

# Wafer-Scale and Deterministic Patterned Growth of Monolayer

## MoS<sub>2</sub> via Vapor-Liquid-Solid Method

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## Growth conditions:

1) 4-inch-wafer-scale growth of monolayer VLS-MoS<sub>2</sub> flakes: A 4-inch SiO<sub>2</sub>/Si wafer was treated with UV-Ozone for 30 minutes to obtain hydrophilic surface. To load Na<sub>2</sub>MoO<sub>4</sub>, ~10 mL of 4 mg/mL Na<sub>2</sub>MoO<sub>4</sub> aqueous solution was drop on the wafer first. Then, spin-coating was conducted at 5000 rpm for 60 seconds. The 4-inch SiO<sub>2</sub>/Si wafer was cut to small pieces to fit the inner-diameter of a 2-inch quartz tube. The growth was performed in a thermal tube furnace at 750 °C for 5 minutes with 100 sccm high-purity Argon as carrier gas. The temperature ramping rate was 30 °C/min. The temperature of sulfur was kept at ~170 °C and ~ 25 mg sulfur was consumed during the growth. (Fig. S1)

2) 2-inch-wafer-scale growth of monolayer VLS-MoS<sub>2</sub> film: 2-inch sapphire substrate was pretreated with UV-Ozone for 30 minutes to obtain highly hydrophilic surface. Here, Na<sub>2</sub>MoO<sub>4</sub> particles was uniformly distributed on sapphire substrate by loading ~1.5 mL of 5 mg/mL Na<sub>2</sub>MoO<sub>4</sub> aqueous solution. And then, spin-coating was conducted at 3000 rpm for 60 seconds. The growth condition is like the growth of VLS-MoS<sub>2</sub> flakes on SiO<sub>2</sub>/Si substrates. To engineer the grain size of as-grown VLS-MoS<sub>2</sub> film, the supply of sulfur and growth time were modified. For large-grain VLS-MoS<sub>2</sub> film (>100 μm), low concentrated sulfur and long growth time were used, ~ 80 mg sulfur was consumed in 30-minute growth. For small-grain VLS-MoS<sub>2</sub> film (<100 μm), high concentrated sulfur and short growth time were required, ~ 60 mg sulfur was consumed in 10-minute growth.

3) Patterned growth of monolayer VLS-MoS<sub>2</sub> film: A photomask was used to intimately contact with a sapphire substrate first. Then vacuum ultraviolet (VUV) was employed to irradiate the sapphire substrate for 2 minutes. As a result, the originally less-hydrophobic sapphire substrate with a contact angle of ~26.3° with 5 mg/mL Na<sub>2</sub>MoO<sub>4</sub> aqueous solution was patterned with an array of highly hydrophilic rectangles. The VUV-exposed sapphire substrate usually has a highly hydrophilic surface with a contact angle of ~8.5°. Then, ~0.5 mL of 5 mg/mL Na<sub>2</sub>MoO<sub>4</sub> was loaded on the sapphire substrate and spin-coated with a speed of 4000 rpm for 30 seconds. A clear difference of the size and area-density of Na<sub>2</sub>MoO<sub>4</sub> particles between the highly hydrophilic rectangular area and surrounding less-hydrophilic area can be observed.

The growth results indicated that high area-density of small  $\text{Na}_2\text{MoO}_4$  particles in the hydrophilic rectangular area were facile for the growth of continuous VLS- $\text{MoS}_2$  film. While the large  $\text{Na}_2\text{MoO}_4$  particles deposited on the surrounding hydrophobic area were only converted to thick  $\text{MoS}_2$  islands. (**Fig. 4**)

4) Patterned growth of monolayer VLS- $\text{MoS}_2$  flakes: A layer of photoresist (AZ5214) was spin-coated on a  $\text{SiO}_2/\text{Si}$  substrate. A standard LED photolithography process was performed to prepare patterns on the  $\text{SiO}_2/\text{Si}$  substrate. Then, the  $\text{SiO}_2/\text{Si}$  substrate was treated with UV-Ozone for 30 minutes to modify the surface to hydrophilic. After spin-coating of  $\sim 0.5$  mL of 5 mg/mL  $\text{Na}_2\text{MoO}_4$  aqueous solution at 3000 rpm for 30 seconds. The patterned  $\text{Na}_2\text{MoO}_4$  was obtained by sequential washing with dehydrate acetone at 50 °C for 30 minutes and IPA for 5 minutes. Then the  $\text{SiO}_2/\text{Si}$  substrate with patterned  $\text{Na}_2\text{MoO}_4$  particles was blew dry with  $\text{N}_2$ . The growth condition was the same as the growth of VLS- $\text{MoS}_2$  flakes on  $\text{SiO}_2/\text{Si}$  substrates. (**Fig. 5**)

