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Atomic insights into hydrodesulfurization

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Chapter 5

Low-temperature synthesis strategy for MoS₂ slabs supported on TiO₂(110)

This chapter is based on:

*Prabhu, M. K.; Groot, I. M. N. Low-Temperature Synthesis Strategy for MoS₂ Slabs Supported on TiO₂(110), Surfaces **2020**, 3(4), 605-621*

Abstract:

MoS₂ supported on oxides like TiO₂ has a broad range of applications. The atomic structure of this system is therefore, very useful to study. Previous research work in this area has made use of high-temperature synthesis methods to gain atomic-level insights for important applications such as catalysis, while the industrial synthesis strategy predominantly makes use of a low-temperature synthesis method. In this chapter, we investigate a low-temperature synthesis strategy for MoS₂ slabs supported on rutile TiO₂(110). Using scanning tunneling microscopy and X-ray photoelectron spectroscopy, we demonstrate that not only flat MoS₂ slabs with irregular shapes but also MoS_x stripes with coordinatively unsaturated Mo atoms are also formed. Furthermore, this work shows that for atomic structural characterization of MoS₂/TiO₂ and similar oxide-supported systems grown by low-temperature synthesis methods, the surface structure of the support becomes highly relevant and cannot be ignored.

5.1 Introduction

Nanostructured MoS₂/TiO₂ composites have attracted a lot of interest as a model system for applications in electronics¹⁻³, photovoltaics⁴, electrocatalysis⁵ and heterogeneous catalysis⁶, combining a transition metal dichalcogenide (TMDC) and a wide-bandgap semiconductor. In particular, the promoted MoS₂/TiO₂ system is widely applied in industry to perform hydrodesulfurization (HDS) and reduce the global SO_x emissions.⁷⁻⁹ More recently, the MoS₂/TiO₂ system has also found application as an efficient hydrogen evolution reaction (HER) catalyst.¹⁰

Despite the widespread applications, many fundamental properties of the MoS₂-TiO₂ system, especially those relevant for catalysis, such as the atomic structure and reactivity of the edges, are disputed due to the difficulty of resolving the edge structure with sufficient contrast in conventional characterization techniques such as electron microscopy.^{11,12} Recent studies on model systems have attempted to tackle some of these challenges using scanning tunneling microscope (STM) and X-ray photoelectron spectroscopy (XPS). For instance, Kibsgaard et al.⁶ have shown that the morphology of MoS₂ slabs supported on rutile TiO₂(110) depends on the atomic structure of the TiO₂(110) surface and the synthesis temperature. The MoS₂ slabs grown using physical vapor deposition (PVD) at 900 K are hexagonal, while at 950 K, elongated particles are formed. Galhenage et al.¹³ have investigated the effects of exposure of MoS₂/TiO₂(110) grown by PVD at 950 K to various gas environments such as D₂, CO and methanol. The MoS₂ slabs grown on TiO₂(110) by alternative strategies, like chemical vapor deposition (CVD), have shown efficient excitonic separation between the MoS₂ and TiO₂ phases and hence, better photocatalytic activity.¹⁴ In all these studies, MoS₂ is grown at temperatures above 900 K and thermodynamically favorable pristine MoS₂ slabs with well-defined edges and the basal planes lying flat on the TiO₂(110) surface are observed.

In industrially relevant systems such as a HDS catalyst however, MoS₂ is typically grown at much lower temperatures between 573-673 K using wet chemical procedures.¹⁵⁻¹⁷ The transmission electron microscopy (TEM) studies of MoS₂ grown at low-temperatures on various facets of rutile and anatase TiO₂ have shown the presence of “edge-on” supported MoS₂ slabs.^{18,19} The X-ray absorption fine structure (XAFS) studies of the Mo K-edge of MoS₂ slabs grown on TiO₂(110) at lower temperature have indicated the presence of MoS₂ clusters with Mo being in five-fold coordination or less.^{20,21} Such unsaturated Mo atoms were assigned to small MoS₂ clusters potentially growing as stripes on the TiO₂ surface.²⁰ On the contrary, the prior STM-based studies on MoS₂/TiO₂(110) fabricated by the high-temperature synthesis procedure have not observed the formation of any such structures. Given the sensitivity of the MoS₂ morphology to the synthesis temperature, it is important to synthesize MoS₂ on the TiO₂ surface at lower temperatures in order to gain atomic level insights, especially those relevant for industrial HDS. However, such attempts are complicated by the reactivity of the TiO₂(110) substrate towards sulfur. Studies performed by other groups have shown that, depending on the temperature and the coverage, sulfur can form a plethora of structures by binding to five-fold coordinated surface Ti atoms, by replacement of the surface bridging oxygen atoms or by replacement of the near-surface in-plane oxygen atoms.²²⁻²⁵ Such complications are conveniently avoided at higher temperatures as the sulfur desorbs from the TiO₂(110) surface.

In this chapter, we report a synthesis procedure to grow MoS₂ on rutile TiO₂(110) at a catalytically relevant low temperature of 650 K. We start with depositing Mo nanoparticles on a clean TiO₂(110)

surface. The Mo nanoparticles are thereafter, sulfided using H_2S as the sulfiding agent. We make use of STM and XPS to study the morphology of MoS_2 . We show that our synthesis procedure yields irregular shaped MoS_2 slabs with their basal planes lying flat on the substrate and “edge-on” MoS_x stripes forming as elongated structures aligned along the $[1\bar{1}0]$ direction of the $\text{TiO}_2(110)$ substrate. At higher initial Mo coverage, we obtain predominantly multilayered MoS_2 slabs with their basal planes lying flat on the substrate. Furthermore, we show that all these structures adhere to a (3×1) lattice on the $\text{TiO}_2(110)$ surface formed by adsorption of sulfur. Additionally, we present possible atomic models supported by our experimental results to explain our findings for future theoretical work.

5.2 Materials and Methods

All the experiments were carried out in the ReactorSTM setup.²⁶ A polished rutile $\text{TiO}_2(110)$ crystal was purchased from Surface Preparation Laboratory, Zaandam, the Netherlands. The $\text{TiO}_2(110)$ crystal was cleaned by repeated cycles of sputtering and annealing. The sputtering was performed using Ar^+ with an ion energy of 1.5 keV and annealing was performed at 873 K for 10 min in the presence of O_2 at 2×10^{-6} mbar. Heating and cooling rates of 10 K/minute were maintained to prevent cracks in the crystals due to thermal shock. The ultimate cleaning cycle involved annealing in ultra-high vacuum (UHV) at 900 K for 10 min to generate atomically flat $\text{TiO}_2(110)$ terraces. The cleanliness was checked with XPS and STM until impurities were below the detection limits. The $\text{TiO}_2(110)$ crystal turned light blue after this cleaning procedure due to the slight bulk reduction in UHV generating oxygen vacancies which act as color centers.

Mo metal was deposited from an Mo rod using an Oxford EGCO4 e-beam evaporator with the TiO_2 substrate held at 300 K. Coverages of Mo were checked using XPS and samples with 0.25, 0.49 and 0.61 ML Mo nanoparticles were prepared as precursors for the sulfidation process. The coverage of the Mo nanoparticles was calculated from the XPS spectra by comparing the peak areas of Mo 3d and Ti 2p signals after correcting for the relative sensitivity factors.²⁷ The sulfidation was carried out by heating the samples to 650 K for 45 minutes in a H_2S atmosphere of 1×10^{-3} mbar. Thereafter, the samples were cooled to room temperature in UHV.

Scanning tunneling microscopy was performed at room temperature using the UHV mode of the ReactorSTM. Polycrystalline Pt-Ir 90-10 wires purchased from Goodfellow were cut and used as STM tips without further processing. Constant-current scans were performed using LPM video-rate scanning electronics described in detail elsewhere.^{28,29} Home-developed Camera software and WSxM were used for STM image processing.^{30,31} Most-common normal filtering was used to obtain a correctly connected surface in order to calculate the height profiles. Line-by-line background subtraction was used otherwise for the ease of viewing. No other processing was performed on the STM images reported in this Chapter.

The XPS measurements were performed in a SPECS Phoibos system equipped with an XRM50 X-ray source set to the Al K-alpha line used along with a monochromator to excite the sample with a beam spot of 0.4 mm diameter at 54.6° incidence. The acceleration voltage was set to 10 kV and a power of 250 W was used for all the measurements. The HSA3500 hemispherical analyzer with a pass energy of 30 eV was used to analyze the photoemission. The bulk Ti 2p peak set to 458.5 eV was used to calibrate the XPS spectra obtained.³² The calibration was further checked using a separate clean Au(111) single crystal by confirming the peak position of Au 4f at 84 eV. The number of integrations was set to 20.

