

# MoS<sub>2</sub>-OH Bilayer Mediated Growth of Inch-Sized Monolayer MoS<sub>2</sub> on Arbitrary Substrates

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**ABSTRACT:** Due to remarkable electronic property, optical transparency and mechanical flexibility, monolayer molybdenum disulfide (MoS<sub>2</sub>) has been demonstrated to be promising for electronic and optoelectronic devices. To date, the growth of high-quality and large-scale monolayer MoS<sub>2</sub> has been one of the main challenges for practical applications. Here we present a MoS<sub>2</sub>-OH bilayer mediated method that can fabricate inch-sized monolayer MoS<sub>2</sub> on arbitrary substrates. This approach relies on a layer of hydroxide groups (-OH) that are preferentially attached to the (001) surface of MoS<sub>2</sub> to form MoS<sub>2</sub>-OH bilayer structure for growth of large area of monolayer MoS<sub>2</sub> during the growth process. Specifically, the hydroxide layer impedes vertical growth of MoS<sub>2</sub> layers along the [001] zone axis, promoting the monolayer growth of MoS<sub>2</sub>, constrains growth of the MoS<sub>2</sub> monolayer only in lateral direction into larger area, and effectively reduces sulfur vacancy and defects according to density functional theory calculations. Finally, the hydroxide groups advantageously prevent the MoS<sub>2</sub> from interface oxidation in air, rendering high-quality MoS<sub>2</sub> monolayers with carrier mobility up to  $\sim 30 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . Using this approach, inch-sized uniform monolayer MoS<sub>2</sub> has been fabricated on the sapphire and mica and high-quality monolayer MoS<sub>2</sub> of single crystalline domains exceeding 200  $\mu\text{m}$  has been grown on various substrates including amorphous SiO<sub>2</sub> and quartz and crystalline Si, SiC, Si<sub>3</sub>N<sub>4</sub> and graphene. This method provides a new opportunity for the monolayer growth of other two-dimensional (2D) transition metal dichalcogenides (TMDs) such as WS<sub>2</sub>, MoSe<sub>2</sub>.

## INTRODUCTION

2D TMDs have drawn extensive attention due to their attractive physical properties, such as outstanding electronic property, optical transparency, and mechanical flexibility.<sup>1-5</sup> It was demonstrated that TMD semiconductors undergo an indirect-to-direct band gap transition when thinned from bulk to a monolayer.<sup>1</sup> Monolayer molybdenum disulfide (MoS<sub>2</sub>) is a representative TMD with a direct bandgap, and has been widely studied for applications in field effect transistors (FETs), photodetectors, piezotronic devices, *etc.*<sup>5-9</sup> The growth of high-quality and large-scale monolayer MoS<sub>2</sub> underpins these technological advancements. Among various methods, the CVD approach has the potential for scaled-up production of high-quality 2D materials.<sup>5, 10-16</sup> However, monolayer MoS<sub>2</sub> growth has still suffered from a high defect density, small domain size and formation of multilayers because of non-uniformity of aggregated/diffusing precursors on growth substrates and nucleation of crystallites occurred preferentially at impurities or defect sites on solid substrates. They prevent the full potential of monolayer MoS<sub>2</sub> to be realized.<sup>17-19</sup> Therefore, the key step

is to find a substrate-independent strategy for the growth of high quality monolayer MoS<sub>2</sub>.

Herein, we report a MoS<sub>2</sub>-OH bilayer mediated method for fabrication of inch-sized monolayer MoS<sub>2</sub> on arbitrary substrates. This method demonstrates that hydroxide (-OH) groups in the aqueous solution are preferentially attached to the (001) surface of MoS<sub>2</sub> during the growth process. They not only suspend the growth along the [001] zone axis which promotes formation of monolayer MoS<sub>2</sub>, but also lead to a lower density of sulfur vacancies and defects. According to density functional theory (DFT) calculations, the -OH surface groups are proved to drive the growth of monolayer MoS<sub>2</sub> on arbitrary substrates. Inch-sized uniform monolayer MoS<sub>2</sub> can be obtained on both sapphire and mica substrates. More importantly, high-quality monolayer MoS<sub>2</sub> with domain size exceeding 200  $\mu\text{m}$  can be grown on various substrates, from crystalline Si, SiC, Si<sub>3</sub>N<sub>4</sub>, and graphene to amorphous SiO<sub>2</sub> and quartz.

## EXPERIMENTAL

**Substrate Preparation:** To improve the wettability of molybdenum precursor during spin coating, the surface of various

substrates was transformed from weakly hydrophilic to hydrophilic by treating with piranha solution (Be cautious: H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> in the ratio of 2:3). After the piranha treatment, the substrates were rinsed with copious amounts of deionized water and dried with the N<sub>2</sub> gun.

**Preparation of hydroxide-assisted aqueous solution:** 0.05 g ammonium molybdate (powder, 98 %) and different proportions of KOH were dissolved in 5 mL deionized water to obtain 0, 0.25, 1 and 4 M KOH precursor solutions, respectively. Those precursor solutions were then spin coated to diverse substrates with 8000 rpm/s to obtain a well-distributed film.

**Growth of monolayer MoS<sub>2</sub>:** An alumina boat loaded with several spin-coated substrates was placed at the heating center of a quartz tube, and another alumina boat loaded with 50 mg sulfur at the upstream of the tube, where the temperature was independently controlled. Then the center of quartz tube was ramped up to 750 °C for 40 min, meanwhile the S powder was heated to 200 °C for 15 min. Growth of MoS<sub>2</sub> was carried out at 750 °C under inert atmosphere (30 sccm Ar) for 10 min, then the furnace was naturally cooled to room temperature.

**In situ TEM observation:** The TEM samples were spin-coated with 1 M and without KOH precursor solution on a Si<sub>3</sub>N<sub>4</sub> membrane (Si<sub>3</sub>N<sub>4</sub> thickness of ~50 nm) supported by a silicon E-Chip, respectively. The TEM observations were conducted in a Cs-corrected environmental TEM (FEI, Titan ETEM, 300 kV). During the observations, the sample was irradiated with the intensity of the e-beam ~200 pA cm<sup>-2</sup>, and the image was recorded with a Gatan SC1000 ORIUS CCD camera with a short exposure time (~1 s).