#### **Transfer of VLS- $\text{MoS}_2$ flakes:**

1) For XPS: To remove the adsorbed Na residuals, the as-grown VLS- $\text{MoS}_2$  flakes were immersed in IPA/ $\text{H}_2\text{O}$  (9/1 vol.) solution for 30 minutes. Then, the as-grown samples were spin-coated with a layer of PMMA. The PMMA film was peeled off from growth substrate using KOH (35 wt%) as etchant. The PMMA film was transferred to an Au (50 nm) coated heavily doped silicon substrate. Finally, the PMMA was removed by resining with acetone and IPA sequentially.

2) For TEM observation: To investigate the Na residuals in the as-grown VLS- $\text{MoS}_2$  flakes on  $\text{SiO}_2/\text{Si}$  substrate, the samples were firstly protected by spin-coating a layer of polycarbonate. The  $\text{SiO}_2$  layer was therefore etched in a diluted HF solution and the polycarbonate along with the  $\text{MoS}_2$  monolayers were peeled off from the growth substrate. The film was rinsed for several times in DI water before transferring to TEM grids. Finally, the polycarbonate film was removed in chloroform and the as-grown VLS- $\text{MoS}_2$  flakes left on a Quantifoil microgrids. (**Fig. S3**)

### **Fabrication of VLS-MoS<sub>2</sub> FETs:**

The VLS-MoS<sub>2</sub> monolayers were grown on silicon substrates with 285-nm-thick SiO<sub>2</sub> layer. First, the substrates were spin-coated with a layer of photoresist (AZ5214). Then, a standard LED photolithography process was conducted to define the patterns of electrodes. After the deposition of Ti/Au (5 nm/50 nm) film, a lift-off process was employed to remove residual photoresist. A second photolithography and oxygen plasma etching were used to define the shape of the channels VLS-MoS<sub>2</sub> FETs. (**Fig. S5**)