The data thus obtained, were characterized and quantified using CASA-XPS and with relative sensitivity factors reported in the literature.²⁷ The XPSPEAK41 software was used for peak fitting the Mo 3d and S 2p spectra. The Mo 3d and S 2p peaks were fit using a mixed Gaussian-Lorentzian (65-35) curves. Shirley background subtraction was applied and a non-linear least squares method was used for peak fitting. The Mo 3d spectrum was fit with components for Mo (228.0 eV), MoO_x (228.7 eV) and MoO₂ (229.8 eV) for the Mo nanoparticles and MoS₂ (229.2 eV), MoS_x (228.8 eV, 228.3 eV) and the S 2s (226.2 eV) component for the Mo sulfide samples. The MoS_x has two components arising from 5-fold and 4-fold coordinated Mo atoms. The S 2p spectra were fit with components for S²⁻ (161.8 eV) and bridging S₂²⁻ (163.1 eV) doublets separated by 3.15 eV and 1.16 eV, respectively. These binding energies are tabulated in Table 1 and they are based on previous experiments reported in literature.³³⁻⁴⁰

Table 1: XPS binding energies for various components used for peak fitting.

Components	Mo metal	MoO _x	MoO ₂	MoS ₂
Binding energy (eV)	228.0	228.7	229.8	229.2
ΔBE (eV)	3.15	3.15	3.15	3.15
Components	MoS _x	S 2s	S ²⁻ 2p	S ₂ ²⁻ 2p
Binding energy (eV)	228.3, 228.8	226.2	161.8	163.1
ΔBE* (eV)	3.15		1.16	1.16

* ΔBE(3d) = BE 3d_{5/2} - BE 3d_{3/2} ; ΔBE(2p) = BE 2p_{3/2} - BE 2p_{1/2}

5.3 Results and Discussion

A clean TiO₂(110) surface with atomic steps produced by our cleaning procedure is shown in Figure 1a. The height of steps (Figure 1b) is measured to be 3.19 Å and it is very close to the monoatomic step height 3.24 Å of TiO₂(110).⁴¹ The terraces show bright and dark rows along the [001] direction (Figure 1c, 1d) characteristic of a slightly reduced UHV-annealed TiO₂(110) surface.^{22,41-43} The bright rows in Figure 1c are attributed to the Ti⁴⁺ atoms with five-fold coordination and the dark rows are attributed to the bridging oxygen atoms of the rutile TiO₂(110) atomic structure.⁴⁴ Figure 1d shows that the presence of dark spots on the bright rows of the (1x1) structure. These features have been interpreted as sub-surface oxygen vacancy sites in a previous study.⁴³ The bright features on the dark rows which are expected for surface oxygen defects are not imaged here.⁴³⁻⁴⁵ The Pt-Ir tips are known to be prone to a tip state where these features are not imaged and the appearance of the dark features are enhanced.⁴³ The bright features observed in Figure 1d are likely due to residual -OH groups on the surface.⁴⁵

Mo metal was deposited onto the clean TiO₂(110) surface by physical vapor deposition from an Mo rod as detailed in the experimental methods. Figure 2a shows the large-scale STM image of the Mo nanoparticles supported on the TiO₂(110) surface grown to a coverage of 0.25 ML of Mo. The Mo nanoparticles are observed to nucleate randomly on the TiO₂(110) terraces and are 1.8-3.2 Å high (Figure 2b). Some nanoparticles of 4-5 Å height are also observed. The Mo nanoparticles uniformly cover the TiO₂(110) surface and preference for any nucleation site was not observed. Furthermore, the Mo 3d XPS

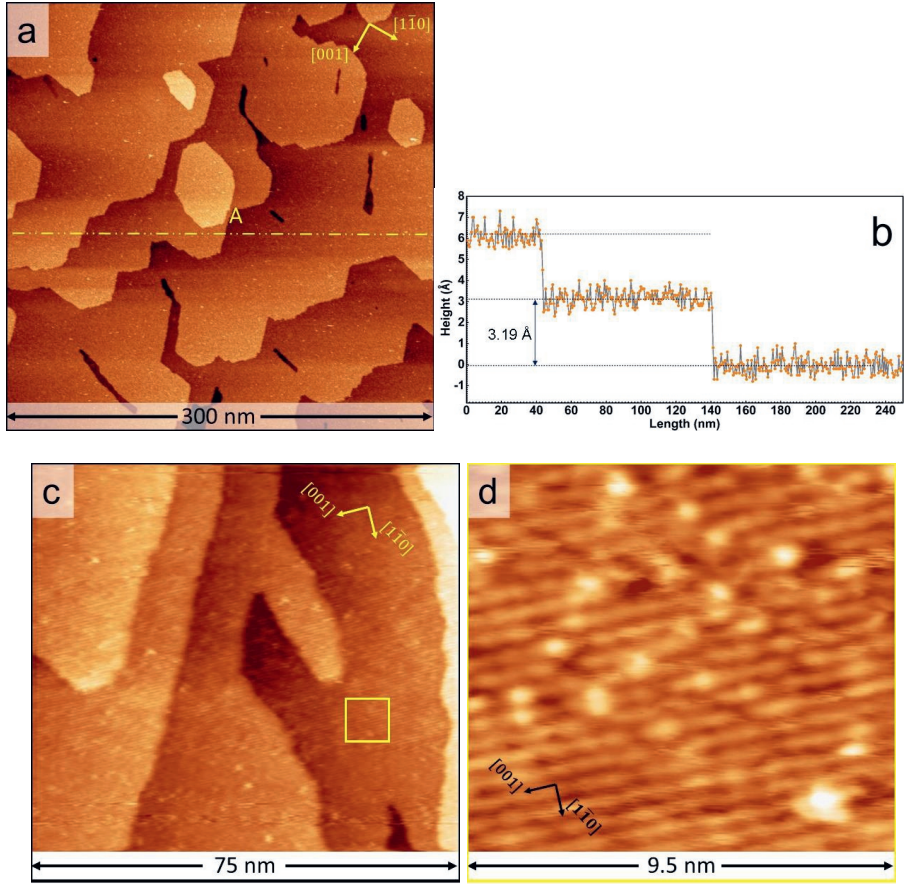


Figure 1: a) Large-scale STM image of a clean $\text{TiO}_2(110)$ surface after sputtering and annealing in UHV at 900 K; sample voltage = +2.2 V, tunneling current = 150 pA. b) Height along line A in Figure 1a shows the measured step height of clean $\text{TiO}_2(110)$ is 3.19 Å. c) Zoom in of the $\text{TiO}_2(110)$ surface showing the alternating bright and dark rows characteristic of the (1x1) structure of slightly reduced rutile titania. d) Zoom-in of the area denoted by the yellow square in Figure 1c.

spectrum (Figure 2c) shows a peak at 228.8 eV which is less than the expected 229.2 eV for Mo^{4+} suggesting that the particles have an overall oxidation state of less than 4. Peak fitting shows the presence of Mo^{4+} as well as a sub-stoichiometric Mo oxide component suggesting that the particles are of the form MoO_{2-x} . The lack of a preferred nucleation site and the spontaneous partial oxidation of Mo nanoparticles on the $\text{TiO}_2(110)$ surface suggests a very strong substrate-overlayer interaction. Such a strong $\text{Mo-TiO}_2(110)$ interaction has been observed in the previous studies on this system.^{33-36,46,47} The nature of interaction between metal nanoparticles and the TiO_2 surface has been found to depend on the initial heat of adsorption of oxygen on the respective metal nanoparticle in comparison to the initial heat of reduction of TiO_2 . In the case of Mo, the heat of absorption of oxygen is greater than the heat of reduction of TiO_2 . Therefore, the transfer of oxygen from the surface to the Mo nanoparticles leading to their partial oxidation is thermodynamically favorable.⁴⁷ The Mo nanoparticles thus formed, are known to have an oxidation state of less than 4, as observed in our experiment. Similar behavior is also observed for reactive metals with high heat of oxygen adsorption such as Re, Al, Hf, Cr, and Mn supported on TiO_2 .⁴⁸⁻⁵⁰ Growing Mo nanoparticles to higher coverages, for instance, to 0.49 ML leads to an increase in their metallicity, as is evident from the overall 0.4 eV shift of the Mo 3d spectrum to lower binding energy (see SI, Figure S1). The peak fits also show a non-zero contribution from metallic Mo signature at 228.0 eV. This increase in the metallicity of Mo is attributed to the kinetic limitations of oxygen diffusion from the bulk TiO_2 to Mo nanoparticles and was observed in the previous studies as well.³³