**Transfer of monolayer MoS<sub>2</sub>:** i) 9 g of PS with a molecular weight of 280000 g/mol was dissolved in 100 mL of toluene and then the PS solution was spin-coated (3500 rpm for 60 s) on as-grown monolayer MoS<sub>2</sub> on any substrates. ii) the sample was baked at 80 °C for 15 min. iii) A water droplet was dropped on top of the sample, resulting in the delamination of the PS-MoS<sub>2</sub> assembly. iv) the floating PS-MoS<sub>2</sub> film was dredged up with a clean SiO<sub>2</sub>/Si substrate or a holeycarbon TEM grid. v) a mild baking at 80 °C for 1 h to remove the water residues and a final baking for 30 min at 150 °C to spread the polymer for the elimination of possible wrinkles. vi) PS was removed by rinsing with toluene several times.

**Structure and optical property characterization:** The morphology of the as-grown MoS<sub>2</sub> was characterized using an optical microscope (Nikon Eclipse LV100) and SEM (FEI Scios, 15 kV). The phase of products was checked by using an XRD (Bruker D8 Advance). X-ray photoelectron spectroscopy (Thermo Fisher Escalab 250Xi) was used to characterize the chemical composition of as-grown MoS<sub>2</sub> sample with -OH. HRTEM imaging was performed on a field emission TEM (FEI Tecnai F20, 200 kV); SAED measurements were performed on a TEM operating at 120 kV (FEI Tecnai T12). Room temperature ADF-STEM imaging was performed using a JEOL ARM200F at 200kV. Raman and PL spectra/maps were collected with a confocal Raman spectrometer (Horiba Jobin Yvon HR Evolution) using a 532-nm laser as the excitation source. The laser spot size was 1 mm and the laser power on the sample surface was kept below 60 mW.

**AFM and KPFM Measurement:** The AFM and KPFM images were obtained using a Bruker Dimension Icon AFM system. An AFM tip (SCANASYST-AIR, Bruker Nano Inc.) was applied to probe the topography and thickness of the samples in the peak-force working mode, while the KPFM measure-

ments were performed using a conductive tip (SCM-PIT-V2, Bruker.) with a resonant frequency of 75 kHz, a lift height of 60 nm, and the ac bias of 0.5 V. To obtain quantitative work function values of as-grown MoS<sub>2</sub>, we calibrated the tip on the gold surface by using the known work function of gold  $\phi_{Au} = 5.10$  eV. The work function of as-grown monolayer MoS<sub>2</sub> can be calculated using the following equations:  $\phi_{tip} = 4.765$  eV,

$$\begin{aligned}\phi_{substrate} &= \phi_{tip} - e(CPD_{tip} - CPD_{substrate}) \\ &= 4.765 - 0.045 = 4.72 \text{ eV},\end{aligned}$$

$$\phi_{MoS_2} = \phi_{substrate} + e\Delta DP = 4.72 - 0.07 = 4.65 \text{ eV}.$$

**Density functional theory calculations:** The first-principles DFT calculations were carried out by using the projector-augmented wave (PAW)<sup>20</sup> method and the Perdew-Burke-Ernzerhof exchange correlation functional<sup>21-22</sup> as implemented in the Vienna Ab-initio Simulation Package (VASP).<sup>23</sup> To include the effects of van der Waals interactions, the approach of Grimme (DFT-D3)<sup>24</sup> was adopted. The calculated equilibrium lattice constants are  $a = b = 3.15180$  Å and  $c = 17.94945$  Å for bulk MoS<sub>2</sub> and  $a = 4.77805$  Å for  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (Sapphire). The cutoff energy for the plane-wave basis set is 500 eV. The  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(001) surface was simulated by a twelve-layer  $p$  (2×2) unit cell containing 80 atoms, with a vacuum region of 15 Å. Here the surface is Al-terminated, which is known as the most stable configuration.<sup>25</sup> The monolayer MoS<sub>2</sub> deposited on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(001) were simulated by a (3×3) unit cell: the lattice mismatch is ~1.0%. The surface Brillouin zone was sampled using a 15×15×1  $k$ -point mesh. All the atoms except the bottom five atomic layers of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (001) were allowed to relax until the forces exerted on each atom are less than 0.02 eV/Å, while the bottom five layers were fixed in their respective bulk positions. The adsorption energies of OH<sup>-</sup> were calculated by using neutral systems with a homogeneous background charge, as described in a previous DFT study.<sup>26</sup>