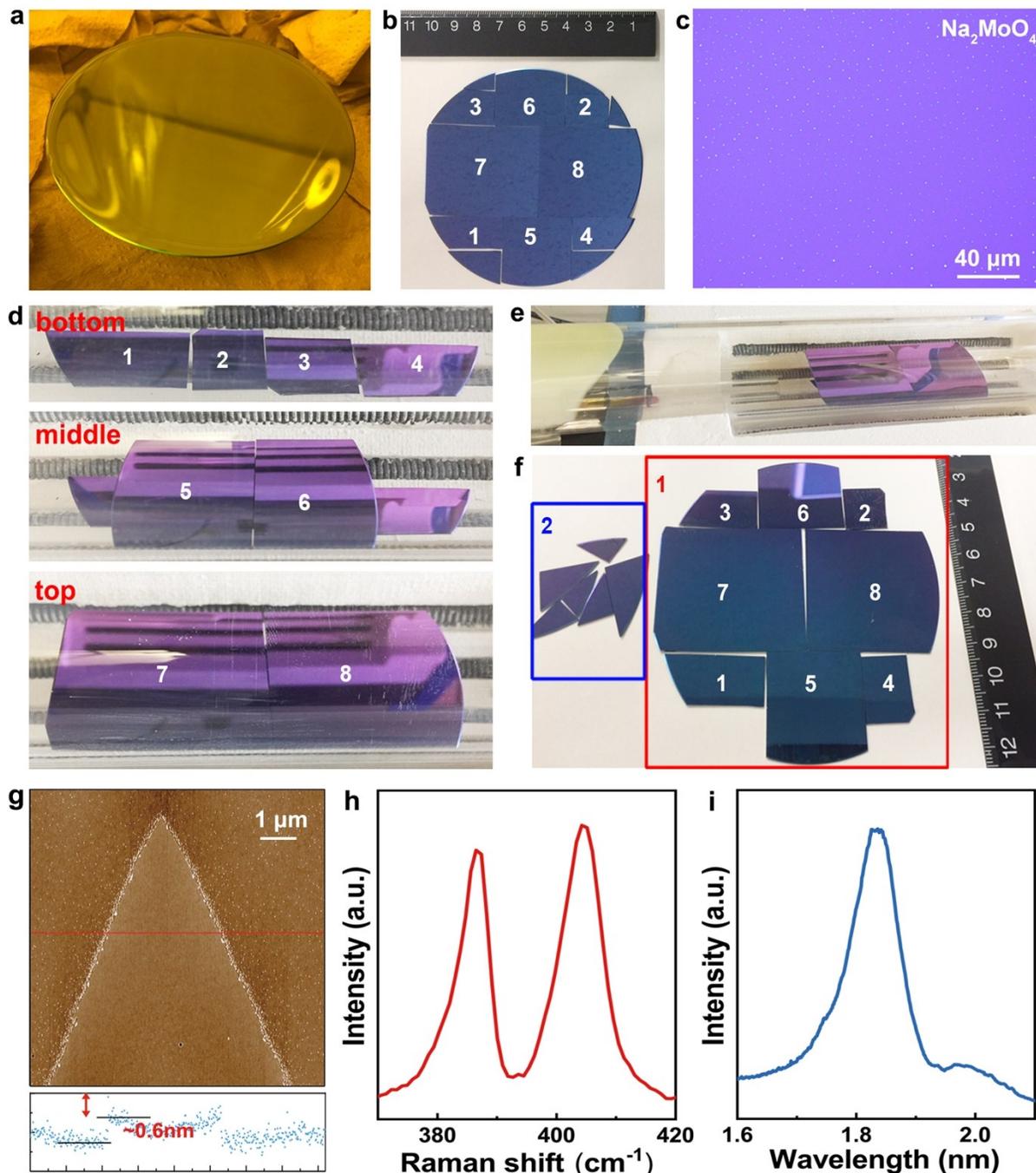
### **Characterization:**

1) Raman and PL: The micro-Raman/PL was performed using a laser confocal microscope (inVia, Renishaw). The 532-nm excitation laser was focused on the sample surface with a 100× objective lens. Then, Raman/PL signals from the MoS<sub>2</sub> samples were detected by an electron multiplying CCD detector (Andor) through a grating with 1800 grooves/mm for Raman and 150 grooves/mm for PL. The laser spot size was about 1 μm in diameter.

2) STEM and EELS: STEM images were acquired by using JEOL 2100F microscope equipped with dodecapole correctors and the cold field emission gun operating at 60 kV. The probe current was about 25-30 pA. The convergence semiangle was 35 mrad and the inner acquisition semiangle was 79 mrad. The EELS core loss spectra were taken by using Gatan low-voltage quantum spectrometer.