The Mo nanoparticles thus prepared, were sulfided at 650 K in a H_2S atmosphere of 1×10^{-3} mbar, as detailed in the experimental methods. Figures 3a and 3b show large-scale STM images of MoS_2 slabs on $\text{TiO}_2(110)$ formed after the sulfidation process. Upon sulfidation, the atomically-flat structures with a dark relative contrast and a bright rim along their perimeter are formed. We identify these structures as MoS_2 slabs with their basal planes lying flat on the $\text{TiO}_2(110)$ support and refer to them as “basal-bonded” MoS_2 slabs in the rest of this chapter. These MoS_2 slabs are of 3-5 nm size and predominantly have an irregular shape (Figures 3b and 3c). The “basal-bonded” MoS_2 slabs, despite their irregular shape, appear to be slightly elongated along the $[1\bar{1}0]$ direction. This is in contrast to the MoS_2 slabs grown by the high-temperature synthesis methods used in prior studies where highly elongated particles with well-defined edges aligned along both the $[001]$ and $[1\bar{1}0]$ directions were observed.^{6,13} Kibsgaard et al.⁶, in particular, observed a strong dependence of the shape of the MoS_2 slabs on the synthesis temperature. The irregular edge shapes of the “basal-bonded” MoS_2 in our experiments are likely driven by the strong interaction of Mo nanoparticles with the $\text{TiO}_2(110)$ substrate as well as the adsorption of S on $\text{TiO}_2(110)$ which, in turn, strongly depends on the temperature.^{22,25,51} Atomic resolution of the basal planes of the “basal-bonded” MoS_2 slabs show an interatomic distance of 3.13 Å (see Figure 3d) which matches well with the reported S-Mo-S distance of 3.15 Å of the (0001) basal plane of single-layer (SL) MoS_2 slabs.⁵² This further shows that the “basal-bonded” MoS_2 slabs grown in this experiment are crystalline in nature. Atomic resolution along the edges was, however, difficult to obtain due to the low conductivity of the titania substrate. Furthermore, the tendency for rapid tip changes due to the mobile sulfur species present on the sample made it difficult to maintain the tip state required for the atomic resolution of the MoS_2 basal planes.

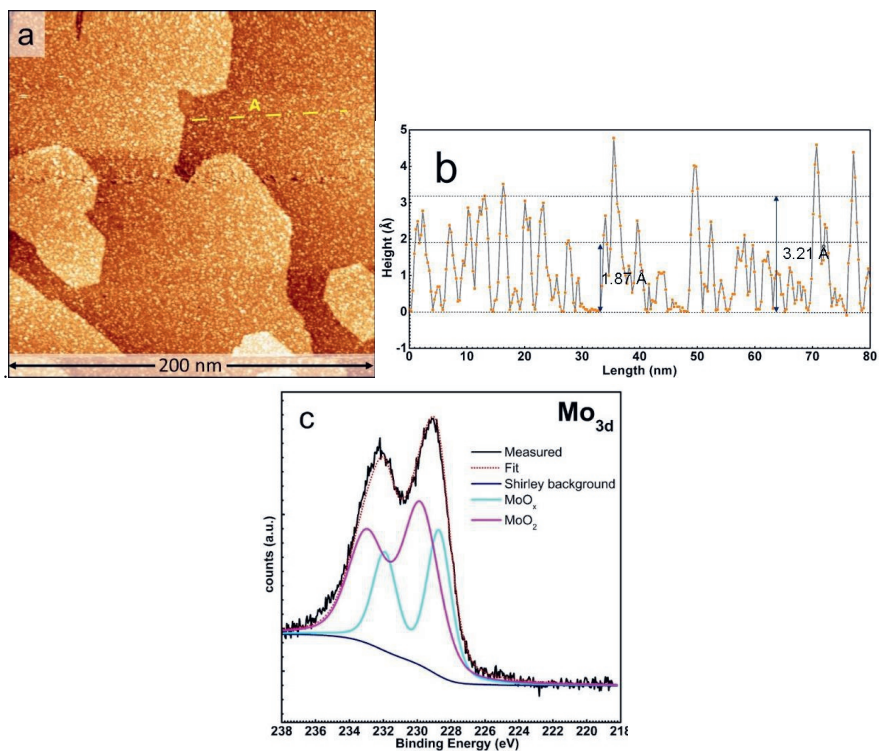


Figure 2: a) Large-scale STM image of Mo nanoparticles supported on TiO₂(110) grown by physical vapor deposition at 300 K; sample voltage = +2.2 V, tunneling current = 200 pA. The Mo coverage is 0.25 ML as determined from XPS. b) Measured height along the line marked A in Figure 2a. c) Mo 3d XPS spectrum of the Mo nanoparticles supported on TiO₂(110).

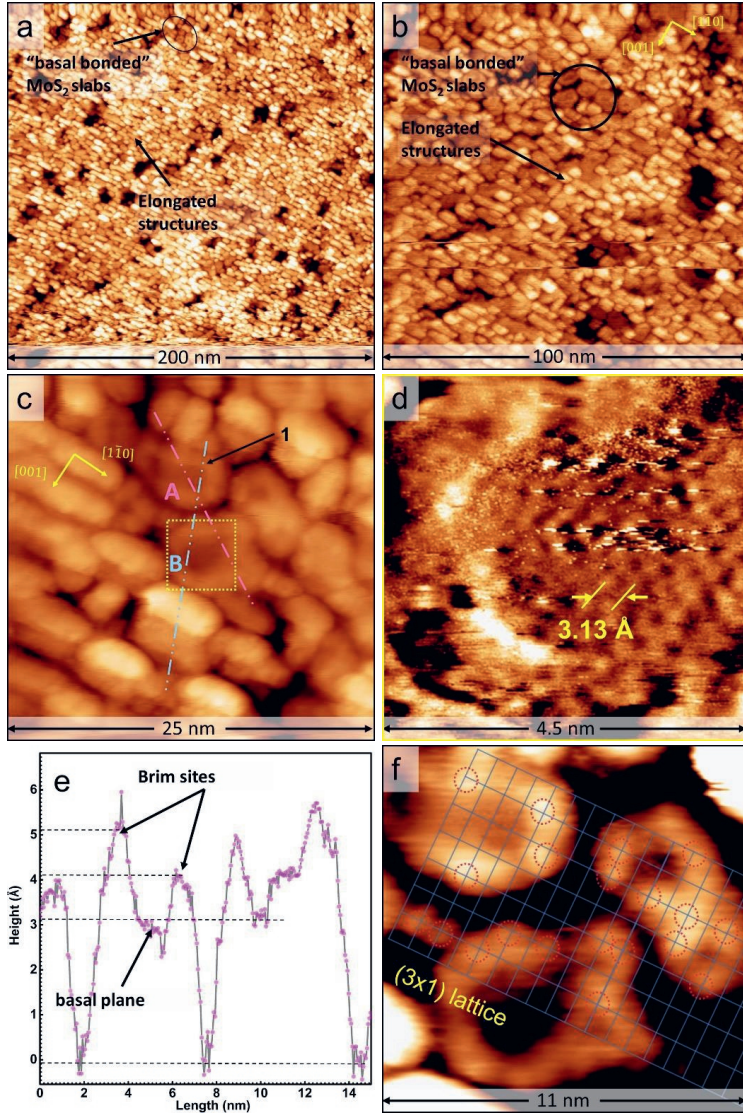


Figure 3: a, b) Large-scale STM images of MoS₂ slabs supported on TiO₂(110) obtained with a sample voltage = +2.1 V and tunneling current = 150 pA. The coverage of Mo determined from XPS is 0.25 ML. c) Zoomed-in STM image showing MoS₂ slabs supported on TiO₂(110). d) Atom-resolved STM image of the “basal-bonded” MoS₂ slab within the area marked by the yellow dotted square in Figure 3c. e) Measured height along the line marked A in Figure 3c, (Measured height along the line B is discussed later in Figure 5a). f) A (3x1) lattice superimposed on the “basal-bonded” MoS₂ slabs in Figure 3c. The red dotted circles show the locations where the bright corner sites match the (3x1) lattice.