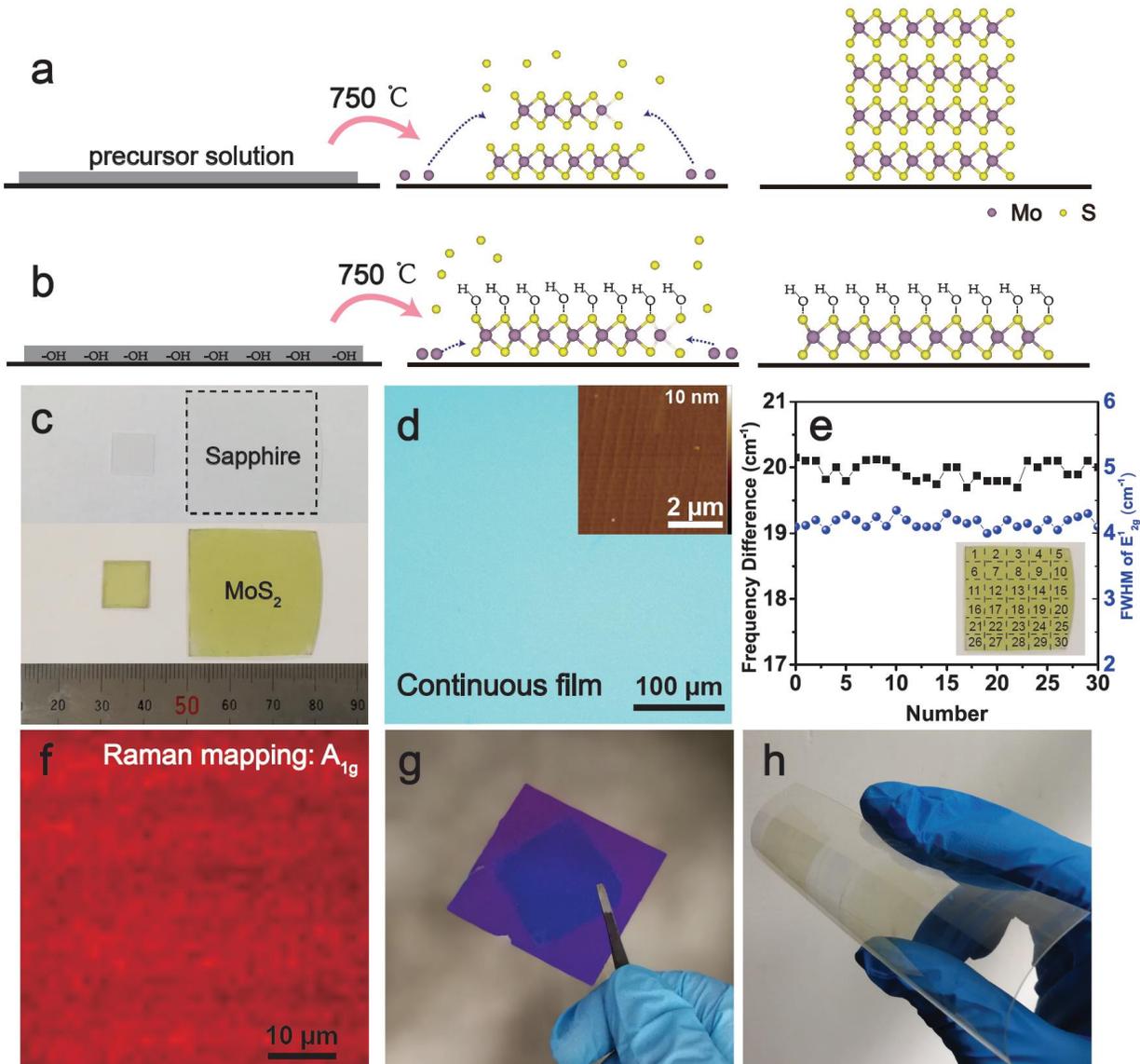
**Electrical Characterization:** Monolayer MoS<sub>2</sub> were transferred to n-doped Si substrates with 300-nm-thick SiO<sub>2</sub>. Subsequently, a conventional photolithography was used to pattern the source and drain electrodes, followed by a thermal evaporation and lift-off process to achieve Ni/Au electrodes with a thickness of 10 nm/50 nm. All the current-voltage (I-V) characteristics of the devices were measured with a Keithley 4200 semiconductor characterization system under ambient environment.

## RESULTS AND DISCUSSION

The growth of monolayer MoS<sub>2</sub> was carried out by forming -OH groups via a solution spin-coating process as depicted in **Figure 1a-b** and **Figure S1**. Ammonium molybdate ((NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub>) was used as the Mo source and sublimed sulfur as the S source. Firstly, KOH (or NaOH) and (NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub> were dissolved in deionized water to obtain an aqueous solution for generation of -OH groups. The precursor solution was spin-coated to a sapphire substrate that was pretreated by a piranha solution to possess good hydrophilicity for a well-distributed precursor film with -OH formed on the sapphire.<sup>27</sup> Afterwards, the as-prepared sapphire substrates were annealed in a furnace tube. **Figure 1a** shows the Mo and S atoms are crystalized layer by layer at 750 °C without -OH. When introduced OH<sup>-</sup> groups from aqueous solution, during the thermal annealed growth process, -OH groups are attached to the MoS<sub>2</sub> (001) surface, forming an S-Mo-S-OH bilayer structure. Further growth of MoS<sub>2</sub> along the [001] zone axis is suspended by

the surface -OH layer, which leads to preferential formation of a MoS<sub>2</sub> monolayer in the lateral direction instead of forming

multilayers along the [001] axis. Under the constraint of the



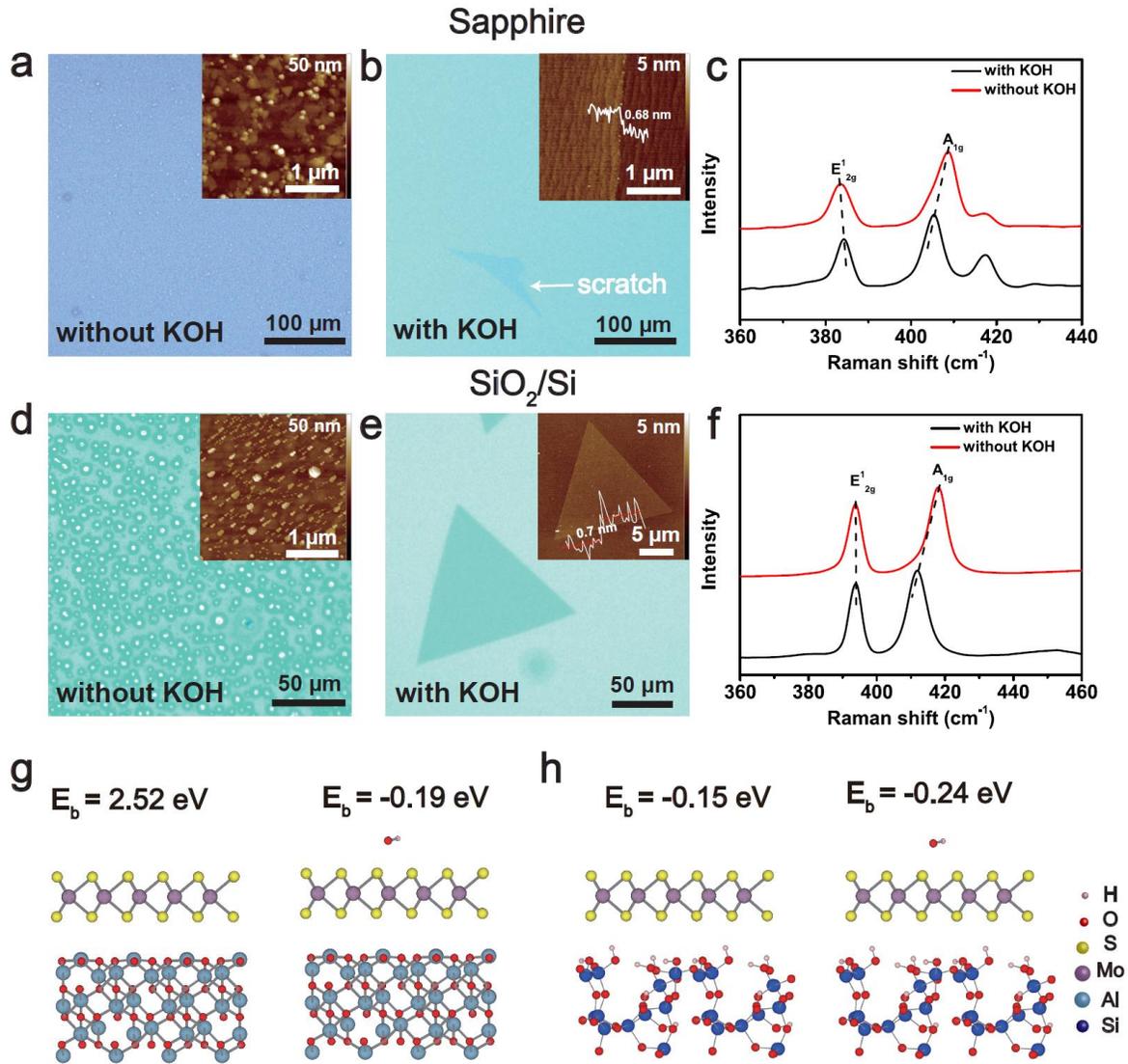
**Figure 1.** MoS<sub>2</sub> growth process in a precursor solution (a) without -OH and (b) with -OH. (c) Photographs of 1×1 and 3×3 cm<sup>2</sup> MoS<sub>2</sub> monolayer films on sapphire. (d) Typical OM image of a continuous MoS<sub>2</sub> film grown on sapphire. The inset is an AFM image, displaying an atomic-flat surface. (e) The statistical  $\Delta$  (left y-axis) and FWHM (right y-axis) values of the  $E_{2g}^1$  peak plotted as a function of numbered sites in the 3×3 cm<sup>2</sup> MoS<sub>2</sub> film (inset photograph). The  $\Delta$  and FWHM values of each site were extracted from the respective Raman spectrum, which was obtained from the central dot of each site. (f) Raman intensity mapping for  $A_{1g}$  peak of the as-grown monolayer MoS<sub>2</sub>. (g, h) Photographs of the inch-size MoS<sub>2</sub> films transferred onto a SiO<sub>2</sub>/Si substrate and a flexible PET substrate, respectively.