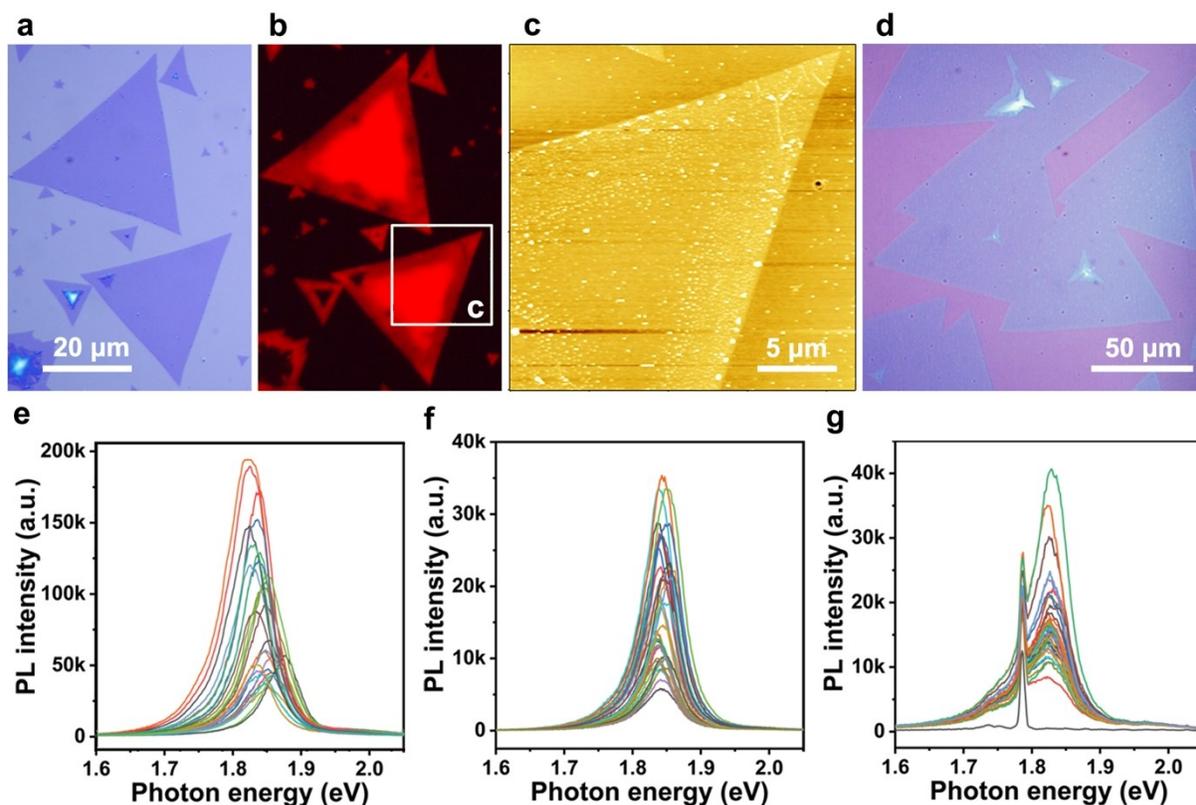
3) Measurement of VLS-MoS<sub>2</sub> FETs: To test the transport properties of VLS-MoS<sub>2</sub> FETs, the devices were loaded in a vacuum chamber with a pressure of  $\sim 10^{-3}$  Pa. The backgate bias ( $V_{gs}$ ) was scanned forward from -20 V to 60 V and backward from 60 V to -20 V, the source-drain bias ( $V_{ds}$ ) is 1 V. To measure the output performance of VLS-MoS<sub>2</sub> FETs, the backgate bias ( $V_{gs}$ ) was scanned from 0 to 60 V with a step of 20 V. The source-drain bias ( $V_{ds}$ ) was swept forward from 0 V to 2 V and backward form

2 V to 0 V with a step of 50 mV. The Y-axis was normalized to conductivity using the channel current and device dimensions.