The observed bright rim along the periphery of the MoS₂ slabs was attributed to the electronic effects of one-dimensional metallic states on the edges of the MoS₂ slabs called Brim sites.⁵³ The bright rim of “basal-bonded” MoS₂ slabs supported on TiO₂(110) is, however, more diffuse as compared to MoS₂ on metallic supports like Au(111). These Brim sites were also observed on MoS₂ slabs grown on TiO₂ at 900 K.⁶ The measured height along the line marked A in Figure 3c (shown in Figure 3e) shows that the “basal-bonded” MoS₂ slabs have the edge protrusions measured up to 5.1 ± 0.1 Å high while the basal planes are measured to be 3.3 ± 0.2 Å high which is close to the theoretical S-Mo-S distance of 3.15 Å. However, the SL MoS₂ slabs with measured height of up to 4.7 Å were reported in previous studies.^{6,13} The measured height of MoS₂ is strongly influenced by electronic effects due to the chemical state of the tip, applied sample voltage, MoS₂-TiO₂ interactions as well as the conductivity of the substrate which in turn is influenced by the cleaning procedure and fate of the substrate due to the inevitable sulfur-TiO₂ chemical reactions at the lower synthesis temperature used in our experiment. Therefore, the comparison of our measured heights with previous literature reports becomes difficult. Since nearly all of the “basal-bonded” MoS₂ slabs have the same relative contrast with respect to the TiO₂(110) steps, we conclude that the synthesis procedure yields predominantly SL “basal-bonded” MoS₂ slabs. Furthermore, we observe that there are two types of Brim sites with a measured height difference of ~ 1 Å. This is attributed to the Mo- and S- terminated edges of the MoS₂ slabs having slightly different electron densities at the respective Brim sites. Furthermore, the electron density at these Brim sites was found to have maxima (bright spots) at the corner sites of the irregular “basal-bonded” MoS₂ slabs. Analysis of the locations of these corner sites of nearby “basal-bonded” MoS₂ slabs showed that the bright spots were located at positions which were integral multiples of ~ 6.2 Å along the $[1\bar{1}0]$ direction and ~ 8.9 Å along the $[001]$ direction, thus fitting a (3x1) TiO₂(110) lattice (see Figure 3f) strongly suggesting that these bright spots are related to bonding of the MoS₂ slabs with the substrate, likely through an edge sulfur atom. Theoretical calculations using density functional theory (DFT) on the influence of the substrate interactions are necessary to correctly assign the edge terminations.

Increasing the initial coverage of Mo nanoparticles to 0.49 ML followed by sulfidation also formed “basal-bonded” MoS₂ slabs. However, the slabs were observed to merge along at least one of their edges and thus, forming effectively larger-size MoS₂ slabs. This effect can be seen in Figure 4a and is better resolved in Figure 4b. The “basal-bonded” MoS₂ slabs thus formed, retain their irregular shape and also have an atomically-flat basal plane with a dark relative contrast. However, we also observed the formation of a significant number of slabs with a brighter contrast in the basal plane. Heightlines along the basal planes of these slabs show a measured height of ~ 5.8 Å suggesting the formation of a second layer (see SI, Figure S2). Upon further increasing the coverage of Mo nanoparticles to 0.61 ML followed by sulfidation, the MoS₂ slabs are predominantly “basal-bonded” and are multilayered, as is evident from their STM contrasts (see Figure 4c). As the substrate is already completely covered at this Mo coverage, determining the number layers of “basal-bonded” MoS₂ slabs from the STM images becomes difficult. However, a layer-by-layer growth of the MoS₂ slabs is evident from our experiments up to a coverage of 0.61 ML Mo.

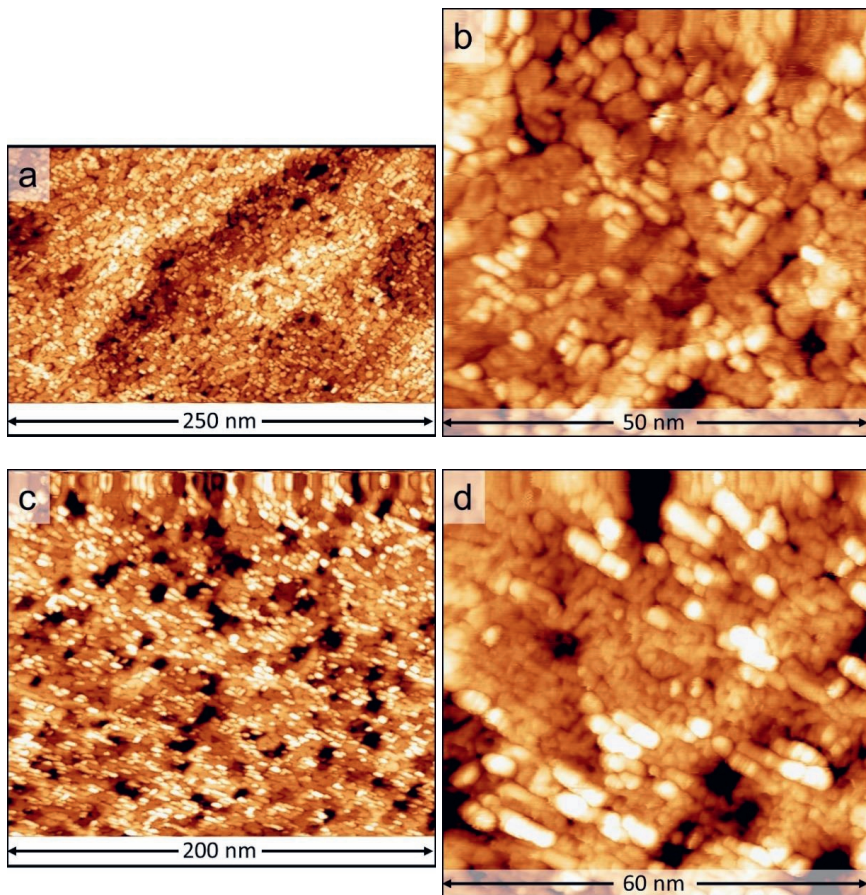


Figure 4: a, b) STM images of MoS₂ slabs supported on TiO₂(110) obtained with a sample voltage = +2.2 V and tunneling current = 150 pA. The coverage of Mo determined from XPS is 0.49 ML. c, d) MoS₂ slabs supported on TiO₂(110) obtained with a sample voltage = +2.2 V and tunneling current = 200 pA. The coverage of Mo determined from XPS is 0.61 ML.

In addition to the “basal-bonded” MoS₂ slabs, we also observe the formation of several elongated structures aligned along the $[1\bar{1}0]$ direction for all the coverages of Mo nanoparticles presented in this work. These elongated structures have both intermediate and bright relative contrasts with respect to the “basal-bonded” MoS₂ slabs as seen in the large-scale STM images in Figures 3a, 4a and 4c. These structures have not been observed to form in the previous studies that use high temperature for the synthesis of MoS₂ on TiO₂ at 900 K and 950 K. The measured height along the line marked B in Figure 3c over one such elongated structures is shown in Figure 5a. The elongated structures were measured to have a height of 7.2 ± 0.2 Å for the intermediate contrast ones and 11.7 ± 0.4 Å for the bright contrast ones. Additionally, the elongated structures are 3-5 nm in length and are formed without a preferred

location as is seen from their uniform distribution on the $\text{TiO}_2(110)$ steps in Figure 4a. Furthermore, these elongated structures are resolved further into a row of bright spots separated by $6.2 \pm 0.1 \text{ \AA}$ (see Figure 5b). The elongated structures typically consist of 2-4 of such rows separated by $8.6 \pm 0.2 \text{ \AA}$ (see Figure 5b and 5c). These distances fit well with a (3×1) $\text{TiO}_2(110)$ lattice suggesting that strong substrate interactions are present and likely play a key role in the formation of these structures. We also observed that the number density of the elongated structures decreases sharply with increasing the Mo coverage from 0.25 to 0.49 ML but only decreases slightly with further increasing the Mo coverage to 0.61 ML (see SI, Figure S3). However, we also observe that the elongated structures always have a higher STM contrast than that of the “basal-bonded” MoS_2 slabs irrespective of the number of layers of MoS_2 grown, suggesting a more metallic nature of the elongated structures. For example, in the case of Mo coverage of 0.25 ML, a relative height difference of up to $8.3 \pm 0.4 \text{ \AA}$ (see Figure 5a) is measured between the elongated structures and the basal planes of nearby “basal-bonded” MoS_2 slabs, while in the case of Mo coverage of 0.61 ML, a height difference of $7.4 \pm 0.2 \text{ \AA}$ (see SI, Figure S2) is measured. However, one may expect that the geometric effect growing multiple layers of “basal-bonded” MoS_2 slabs eventually offsets the electronic effects of an adjacent, more metallic elongated structure and, therefore, the contrast difference between the MoS_2 phase and the elongated structures should decrease with increasing coverage of Mo. The measured height difference however, contradicts this expectation. This observation can, however, be explained by the vertical growth of the elongated structures with respect to the TiO_2 substrate.