surface layer of -OH groups anchored on the MoS<sub>2</sub> (001) surface, Mo and S atoms can only attach to the edges of the monolayer MoS<sub>2</sub>. As a result, monolayer MoS<sub>2</sub> grows only in lateral direction into larger area (**Figure 1b**). Figure 1c shows representative uniform MoS<sub>2</sub> monolayers that are grown with 100% coverage on 1×1 and 3×3 cm<sup>2</sup> sapphire using the surface -OH groups assisted method, and the transparent sapphire substrate becomes light brown after growth of the MoS<sub>2</sub> monolayer (**Figure 1c**). Optical microscopy (OM) and atomic force microscopy (AFM) images in **Figure 1d** show that the sapphire is completely covered by a uniform and atomically flat MoS<sub>2</sub> film with a surface roughness of ~ 0.12 nm. The layer thickness of the MoS<sub>2</sub> film was determined by Raman spectroscopy. The peaks of  $E_{2g}^1$  and  $A_{1g}$

in Raman spectra originate from in-plane and out-of-plane phonon modes, respectively.<sup>28-29</sup> Each phonon oscillation is sensitive to the thickness of MoS<sub>2</sub>, and the Raman shift difference between the  $E_{2g}^1$  and  $A_{1g}$  modes depends on the layer numbers of MoS<sub>2</sub>, which is about 20 cm<sup>-1</sup> for monolayer MoS<sub>2</sub> and 25 cm<sup>-1</sup> for bulk MoS<sub>2</sub>.<sup>30</sup> In **Figure S2**, the characteristic Raman peaks obtained from the randomly selected site in MoS<sub>2</sub> monolayer are located at 384.3 cm<sup>-1</sup> and 404.6 cm<sup>-1</sup>, corresponding to  $E_{2g}^1$  and  $A_{1g}$  Raman modes, respectively. The specific frequency difference between the two peaks ( $\Delta$ ) is 20.3 cm<sup>-1</sup>, suggesting the monolayer nature, and the narrow full width at half maximum (FWHM) ~ 4 cm<sup>-1</sup> of the  $E_{2g}^1$  peak indicates a very low defect density of the as-

grown monolayer MoS<sub>2</sub> film.<sup>28</sup> The statistical analysis for  $\Delta$  and FWHM values of the  $E_{2g}^1$  peak, both obtained from the

numbered 30 sites, is shown in **Figure 1e**, demonstrating a good film uniformity across the entire sapphire. In addi



**Figure 2.** Critical role of the surface -OH groups in growth of monolayer MoS<sub>2</sub>. OM and AFM images of MoS<sub>2</sub> grown on sapphire (a) without and (b) with -OH, respectively. The inset AFM image in (b) shows that the MoS<sub>2</sub> film thickness is  $\sim$  0.68 nm, corresponding to the monolayer thickness. (c) The Raman spectra of MoS<sub>2</sub> films grown without and with -OH on sapphire. OM and AFM images of MoS<sub>2</sub> grown on SiO<sub>2</sub> (d) without and (e) with -OH, respectively. (f) The Raman spectra of MoS<sub>2</sub> films grown without and with -OH on SiO<sub>2</sub>. The optimized structures of monolayer MoS<sub>2</sub> on (g) sapphire (001) and (h) amorphous SiO<sub>2</sub> substrates, together with the calculated binding energy ( $E_b$ ) in the absence (left) and presence (right) of -OH, respectively.