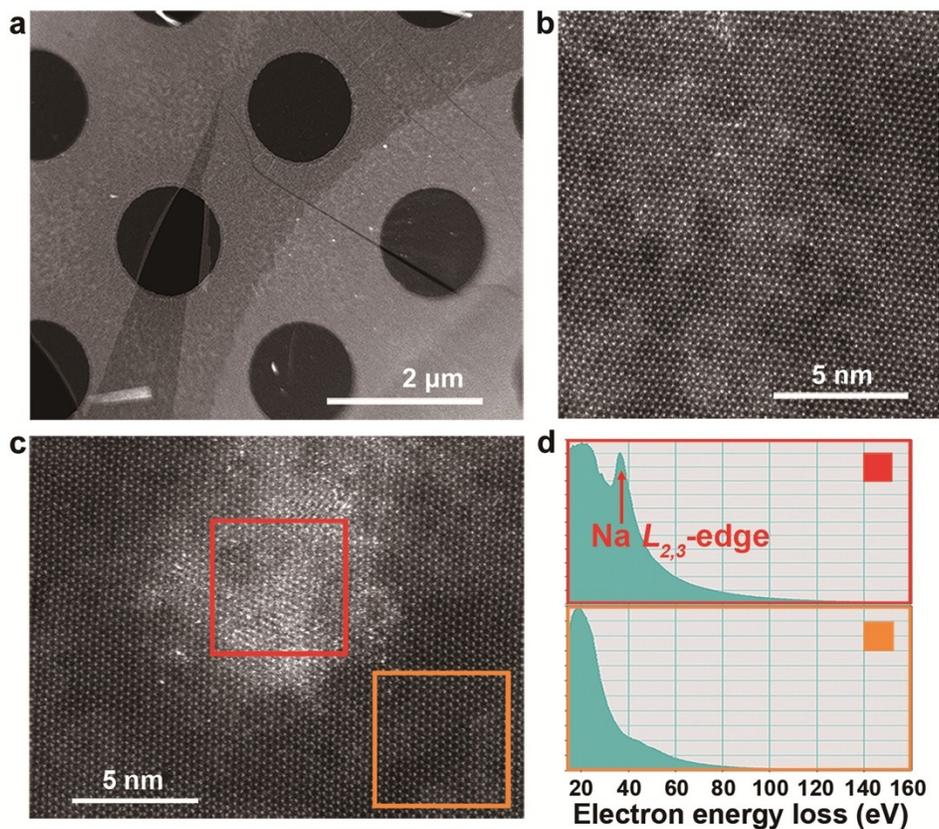


**Fig. S1. 4-inch-wafer-scale growth of monolayer VLS-MoS<sub>2</sub> flakes.** (a) Spin-coating of Na<sub>2</sub>MoO<sub>4</sub> aqueous solution on a 4-inch SiO<sub>2</sub>/Si wafer. (b) A photo of the SiO<sub>2</sub>/Si substrates cut with different widths (~15, 30 and 44 mm). (c) An optical image of Na<sub>2</sub>MoO<sub>4</sub> particles deposited on the SiO<sub>2</sub>/Si substrate. (d) Photos of the SiO<sub>2</sub>/Si substrates loaded in a 2-inch quartz tube furnace as three layers. (e) A photo of the

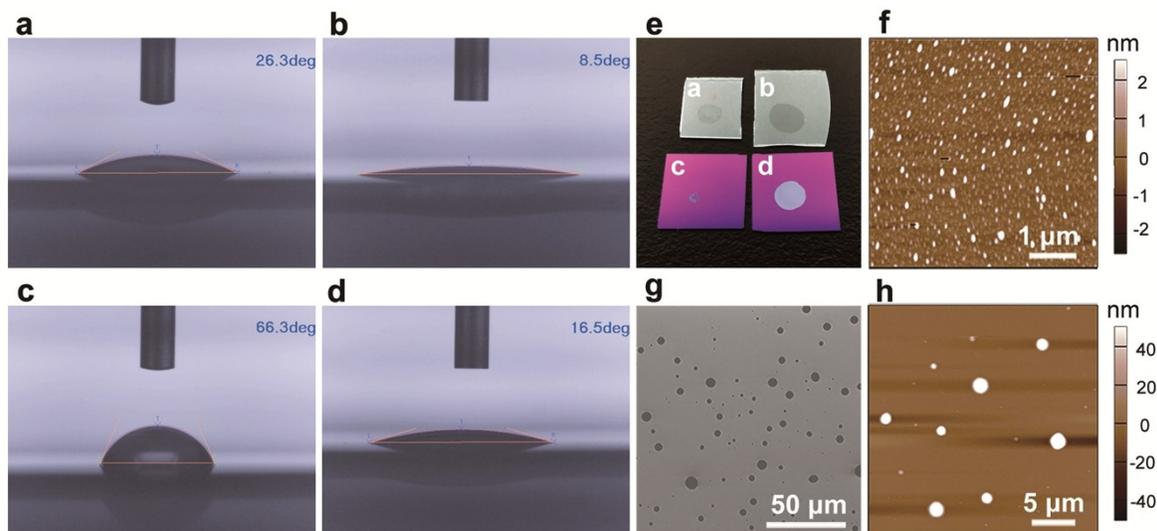
tube furnace after VLS growth of MoS<sub>2</sub>. (f) A photo of the 8 pieces of SiO<sub>2</sub>/Si substrates after VLS growth of MoS<sub>2</sub>. (g) A typical AFM image of a VLS-MoS<sub>2</sub> flake with a height of ~0.6 nm. (h, i) Typical (h) Raman and (i) PL spectra of the as-grown monolayer VLS-MoS<sub>2</sub> flakes.