The Mo 3d and S 2p spectra of all the sulfided samples are shown in Figure 6. After sulfidation, irrespective of the coverage, all the Mo 3d spectra show a doublet with peaks at 229.2 eV and 232.3 eV which are identified as those of MoS_2 and a shoulder at 226.1 eV which is identified as the expected S 2s feature. The Mo 3d doublets were fit based on the interpretations by Bruix et al.³⁷. The observed Mo 3d signal has no components of Mo^{5+} and Mo^{6+} states suggesting complete conversion to MoS_2 and no residual Mo oxysulfides within the detection limits of the XPS measurements. This matches very well with our STM observations. Furthermore, the data also suggest the presence of sub-stoichiometric MoS_x due to non-zero components at 228.7 eV and 228.3 eV. These two components have been assigned by Bruix et al. to coordinatively unsaturated Mo atoms bound to sulfur, such as the edge Mo atoms of an MoS_2 slab. Such coordinatively unsaturated Mo atoms have a lower oxidation state than that of the Mo atoms in the basal plane of an MoS_2 slab and hence, a lower binding energy signal in XPS. Upon increasing the coverage of Mo from 0.25 to 0.49 ML, it is observed that the $\text{MoS}_2 : \text{MoS}_x$ ratio increases. But further increase of Mo coverage to 0.61 ML does not change this relative ratio significantly, as it is seen in Table 2. The S 2p peak shows a slight red-shift from 162.2 eV to 162 eV upon increasing the coverage of Mo. The corresponding S 2s spectra also show this behavior. Furthermore, the S 2p peak for low coverage MoS_2 shows an asymmetry on the higher binding energy side of the peak. Fitting is performed with components for S^{2-} and S_2^{2-} .^{38-40,54} The S_2^{2-} states are attributed to the presence of double S atoms on the edges of the MoS_2 slabs.^{39,40} Our fits indicate an increase in the $\text{S}^{2-}:\text{S}_2^{2-}$ ratio (see Table 2) upon increasing the Mo coverage to 0.49 ML, but the ratio remains the same within experimental errors upon further increase of the amount of Mo. This observation also corresponds to the changes in the $\text{MoS}_2:\text{MoS}_x$ ratio observed from the Mo 3d spectra. Furthermore, the Mo:S ratio remains fairly constant at $\sim 1:2.2$ upon increasing the coverage of Mo. The ratio of 1:2.2 is very close to the expected value of 1:2 for MoS_2 . The extra sulfur is attributed to the adsorption of S on TiO_2 . The component for these

sulfur atoms could not be satisfactorily resolved in the peak fits for S 2p due to overlap with the S₂²⁻ component.²⁴

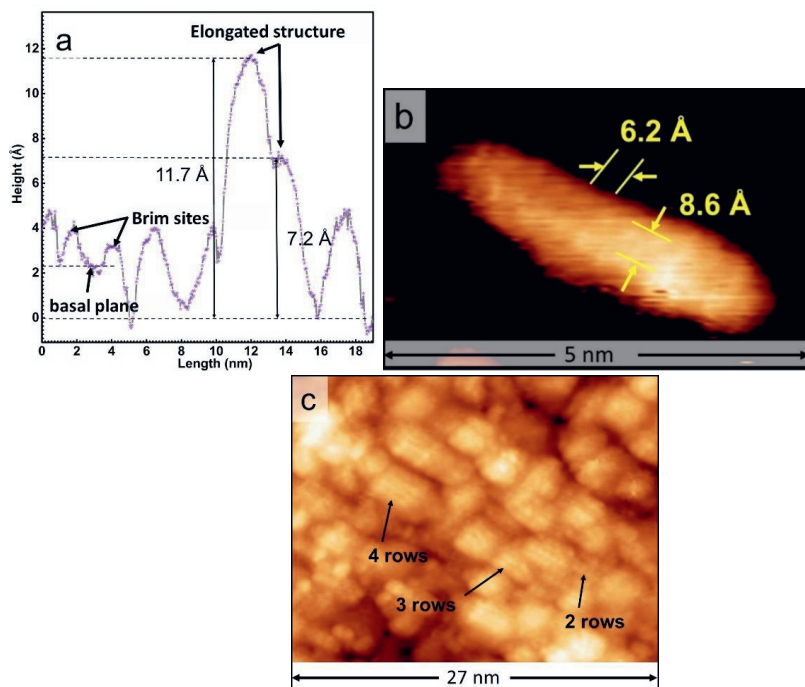


Figure 5: a) Measured height along the line marked B in Figure 3c over the elongated structures, b) Zoom-in of an elongated structure at high contrast resolving rows of bright spots. The STM image is obtained with a sample voltage = +2.2 V and tunneling current = 400 pA. The coverage of Mo determined from XPS is 0.25 ML. c) STM image showing the elongated structures formed as 2-4 rows.

In order to gain insights into the fate of the TiO₂(110) support after the sulfidation of the Mo nanoparticles, the STM images of the sample obtained after sulfiding 0.25 ML Mo nanoparticles were analyzed at high contrast to highlight the substrate (see SI, Figure S4). A characteristic (3x1) structure on the substrate that is identical to the well-known (3x1) sulfur adsorption structure of TiO₂(110) was observed to form on the exposed areas of the TiO₂ support.^{22,24} It is expected that the exposure to H₂S at elevated temperatures drastically changes the surface structure of the TiO₂(110) surface. The extensive studies on S-TiO₂ interactions in the past have shown that the interaction is very complex and can result in a wide variety of structures depending on the S coverage and temperature of adsorption.^{22-25,51,55,56} For instance, at room temperature, sulfur adsorbs on the exposed titanium atoms (five-fold coordinated) of TiO₂(110) but does not form ordered structures. When the temperature is increased to 573 K, the bridging oxygen atoms are systematically replaced by sulfur which eventually forms a (3x1) ordered structure. At 673 K, the in-plane oxygen atoms are also replaced by sulfur atom pairs, forming an ordered

(3x3) and ultimately, a (4x1) structure.^{23,24} Typically, the $\text{TiO}_2(110)$ surface has multiple structures co-existing depending on the sulfur coverage at that given temperature as has been demonstrated by STM and low-energy electron diffraction (LEED) experiments.²⁴ Based on these studies, at 650 K, the temperature used for MoS_2 synthesis in our experiments, the formation of (3x3) and (4x1) domains is expected on $\text{TiO}_2(110)$. We did not observe such structures in any of the STM images where the substrate is exposed. Instead, only a (3x1) structure associated with a slightly lower coverage of sulfur was observed to form on the exposed areas of the substrate. This can be explained by considering the presence of the overlayer of partially oxidized Mo nanoparticles which can act as a sulfur sink and compete with TiO_2 for the sulfur atoms thereby resulting in an effectively lower sulfur coverage on the TiO_2 substrate, since Mo nanoparticles have a higher affinity for sulfur. Therefore, a (3x1) structure, corresponding to a lower sulfur coverage, is likely to form. We also point out that (3x1) domains are also formed at elevated temperatures as have been observed in previous experiments.²⁴

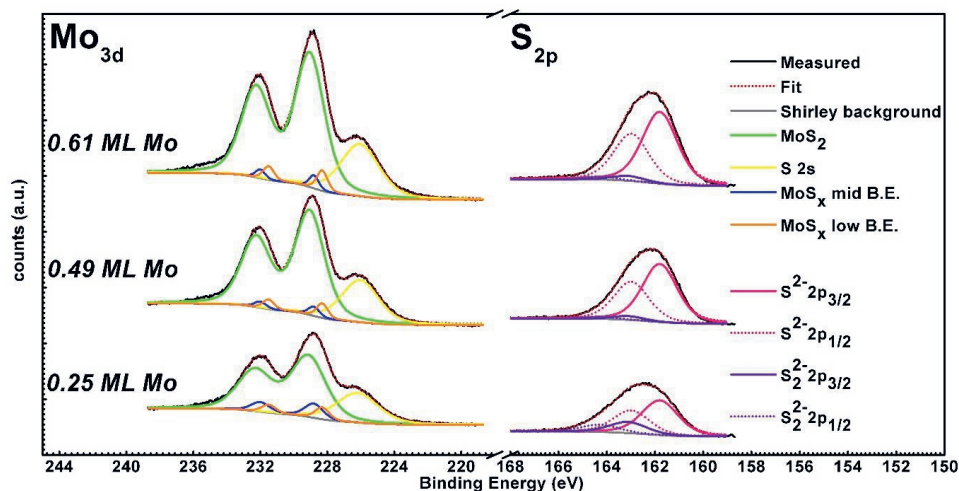


Figure 6: Mo 3d and S 2p XPS spectra of MoS_2 slabs supported on $\text{TiO}_2(110)$ at various initial coverages of Mo.