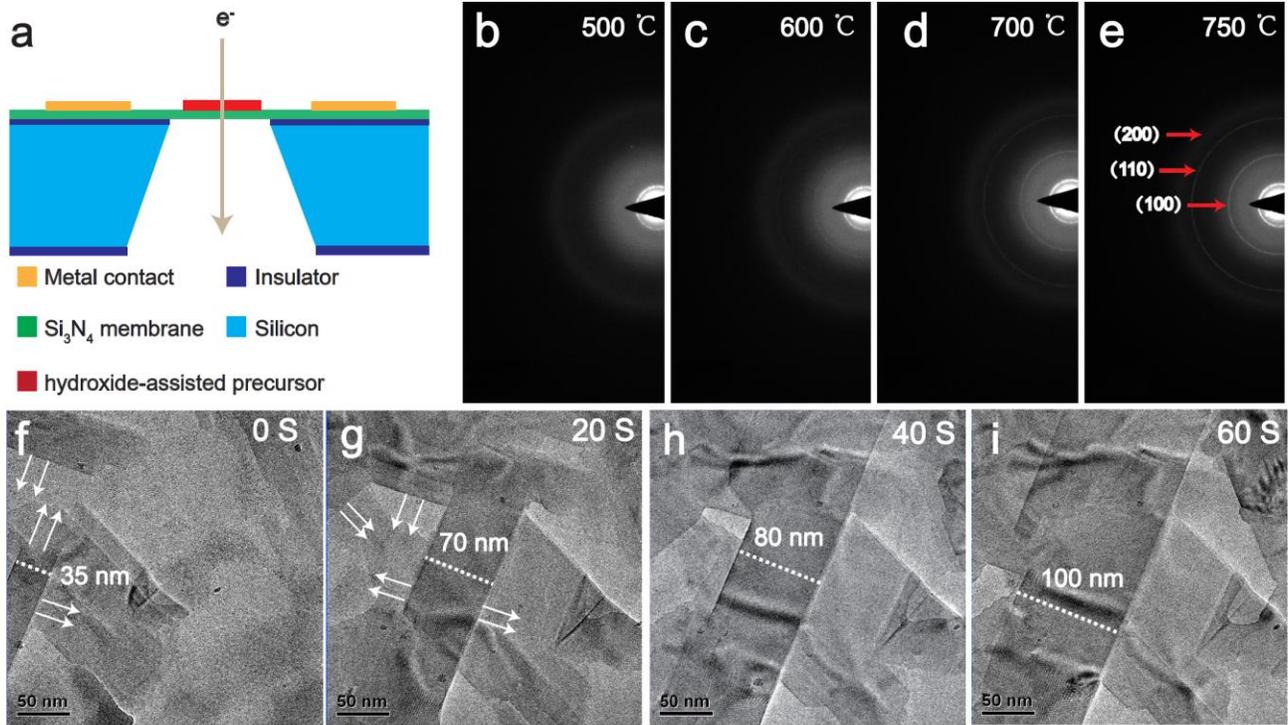
tion, Raman intensity mapping of the  $A_{1g}$  band of a  $50 \times 50 \mu\text{m}^2$  square area (**Figure 1f**) also manifests a uniform color contrast, further demonstrating the high degree of uniform spectroscopic quality of the resultant MoS<sub>2</sub> monolayer. After achieving large-scale monolayer MoS<sub>2</sub>, transferring them is of much importance for the practical applications. Current transfer methods predominantly use poly (methyl methacrylate) (PMMA) as the supporting layer and NaOH or KOH solution bath is used to etch the substrate to separate the films, which may severely damage the film and substrate.<sup>30-31</sup> Thanks to the growth of hydrophobic MoS<sub>2</sub> films on hydrophilic substrates,<sup>32</sup> the inch-size monolayer MoS<sub>2</sub> can be readily transferred to arbitrary substrates without etching the growth substrates. As shown in **Figure 1g and h**, the inch-

size monolayer MoS<sub>2</sub> was transferred to SiO<sub>2</sub>/Si and polyethylene terephthalate (PET) substrates from sapphire by a polystyrene (PS)-assisted method. Notably, the PS-assisted method effectively avoided the damages caused by chemical etchants, so the transferred films on SiO<sub>2</sub>/Si and PET well preserved their original quality. Meanwhile, the growth substrates avoided unnecessary contamination and irreversible damage. Indeed, as presented by the photographs and Raman spectra in **Figure S3**, the sapphire substrate was reused to grow high-quality and inch-size monolayer MoS<sub>2</sub> for multiple times.

To verify the critical role of the surface -OH layer in the growth of large-scale monolayer MoS<sub>2</sub>, we compared MoS<sub>2</sub> samples grown on sapphire and SiO<sub>2</sub> substrates treated with-

out and with -OH (1 M KOH), respectively. The MoS<sub>2</sub> sample grown on sapphire without -OH (**Figure 2a**), shows

many multilayers and small MoS<sub>2</sub> domains with average side length of ~ 500 nm. It is ascribed to the absence of surface



**Figure 3.** (a) Schematic side view of the experimental set-up of *in situ* TEM heating stage. (b - e) The evolution of SAED patterns across a temperature range: (b) 500 °C, (c) 600 °C, (d) 700 °C and (e) 750 °C. (f - i) Time-resolved TEM images of the horizontal growth of MoS<sub>2</sub> at 750 °C. (f) 0 s, (g) 20 s, (h) 40 s and (i) 60 s. Sequences of *in situ* TEM images display the controlled growth orientation of MoS<sub>2</sub> in the horizontal direction.

