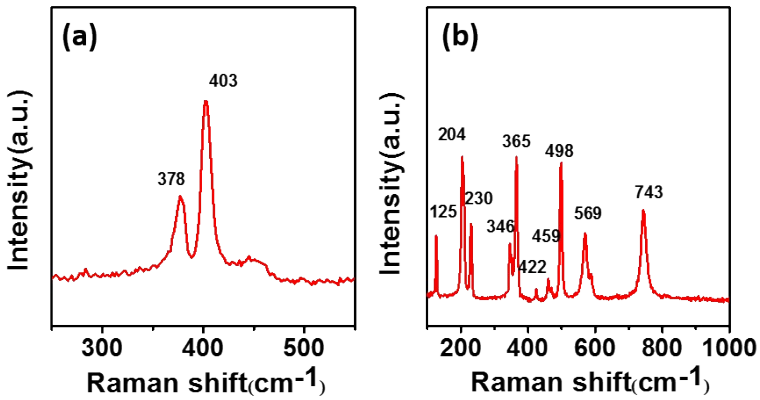

Figure S3 Raman measurements on the thermal decomposition products of Mo-DMDTC. (a) Raman spectroscopy of Mo-DMDTC after TG test. (b) Raman spectroscopy of the remained materials of Mo-DMDTC that deposited on the substrate after annealing at 400 °C in our CVD system.

4. More characterizations on as-grown MoS_2

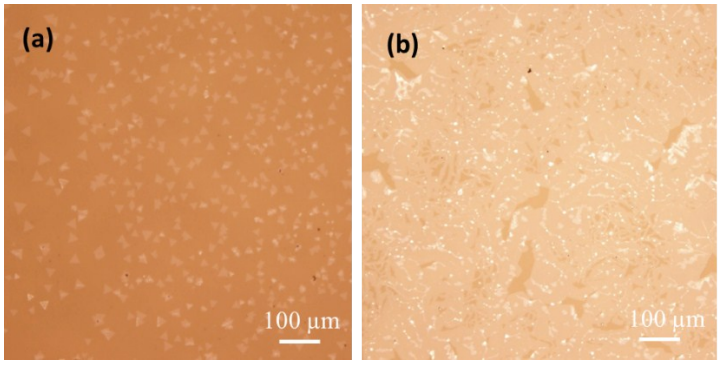

Figure S4 Low magnification optical images of typical growth results. (a) Individual MoS_2 flakes. (b) Continuous MoS_2 film.

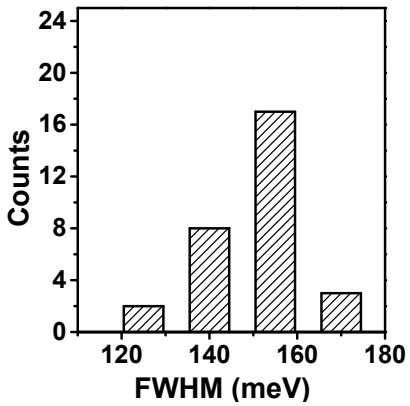

Figure S5 The distribution of A-exciton PL peak FWHM in 30 MoS_2 flakes

5. Effects of growth temperature and substrate

The optimized growth temperature for MoS_2 was 800 ^oC. At a lower growth temperature of 600 ^oC, only small MoS_2 pieces could be found on the growth substrate (Figure S6b). At a higher growth temperature of 900 ^oC, the obtained MoS_2 flakes were larger in size (~60 μm) but the edges were not straight and multiple layers were grown on the top of the 1L flakes (Figure S6d). Besides sapphire, the growth of MoS_2 can also be achieved on SiO_2/Si substrates, but the shape of the obtained flakes is not as regular as those grown on sapphire substrates (Figure S7).

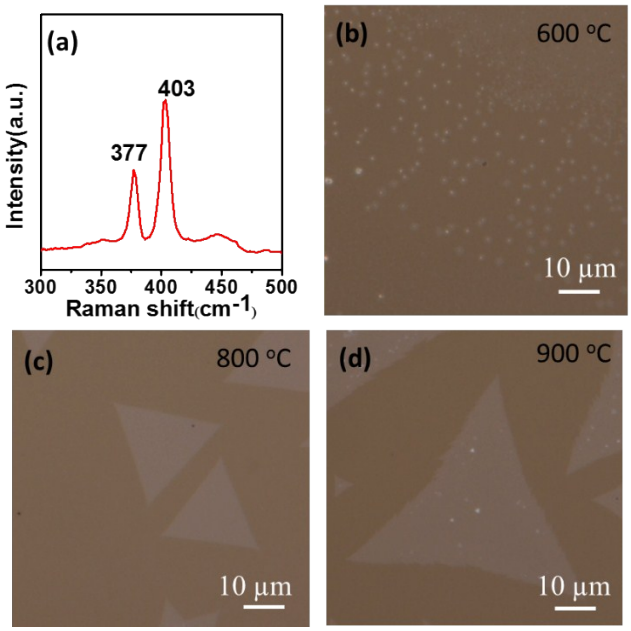

Figure S6 (a) Raman spectrum of the remained materials after the TGA tests. (b, c, d) MoS_2 flakes grown at different temperatures.