Given our observation that the bright spots on the “basal-bonded” MoS_2 slabs confirm to a (3x1) lattice, we propose that the overall curved structure of the MoS_2 slabs is due to interactions of the edges with the (3x1) S adsorption structure on $\text{TiO}_2(110)$. This is not surprising as prior studies have shown that the morphology and stoichiometry of Mo sulfides strongly depend on the interactions with the support.^{57–61} Taking into account the observation that the “basal-bonded” MoS_2 slabs are oriented along the $[1\bar{1}0]$ direction, we present a possible atomic model to account for our experimental findings. We take the case of the “basal-bonded” MoS_2 slab marked 1 in Figure 3c. The proposed atomic model for this MoS_2 slab is shown in Figure 7a. In our model, a pair of opposite edges of the MoS_2 slab with S- and Mo-terminations are oriented along the $[1\bar{1}0]$ direction of the $\text{TiO}_2(110)$ surface with the (3x1) sulfur structure. The terminating S atoms along these edges interact with both the five-fold and four-fold coordinated Ti atoms of the (3x1) structure. The S-S distance in the basal plane of MoS_2 is 3.15 Å which

matches well with the distance of 6.2 Å of the alternate Ti rows in the (3x1) structure of TiO₂(110) facilitating an MoS₂ edge - substrate Ti interaction for every alternating S atom of the MoS₂ edges. This may also be visualized by considering alternating lower edge S atoms lying close to the TiO₂(110) surface as belonging to the (3x1) TiO₂(110) structure. Furthermore, the STM images of all the “basal-bonded” MoS₂ slabs show that the corner sites of the slabs appear very bright, suggesting a high metallicity of these sites. Similar bright corner sites have been observed in Ni-promoted MoS₂ slabs supported on gold where some slabs adopt a curved shape with corner sites having coordinatively unsaturated Ni and Mo atoms.⁵³ The edge sites in these experiments have coordination numbers less than 5. Furthermore, the XAFS studies of promoted and unpromoted MoS₂ catalysts supported on TiO₂ showed that, for small MoS₂ slabs, Mo atoms tend to have coordination numbers between 4-5.5 resulting in sulfur-deficient edge terminations which are stabilized by bonding to the TiO₂ substrate.^{20,21} We propose that the terminating corner sites in the “basal-bonded” MoS₂ slabs in our experiments are formed due to an unsaturated Mo atom of less than 6 coordination number. The conformation of the MoS₂ slab to the (3x1) sulfur structure likely stabilizes these coordinatively unsaturated Mo sites. As a comparison, we overlay the particle marked 1 in Figure 3c over our atomic model (see SI, Figure S5). A visual comparison clearly shows a close match between the locations of the bright spots in the STM image and locations of coordinatively unsaturated Mo corner sites in our atomic model.

Table 2: Ratio between various components of the XPS spectra in Figure 6.

Mo coverage (ML)	Mo:S	MoS ₂ :MoS _x	S ²⁺ :S ₂ ²⁻
0.25	1:2.31	1:0.241	1:0.329
0.49	1:2.22	1:0.096	1:0.056
0.61	1:2.24	1:0.093	1:0.062

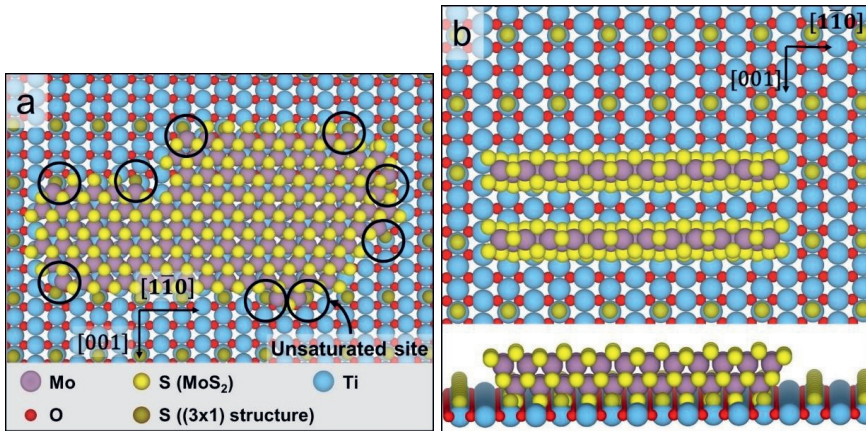


Figure 7: a) Possible atomic model of the “basal-bonded” MoS₂ slab supported on TiO₂(110) with a (3x1) structure due to S adsorption, b) Possible atomic model of “edge-on” MoS_x stripes supported on TiO₂(110) with a (3x1) structure due to S adsorption.

In addition to the “basal-bonded” MoS₂ slabs, the elongated structures are also oriented along the $[1\bar{1}0]$ direction of the TiO₂ substrate. Furthermore, these structures have rows of bright spots that also closely fit a (3x1) lattice suggesting strong substrate interactions. We first consider the possibility of the elongated structures being formed by S atoms reacting with the TiO₂(110) substrate. The well-known (4x1) structure of sulfur on TiO₂(110) also has a similar geometry, albeit with the rows of bright spots separated by 3.2 Å.²⁴ The previous experiments on S-TiO₂(110) interactions showed that the measured height difference of this structure with respect to areas of the substrate with the (3x1) structure is, however, only about 0.5 Å in contrast to the 7.2±0.2 Å and 11.7±0.4 Å measured for the elongated structures in our experiments. The excess sulfur atoms are also not known to form any ordered structures on TiO₂(110) at 650 K. Thus, we rule out the possibility that the elongated structures are formed by sulfur atoms alone. Leliveld et al.^{20,21} have observed the formation of small MoS₂ clusters on a TiO₂ support with only 4-15 Mo atoms per slabs with most of the Mo in likely bonding with the substrate. They have suggested the formation of linear chains of MoS₂ oriented along the $[1\bar{1}0]$ direction of rutile TiO₂ as a possible candidate structure. Chen et al.⁶² and Uetsuka et al.¹⁹ have observed the edge-on coupling of MoS₂ slabs to anatase TiO₂ surfaces. Uetsuka et al.¹⁸, in another study, also reported the formation of edge-on coupled MoS₂ slabs on rutile TiO₂(110) when pure H₂S was used as a sulfiding agent using high-resolution transmission electron microscopy (HRTEM) experiments. Furthermore, many MoS_x-type molybdenum sulfides are known to form striped phases on suitable substrates.^{59,61} We consider the possibility of the elongated structures in our experiments being Mo sulfide stripes. From the STM images of the sample obtained after sulfiding 0.25 ML Mo nanoparticles, we estimated that the coverage of Mo present in the “basal-bonded” MoS₂ slabs is only 0.11±0.02 ML (see SI, S6) in contrast to the 0.25 ML calculated from the XPS spectra. Prior experiments of Mo on TiO₂ showed that the diffusion of Mo into the bulk of TiO₂ is negligible as the process is thermodynamically not favorable.^{34,36} We therefore conclude that the missing Mo is present on the surface and attribute this Mo to the elongated structures observed in the STM images. Furthermore, the observation that the elongated structures are more metallic suggests that they are likely composed of unsaturated Mo atoms, for instance, as MoS_x structures with 1<x<2.