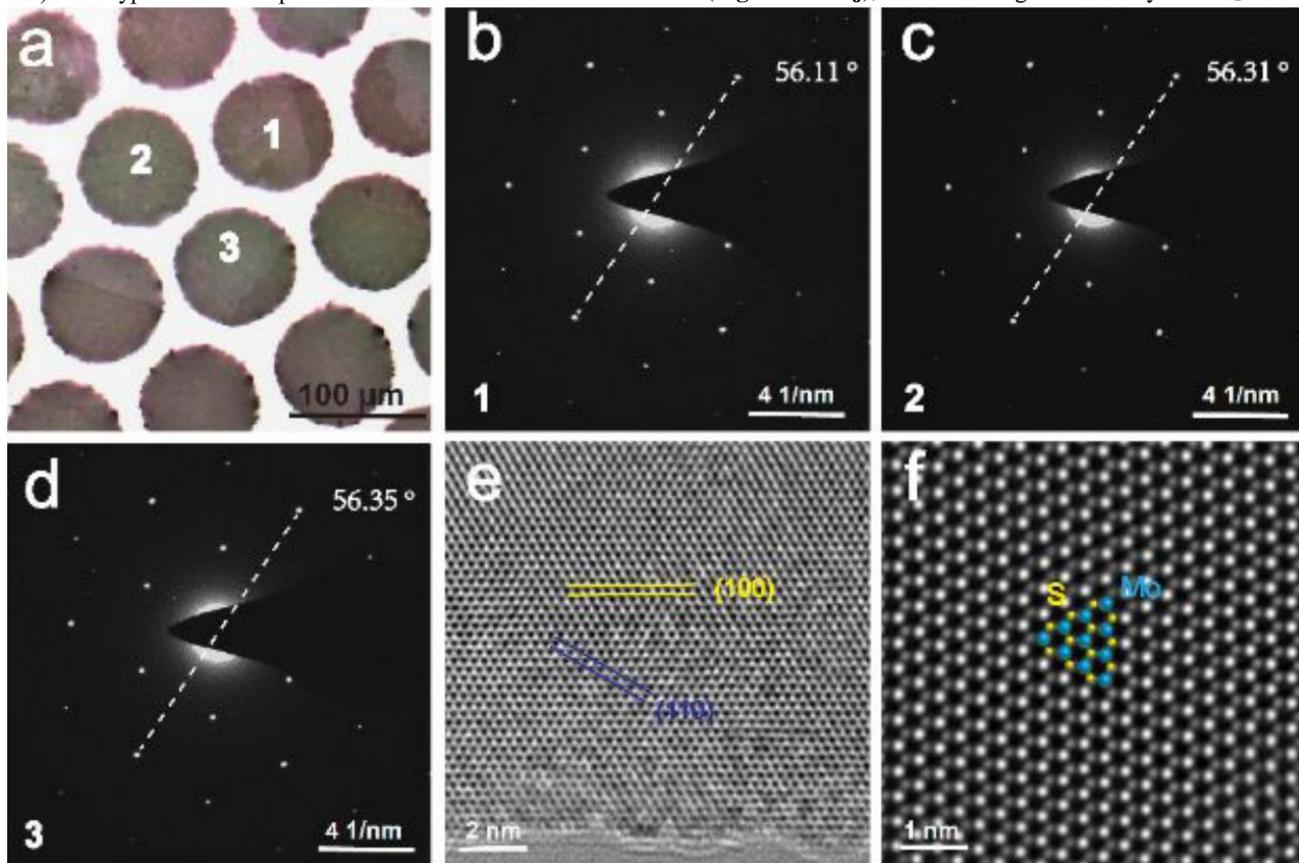
-OH groups that block the attachment of subsequent Mo and S atoms on the (001) surface, and thus, MoS<sub>2</sub> flakes were grown into multilayer and smaller islands.<sup>33-34</sup> In contrast, the MoS<sub>2</sub> monolayer film grown in the S-Mo-S-OH mode, completely and uniformly covers the sapphire substrate (**Figure 2b**). The AFM height profile of MoS<sub>2</sub> film with a scratch shows a thickness of ~ 0.68 nm, which is a typical monolayer thickness. The characteristic Raman spectra of MoS<sub>2</sub> grown on sapphire without and with -OH are shown in **Figure 2c**.  $\Delta$  was measured to be 20.5 and 25 cm<sup>-1</sup> for the MoS<sub>2</sub> grown without and with -OH (1 M KOH), respectively, further confirming the distinct advantage of forming S-Mo-S-OH structure when growing monolayer MoS<sub>2</sub>. To exclude the substrate induced influences on the growth, we also performed growing monolayer MoS<sub>2</sub> on SiO<sub>2</sub>, a typical amorphous substrate. Similarly, the growth carried out without -OH displays multilayer configuration and small MoS<sub>2</sub> flakes (**Figure 2d**). The inset AFM image shows a lot of multilayer islands and average side length of ~ 250 nm. Nevertheless, the MoS<sub>2</sub> sample grown with KOH shows large-scale monolayer domains with a large lateral size (~ 150  $\mu$ m). The inset AFM image in **Figure 2e** shows a clean and flat surface of the triangular domain, confirming the monolayer nature of the domain (thickness ~ 0.7 nm). The monolayer MoS<sub>2</sub> keeps good uniformity in thickness, which is evidenced by both the Raman intensity map of A<sub>1g</sub> peak and the photoluminescence map from the A-exciton (**Figure S4a-b**). The typical Raman spectra (**Figure 2f**) verify the

forming the monolayer S-Mo-S-OH structure. To gain further insight into the key role of -OH groups, we performed density function theory (DFT) calculations for monolayer MoS<sub>2</sub> crystalized on single-crystalline sapphire and amorphous SiO<sub>2</sub> substrates (**Figure 2g, h**). For sapphire substrate, the calculated binding energy of MoS<sub>2</sub> in the absence of -OH is 2.52 eV that is much larger than -0.19 eV in the presence of -OH, indicating that the addition of -OH substantially stabilizes the monolayer MoS<sub>2</sub>. It is noticeable that the deposition process of MoS<sub>2</sub> is converted from endothermic to exothermic by inclusion of -OH, which explains the hydroxide driven growth of monolayer MoS<sub>2</sub> observed in our experiments. For the amorphous SiO<sub>2</sub> substrate, the corresponding binding energy of MoS<sub>2</sub> in the absence of -OH is -0.15 eV that is higher than -0.24 eV in the presence of -OH, confirming that -OH further stabilizes the monolayer MoS<sub>2</sub>. In addition, the formation of a hydroxide-covered MoS<sub>2</sub> is energetically favorable: the formation energy is -0.24 eV per (1 $\times$ 1) MoS<sub>2</sub>, which is consistent with the formation of the MoS<sub>2</sub>-OH bilayer structure.

Besides sapphire and amorphous SiO<sub>2</sub> substrates, we also successfully grew high-quality monolayer MoS<sub>2</sub> on Si, quartz, SiC, graphene and mica (**Figure S5a - e**). Analogous to sapphire and SiO<sub>2</sub>, MoS<sub>2</sub> samples grown on the above substrates without the participation of -OH displayed smaller domain sizes and multilayer structure (**Figure S5-i**). To one's expectation, large-scale MoS<sub>2</sub>-OH surface was obtained on those substrates when introducing KOH (**Figure**

S5-ii). The typical Raman spectra all show the  $\Delta \sim 20 \text{ cm}^{-1}$

(Figure S 5f - j), demonstrating the monolayer MoS<sub>2</sub> nature.



**Figure 4.** Microstructural characterization of monolayer single-crystal MoS<sub>2</sub> domains. (a) OM image of a side length  $\sim 150 \mu\text{m}$  monolayer MoS<sub>2</sub> domain transferred on a TEM grid. (b - d) SAED patterns taken from the areas labelled 1, 2, 3 in a, the dashed lines indicate the rotation angles ( $56.11^\circ$ ,  $56.31^\circ$ , and  $56.35^\circ$ ) from the horizontal direction, displaying a single-crystalline lattice structure of the monolayer MoS<sub>2</sub>. (e) Aberration-corrected HRTEM image. (f) aberration-corrected ADF-STEM image of monolayer MoS<sub>2</sub>, the bright and gray spots correspond to molybdenum and two stacked sulfur atoms, respectively.