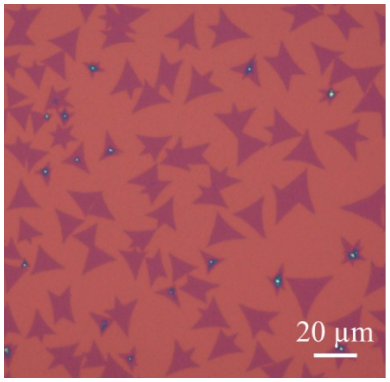

Figure S7 MoS_2 flakes grown on SiO_2/Si substrate

6. Promotion effect of Mo-DMDTC ligand

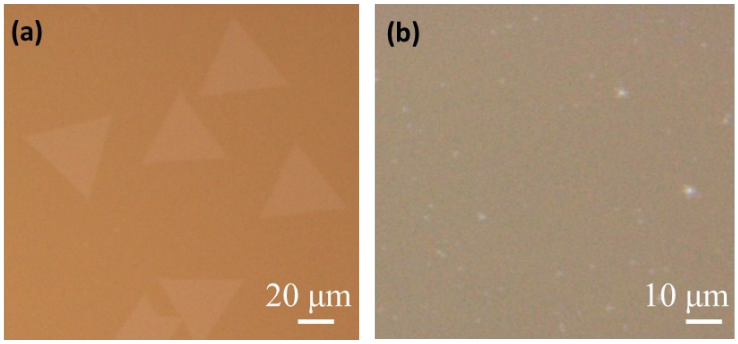

Figure S8 (a) Typical growth result using Mo-DMDTC as precursor. (b) MoS_2 particles grown from Mo-DMDTC after the removal of organic ligands by heating at 1000 °C in Ar.

7. AES measurement on the transferred MoS_2 flakes

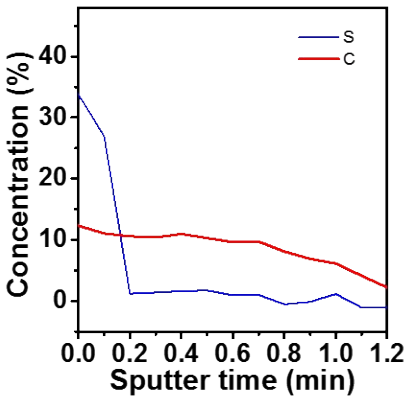

Figure S9 Depth profiling analysis of S and C atomic concentrations on the transferred MoS_2 flakes with Auger electron spectroscopy (AES).

8. More electrical data on MoS_2 devices

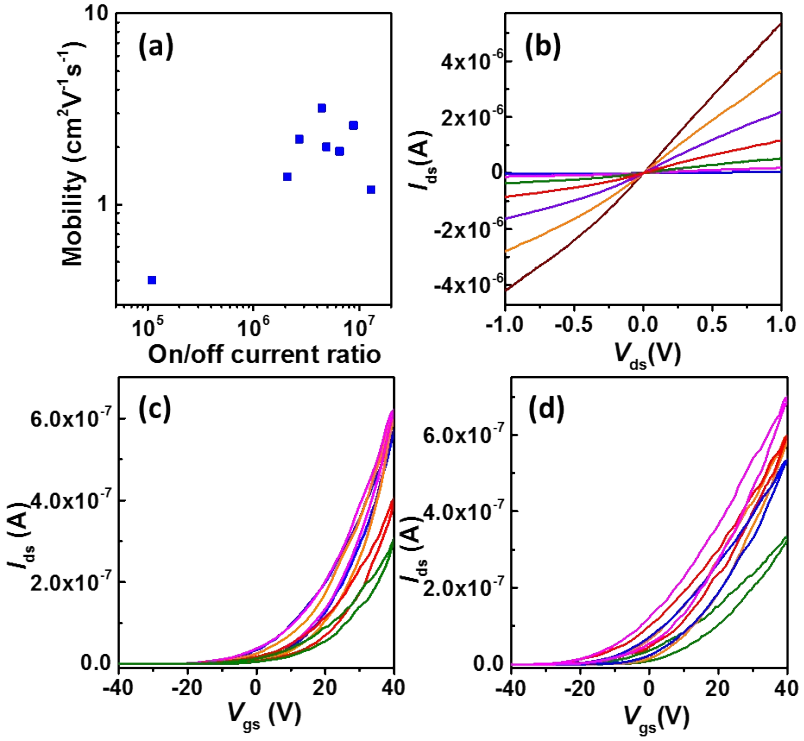

Figure S10 (a) The distribution of mobility and on/off current ratios of 8 MoS_2 FETs. (b) I_{ds}−V_{ds} curves for the device in Figure 5(a) at varied V_{gs} from −40 to 40 V at steps of 10 V from bottom to top. (c, d) Hysteresis in I_{ds}-V_{gs} curves for ten FETs made on MoS_2 flakes grown with Mo-DMDTC and MoO_3 (five devices for each type) at V_{ds}=0.5 V, respectively.

9. Comparison of MoS_2 grown with different approaches

The comparison on grain size and mobility between our MoS_2 flakes and several previous results were listed in the following table. The grain size and mobility of our flakes showed a reasonable value among the existing results with similar device configurations.

Table S1 Comparison of 1 L MoS_2 flakes grown with different approaches

CVD MoS_2	**Grain size**	**Mobility ($cm^2V^{-1}s^{-1}$)**
This work	20-30 μm	1.2-3.2
Y. H. Lee. et al. *Adv. Mater.*, 2012, **24**, 2320-2325.	~160 nm	0.02
X. Wang. et al. *J Am. Chem. Soc.*, 2013, **135**, 5304-5307.	~10 μm	0.1-0.7
Najmaei, S. et al. *Nano Lett*. 2014, **14**, 1354-1361.	~20 μm	1.9
Q. Zhang. et al. *Angew. Chem. Int. Ed.*, 2015, **54**, 8957-8960	20-40 μm	~ 6

Note: The FETs in the table were all fabricated with CVD grown MoS_2 flakes transferred onto SiO_2/Si substrate with similar device configuration and similar post-fabricated thermal treatments.

References

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