Based on these observations from the STM and XPS data, we attempt to arrive at a possible atomic model for the elongated structures. We first consider the possibility of MoS₂ stripes formed with their (0001) basal plane parallel to the TiO₂ (110) surface. This may be visualized as a 1D “basal-bonded” MoS₂ slab. We expect such an orientation of MoS₂ stripes to be highly unlikely due to the high energy cost of such a morphology in comparison to a 2D slab containing the same number of Mo atoms. An alternative possibility is that stripes are formed with an “edge-on” orientation such that one of their edges are directly bonded to the TiO₂ support (see Figure 7b) and with the (0001) plane being perpendicular to the TiO₂(110) surface. Considering the closely matching lattice constants of MoS₂ and TiO₂(110) along the $[1\bar{1}0]$ direction, it is likely that the S edge is bonded to the TiO₂ surface such that alternate sulfur positions match with the location of an S atom of the (3x1) structure, hence the observed periodicity in the STM images. Such “edge-on” MoS₂ stripes growing on adjacent rows of the (3x1) structure could appear as the group of 2 to 5 rows observed in the STM images. The observed STM contrasts of the row of bright spots (such as in Figure 4b) could be due to the structure of the Mo-terminated edge of the “edge-on” MoS₂ stripe that is oriented upwards towards vacuum (see Figure 7b). Based on our assignment of these stripes to the MoS_x signal in XPS, majority of the Mo atoms in such a stripe, including those on the edges, will be unsaturated. An example of such an unsaturated Mo edge

is shown in our model with alternating S^{2-} and S_2^{2-} units. The elongated structures which appear with a higher contrast and have a measured height of $11.7 \pm 0.4 \text{ \AA}$ (see Figure 3c) in the STM images can be explained by the formation of a second -Mo-S layer over the “edge-on” MoS_2 stripe. The height difference of $\sim 4 \text{ \AA}$ matches closely with the theoretical distance of 3.2 \AA . One also cannot rule out the electronic effects of charge transfer due to chemical bonding with the substrate. Thus, the “edge-on” MoS_x stripes described in our model predominantly consist of Mo in less than the ideal coordination number of 6. The presence of under-coordinated Mo atoms leads to an increased metallicity of these MoS_x stripes, thus explaining the higher contrasts in the STM images in comparison to that of the “basal-bonded” MoS_2 slabs. In fact, our observation that the number density of the elongated structures decreases upon increasing the amount of Mo from 0.25 to 0.49 ML, but remains relatively the same upon increasing the amount of Mo further up to 0.61 ML is in direct correlation with the XPS observations of the change in the $\text{MoS}_2:\text{MoS}_x$ and $S^{2-}:S_2^{2-}$ ratios, and can be fully explained by considering the elongated structures as unsaturated “edge-on” MoS_x stripes as in our atomic model. Given the correlations between our proposed atomic models and the STM and XPS data, these models could be good candidate structures for future theoretical research using DFT calculations. This, however, is outside the scope of this current work.

5.5 Conclusions

We have presented a low-temperature synthesis strategy for MoS_2 slabs supported on $\text{TiO}_2(110)$ using partially oxidized Mo nanoparticles as a precursor. We have studied the MoS_2 slabs using STM and XPS and have proposed possible atomic models. When MoS_2 is grown by similar low-temperature synthesis methods on single-crystal metal substrates like $\text{Au}(111)$ with weak interactions, only the “basal-bonded” MoS_2 slabs with the thermodynamically favored edges have been observed to form. In particular, the $\text{MoS}_2 - \text{Au}$ system has been used to study the many well-known remarkable properties of SL MoS_2 slabs. A similar effect is achieved by growing MoS_2 at high-temperatures on TiO_2 where the sulfur-substrate interactions are circumvented due to extensive desorption of S. The low-temperature synthesis method presented in this work is very relevant for fields such as catalysis where this system is synthesized industrially at similar low-temperatures and is widely used to produce cleaner fuels. In particular, our work shows that the reaction of the substrate with sulfur needs to be taken into account for atomic structural characterization. Furthermore, the lower temperature not only leads to the formation of flat MoS_2 slabs with irregular shapes (thermodynamically less favorable), but also to MoS_x stripes with large number of coordinatively unsaturated Mo atoms which are likely very reactive.

5.6 References

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Chapter 5 - Supporting Information

1. Comparison of Mo/TiO₂(110) precursors at Mo coverages of 0.25 ML and 0.49 ML

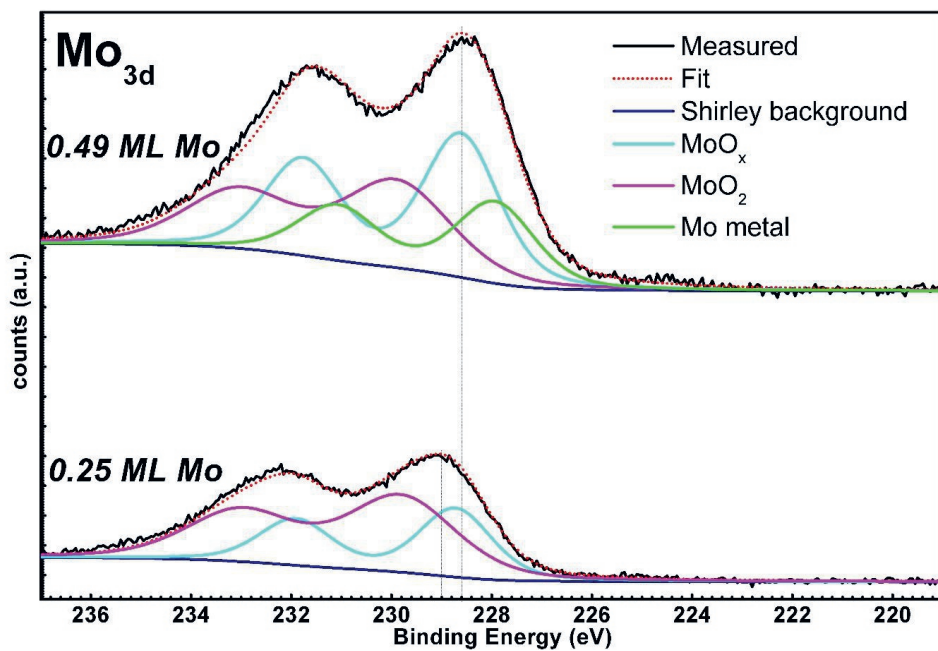


Figure S1: Mo 3d spectra of Mo nanoparticles supported on TiO₂(110) at initial Mo overages of 0.25 ML and 0.49 ML

2. MoS₂ slabs grown on TiO₂(110) at Mo coverages of 0.49 and 0.61 ML

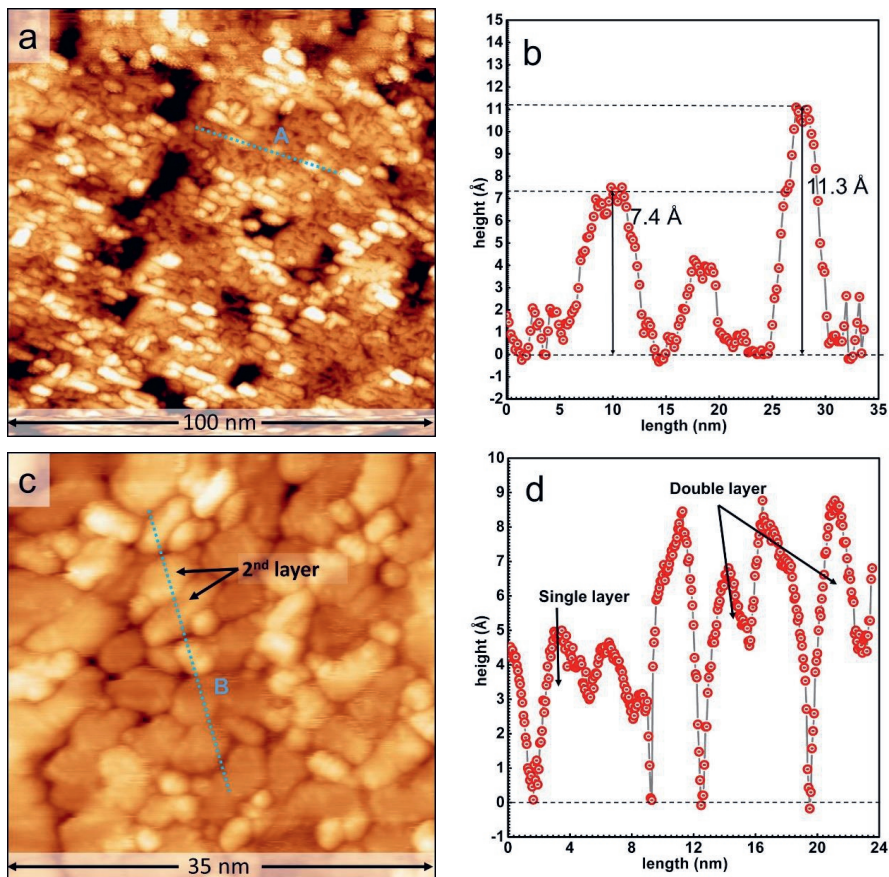


Figure S2: a) Large-scale STM image of MoS₂ supported on TiO₂(110) obtained with a sample voltage = +2.2 V and tunneling current = 250 pA. The coverage of Mo is 0.61 ML. b) Measured height along the line marked A in Figure S2a. c) Large-scale STM image of MoS₂ supported on TiO₂(110) obtained with a sample voltage = +2.1 V and tunneling current = 300 pA. The coverage of Mo is 0.49 ML. d) Measured height along the line marked B in Figure S2c.