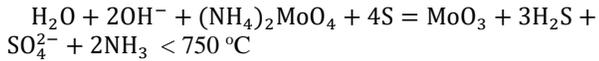
In addition, to investigate the influence of different KOH concentrations on the growth, we also grew MoS<sub>2</sub> films with 0.25 and 4 M KOH. MoS<sub>2</sub> grown on sapphire with 0.25 M KOH shows the side length of the triangular domain of  $\sim 50 \mu\text{m}$  (Figure S6a), and zoomed-in AFM image of the edge shows an irregular terrace structure. It is believed that the amount of -OH is insufficient to cover the upper S atom layer, leading to the partial growth of monolayer. When the concentration of [OH] was further increased to 4 M, the as-grown monolayer MoS<sub>2</sub> domains show side length of  $\sim 40 \mu\text{m}$  (Figure S6b). Likewise, multilayer and monolayer MoS<sub>2</sub> domains were crystallized on SiO<sub>2</sub> with 0.25 and 4 M KOH, respectively (Figure S6c and d). However, the excess of -OH can etch the surface of SiO<sub>2</sub> substrate at 750 °C, resulting in small holes (Figure S6d). Therefore, the appropriate amount of -OH (1 M KOH) determines high-quality growth of monolayer MoS<sub>2</sub>.

*In situ* transmission electron microscopy (TEM) was used to reveal the dynamic behavior of low-dimensional materials with high spatial and temporal resolution.<sup>35-37</sup> We used a heating stage with a Si<sub>3</sub>N<sub>4</sub> membrane inside the TEM to *in situ* observe the dynamic crystallization process of MoS<sub>2</sub> (Figure 3a). Firstly, the Si<sub>3</sub>N<sub>4</sub> membrane was heated from room temperature to 750 °C within 5 min. Figure 3b-e and Supporting Movie 1 display the evolution of selected-area

electron diffraction (SAED) patterns during the crystallization process. From room temperature to 500 °C, there was no diffraction pattern (Figure 3b), suggesting the precursor was kept at an amorphous state. When the temperature was reached up to 600 °C, indistinct diffraction rings emerged in Figure 3c. After the Si<sub>3</sub>N<sub>4</sub> substrate being heated to 700 °C and 750 °C, the diffraction rings became clearer and brighter (Figure 3d and 3e). Meanwhile, the distinct SAED patterns can be well indexed to MoS<sub>2</sub> structure with the space group of P6<sub>3</sub>/mmc (JCPDS card No. 37-1492). The analysis illustrated a very high crystallization rate of the MoS<sub>2</sub> with -OH. In addition, X-ray diffraction is also used to identify the phase and crystallinity of the MoS<sub>2</sub> products grown at different temperatures. MoS<sub>2</sub> samples (Figure S7) have poor crystal quality when they were at 500 and 600 °C. In contrast, the MoS<sub>2</sub> sample grown at 750 °C has high quality crystallinity, in agreement with the above *in situ* observation. When the temperature was kept at 750 °C, the dynamic behavior of the increased flake size was clearly recorded and presented in Figure 3f - i and Supporting Movie 2. As shown in Figure 3f, a MoS<sub>2</sub> nanobelt with size of  $\sim 100 \text{ nm} \times 35 \text{ nm}$  (length by width) was grown. After being maintained at 750 °C for 20 s, the nanobelt grew laterally, and the length and width increased to 200 nm and 70 nm, respectively (Figure 3g). With further increasing the growth duration, the width of

MoS<sub>2</sub> flake increased to 80 and 100 nm after 40 and 60 s, respectively (**Figure 3h and i**). As a comparison, we grew MoS<sub>2</sub> on Si<sub>3</sub>N<sub>4</sub> membrane without the participation of -OH. As shown in **Figure S8a**, at 750 °C from 0 to 480 s, the size of a MoS<sub>2</sub> flake was almost unchanged apart from the increased thickness. **Figure S8b** displays the lateral growth of a MoS<sub>2</sub> flake with -OH for extended time. The final size of the MoS<sub>2</sub> flake reached to 600 nm at 750 °C for 480 s, which is much larger than ever achieved by *in situ* growth inside TEM.<sup>37-38</sup> These results directly confirmed the critical role of -OH in growth of high-quality monolayers MoS<sub>2</sub>.

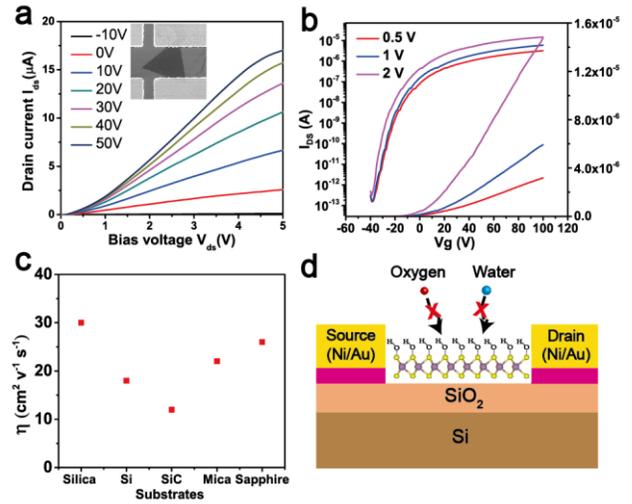
We also used X-ray photoelectron spectroscopy (XPS) to investigate the chemical composition of the product during the growth process. As shown in **Figure S9a**, binding energy of the Mo 3d<sub>5/2</sub> electron peaks of the samples grown at 500 and 600 °C both have the same value of 232.2 eV, corresponding to Mo<sup>6+</sup>. It means the non-sulfidized MoO<sub>3</sub>.<sup>39</sup> Moreover, the binding energy of the S 2p<sub>3/2</sub> peak appears at 168.2 eV, since the sulfurization could not accomplish at temperature below 600 °C. Once the growth temperature was reached to 750 °C and kept for 5 min, the signal of the Mo 3d<sub>5/2</sub> peak shifts to a lower binding energy at 229.4 eV, indicative of Mo<sup>4+</sup> (**Figure S9a**). Meanwhile, the S 2p<sub>1/2</sub> and S 2p<sub>3/2</sub> peaks correspondingly located at 163.2 and 162 eV (**Figure S9b**) imply the formation of MoS<sub>2</sub>.<sup>40-41</sup> As shown in **Figure S9c**, the binding energy of K 2p peaks remained unchanged during growth, illustrating K<sup>+</sup> did not participate in redox reaction. Accordingly, the chemical equations are derived below:



Additionally, XPS spectra of oxygen atoms in **Figure S9d** are also used to verify the presence of -OH in the MoS<sub>2</sub> product. The MoS<sub>2</sub> sample prepared with 1 M KOH precursor solution possesses O peaks at 532.5 and 530 eV, corresponding to the SiO<sub>2</sub> and -OH bonds, respectively, while the MoS<sub>2</sub> sample grown without KOH only has the O peak came from SiO<sub>2</sub>.<sup>42</sup> The presence of -OH in the product demonstrates the MoS<sub>2</sub>-OH bilayer structure.