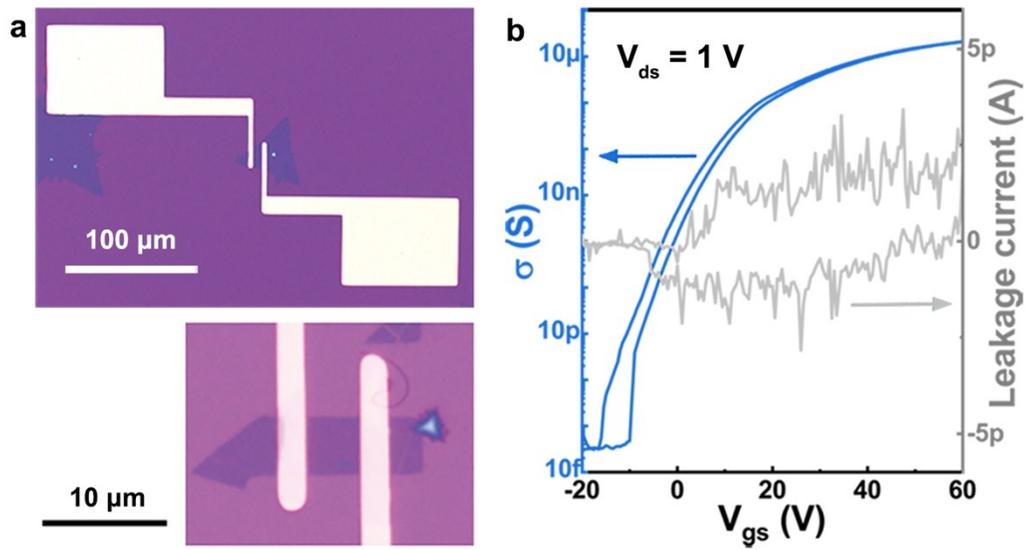
**Fig. S2** (a) An optical image and (b) corresponding fluorescence image of MoS<sub>2</sub> flakes on a SiO<sub>2</sub>/Si substrate grown by powder CVD. (c) An AFM image shows the MoS<sub>2</sub> flake with non-uniform fluorescence is monolayer. (d) An optical image of monolayer VLS-MoS<sub>2</sub> flakes (corresponding to **Fig. 2i**). (e) PL spectra of monolayer MoS<sub>2</sub> flakes on a SiO<sub>2</sub>/Si substrate grown by powder CVD. (f) PL spectra of monolayer VLS-MoS<sub>2</sub> flakes grown on a SiO<sub>2</sub>/Si substrate. (g) PL spectra of monolayer VLS-MoS<sub>2</sub> film grown on a 2-inch sapphire substrate. The peak at ~1.78 eV comes from the sapphire substrate.



**Fig. S3. STEM images and EELS spectra of monolayer VLS-MoS<sub>2</sub> flakes.** (a) A low-magnification STEM image of a VLS-MoS<sub>2</sub> flake transferred on a Quantifoil microgrid. (b) A high-magnification STEM image of a VLS-MoS<sub>2</sub> flake with a high crystallinity. (c) A high-magnification STEM image of a VLS-MoS<sub>2</sub> flake with residual nanoparticle on surface. (d) EELS spectra taking from the residual nanoparticle (red square in (c)) and the clean area (orange square in (c)), respectively. The residual nanoparticle contains Na and shows EELS  $L_{2,3}$ -edge at  $\sim 35$  eV.



**Fig. S4. Contact angles of  $\text{Na}_2\text{MoO}_4$  aqueous solution and as-deposited  $\text{Na}_2\text{MoO}_4$  particles on  $\text{SiO}_2/\text{Si}$  and sapphire substrates, respectively.** (a, b) Optical images showing the contact angles of 2  $\mu\text{L}$  of 5 mg/mL  $\text{Na}_2\text{MoO}_4$  aqueous solution on (a) original and (b) UV-Ozone treated sapphire substrates. (c, d) Optical images showing the contact angles of  $\text{Na}_2\text{MoO}_4$  aqueous solution on (c) original and (d) UV-Ozone treated  $\text{SiO}_2/\text{Si}$  substrates. (e) A photo showing the dried  $\text{Na}_2\text{MoO}_4$  marks on the four substrates corresponding to **Fig. S4a-d**. (f) An AFM image of spin-coated  $\text{Na}_2\text{MoO}_4$  particles on a sapphire substrate. (g) A SEM and (h) an AFM image of spin coated  $\text{Na}_2\text{MoO}_4$  particles on a  $\text{SiO}_2/\text{Si}$  substrate. Substrates in **Fig. S4b** and **S4d** were treated with UV-Ozone for 30 minutes. For **Fig. S4f-h**, 5 mg/mL  $\text{Na}_2\text{MoO}_4$  aqueous solution was used for spin-coating at a speed of 3000 rpm for 60 seconds.



**Fig. S5. VLS-MoS<sub>2</sub> FETs.** (a) Optical images of an as-fabricated VLS-MoS<sub>2</sub> FET. (b) Typical transfer curve and leakage current of the VLS-MoS<sub>2</sub> FET shown in **Fig. 5e**.