3. Estimation of the number density of the elongated structures from STM images

Table S3. Table for estimation of the projected coverages of the elongated structures from STM images of various locations of the samples

absolute Mo coverage from XPS	Area fraction - elongated structure
0.25	0.44 ± 0.02
0.49	0.32 ± 0.04
0.61	0.29 ± 0.03

The number of elongated structures per unit area of the substrate is proportional to the projected area fractions as measured from the STM images, taking into account the elongated structures with both the intermediate and bright STM contrasts. Estimation of the projected area fraction of the elongated structures requires statistical averaging of the number of pixels over large substrate areas. For this, STM images of various areas of substrate totaling to $\sim 2 \mu\text{m}^2$ for each of the three Mo coverages were analyzed. Using the Gwyddion 2.47 software, masks were drawn over areas occupied by the elongated structures. The statistically averaged area coverages of the elongated structures are mentioned in Table S3.

4. STM images of the exposed areas of the $\text{TiO}_2(110)$ substrate

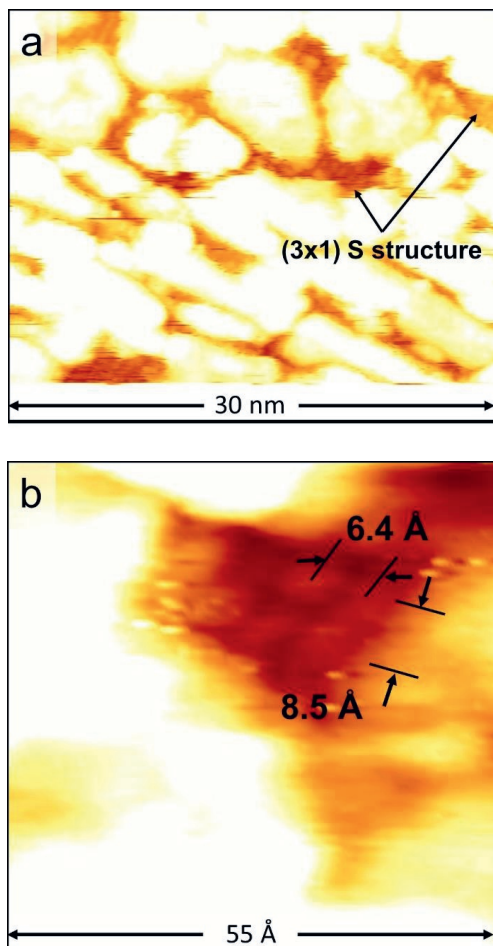


Figure S4: a) High-contrast STM image highlighting the exposed $\text{TiO}_2(110)$ substrate with the (3×1) sulfur structure; obtained with a sample voltage = +2.3 V and tunneling current = 500 pA. b) Zoom-in of a (3×1) structure near the edge of a "basal-bonded" MoS_2 slab.

5. Atomic model of “basal-bonded” MoS₂ slabs

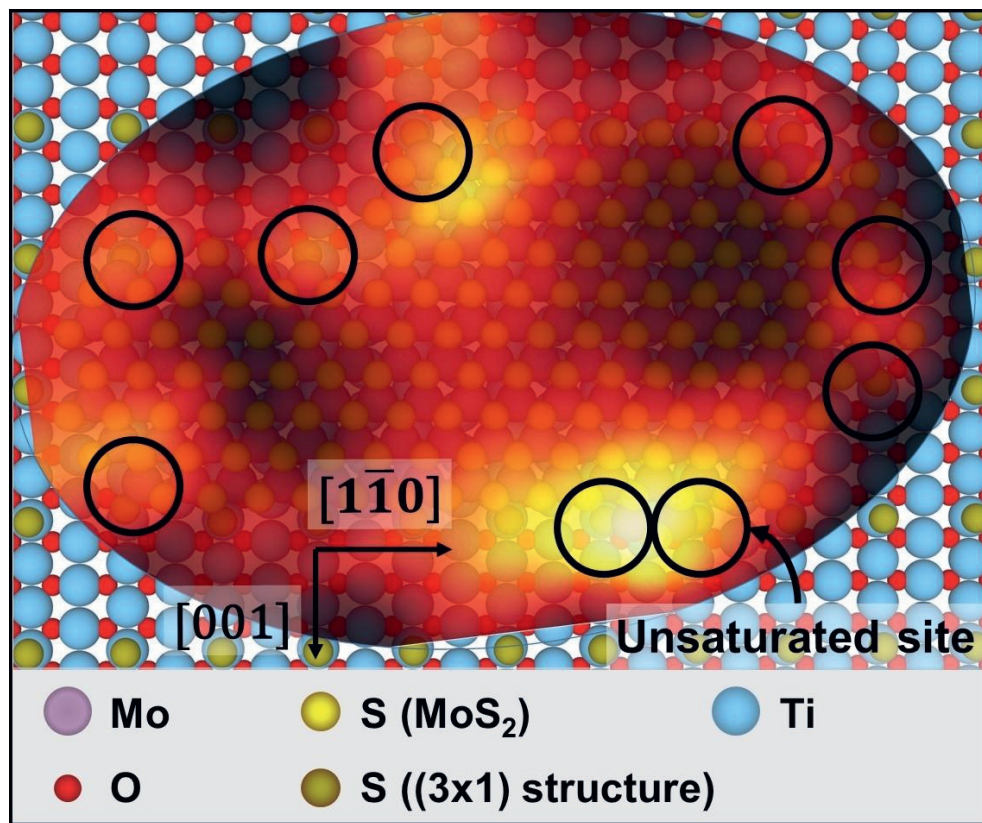


Figure S5: Atomic model of a “basal-bonded” MoS₂ slab from Figure 7a with the STM image of the slab marked 1 in Figure 3c superimposed. Note the close match between the bright spots and the coordinatively unsaturated corner Mo sites marked with black circles.

6. Estimation of Mo coverage from the STM images

In order to estimate the amount of Mo present in the “basal-bonded” MoS₂ slabs, the statistically averaged projected area needs to be determined. For this purpose, we make use of the same method as in S3, but mask the areas occupied by the MoS₂ slabs instead. Analyzing an area of 1.25 μm², we obtain:

Projected area fraction of the “basal-bonded” MoS₂ slabs = 0.117 (*measured from the masking*)

Area occupied by MoS₂ slabs for every (100 x 100) nm² of TiO₂(110)
= 1170 nm²

Side length of a hexagon of the same area = $\{(1170) \times \frac{2}{3\sqrt{3}}\}^{1/2}$ (*assuming that the MoS₂ slabs are perfectly hexagonal*)

$$= 21.23 \text{ nm}$$

distance in MoS₂ is 0.315 nm.)

$$= 21.23/0.315 \text{ Mo atoms, (S-Mo-S)}$$

$$\sim 67 \text{ atoms}$$

Therefore, number of Mo atoms in MoS₂ for every (100 x 100) nm² of TiO₂

$$= \frac{3\sqrt{3}}{2} \times 67^2 \text{ (area of a regular hexagon)}$$

$$= 11805 \text{ atoms}$$

Number of Ti atoms for every (100 x 100) nm² of TiO₂

$$= \left(\frac{100}{0.298}\right) \times \left(\frac{100}{0.32}\right) \text{ where 0.298 and 0.32}$$

nm are the experimentally measured Ti-Ti distances of the TiO₂(110) unit cell [22][40-42].

$$= 104865 \text{ atoms}$$

Since for low coverage, nearly all MoS₂ slabs are single-layer, coverage of Mo in “basal-bonded” MoS₂;

$$= 11805/104865$$

$$= 0.113 \text{ ML}$$

< 0.25 ML estimated from XPS data.