Electron microscopy was used to probe the microstructure of monolayer MoS<sub>2</sub>. The OM image of a typical triangular MoS<sub>2</sub> crystal transferred onto a TEM grid is shown in **Figure 4a**. To identify whether the domain is a single-crystal, we carried out a series of SAED measurements on 3 different regions (**Figure 4a**), and all of the hexagonal diffraction spots have the same crystallographic orientations (deviation smaller than ± 0.3°) in **Figure 4b-d**, confirming the single-crystal nature of the as-grown MoS<sub>2</sub> and uniformity across large area of the sample.<sup>43</sup> **Figure 4e** shows representative high-resolution TEM (HRTEM) images of the single-crystal MoS<sub>2</sub> sample. The lattice distances were measured to be ~ 0.274 nm and 0.158 nm, corresponding to the (100) plane (marked as yellow lines) and (110) plane (marked as blue lines), respectively. Specially, aberration-corrected annular dark field scanning transmission electron microscopy (ADF-STEM) measurement was operated at 200 kV to further identify the structure of the as-grown MoS<sub>2</sub>. ADF-STEM image (**Figure 4f**) shows a clearly discernible hexagonal symmetry. The bright/dim areas correspond to Mo/S atoms, respectively.<sup>44-46</sup> The uniform intensity difference between

the bright and dim spots indicates that there is no sulphur



**Figure 5.** Single-domain MoS<sub>2</sub> FETs. (a) Output characteristics of the device with gate voltages sweeping from -10 to 50 V. Inset: OM image of the device. (b) Transfer characteristics of the device at different V<sub>DS</sub>. The on/off ratio is ~ 10<sup>7</sup>, and V<sub>th</sub> ≈ -35 V. (c) The distributions of the carrier mobility of the MoS<sub>2</sub> FETs based on different substrates. (d) Schematic of the monolayer MoS<sub>2</sub> FET structure. The attached -OH surface layer on the S atom prevents from being oxidized by in air.

vacancy or topological defect. Notably, the high crystal quality and perfect lattice structure benefit from the -OH groups that protect surface S atoms during growth (**Figure 1b**). As a result, the formation of sulphur vacancies and point defects are effectively suppressed.

To evaluate the electrical properties of the resultant monolayer MoS<sub>2</sub>, we transferred the MoS<sub>2</sub> monolayer onto clean 300 nm thick SiO<sub>2</sub> (SiO<sub>2</sub>/Si) substrates to fabricate back-gate FETs. All the electrical measurements of monolayer MoS<sub>2</sub> were performed in air. A typical device has a channel length (L) of ~ 30 μm and a channel width (W) of ~ 10 μm. **Figure 5a** shows the I-V characteristics of a typical device. The linear curves suggest that ohmic contacts were formed at the source and drain electrodes.<sup>47</sup> The transfer curves in **Figure 5b** show a typical n-type behavior, and the maximum on/off current ratio is > 10<sup>7</sup>. The field-effect carrier mobility is estimated using the following equation.

$$\mu = \frac{dI_{ds}}{dV_{bg}} \cdot \frac{L}{WC_i V_{ds}}$$

The carrier mobility was calculated to be as high as 30 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, which is the highest value ever reported in air.<sup>48-50</sup> In addition, **Figure 5c** displays the carrier mobility of FETs based on the monolayer MoS<sub>2</sub> grown on different substrates. The mobility of these devices is in the range of 12 - 30 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. Recent studies have shown that monolayer MoS<sub>2</sub> is prone to be oxidized in air, which can degrade the performance of the devices. To our surprise, the monolayer MoS<sub>2</sub> with surface -OH layer can effectively suppress oxidation in air (**Figure 5d**). Kelvin probe force microscopy (KPFM) images verify that both the as-grown and transferred monolayer MoS<sub>2</sub> keep the MoS<sub>2</sub>-OH bilayer structure. The as-grown and transferred monolayer MoS<sub>2</sub> on SiO<sub>2</sub> substrates show almost the same surface potential of ~ 4.65 eV (**Figure S10**). This value is greater than that measured from the mechanically exfoliated MoS<sub>2</sub> due to the presence of -

OH on the surface MoS<sub>2</sub> monolayer.<sup>51-52</sup> This evidence of -OH attachment well agrees with the DFT calculation and XPS measurement (**Figure S9**).

## CONCLUSION

In summary, we demonstrated the MoS<sub>2</sub>-OH bilayer mediated method for growth of inch-sized monolayer MoS<sub>2</sub> and this method can be applied to various crystalline and amorphous substrates, including sapphire, SiO<sub>2</sub>, Si, Si<sub>3</sub>N<sub>4</sub>, SiC, quartz, mica and graphene. During the crystallization, the -OH groups are attached to the (001) surface of MoS<sub>2</sub>, forming a MoS<sub>2</sub>-OH bilayer structure. The surface -OH layer not only suspended the growth along the [001] axis and led to preferential growth of MoS<sub>2</sub> monolayers, but also protected the MoS<sub>2</sub> surface from oxidation in air. Moreover, the attached -OH groups on the (001) surface lead to a lower density of sulfur vacancies and defects and enabled the FETs to have the highest electron mobility of MoS<sub>2</sub> in air. The electron microscopy results and high performance of devices both confirmed the high crystalline quality of the monolayer MoS<sub>2</sub>. This method provides a new opportunity for the growth of other 2D TMDs such as WS<sub>2</sub>, MoSe<sub>2</sub>, etc.

## ASSOCIATED CONTENT

### Supporting Information

*In situ* Raman, XPS, TEM, KPFM images of the grown MoS<sub>2</sub>. The Supporting Information is available free of charge on the ACS Publications website.

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