

# Chemical Vapor Deposition Synthesis of MoS<sub>2</sub> Layers from the Direct Sulfidation of MoO<sub>3</sub> Surfaces Using Reactive Molecular Dynamics Simulations

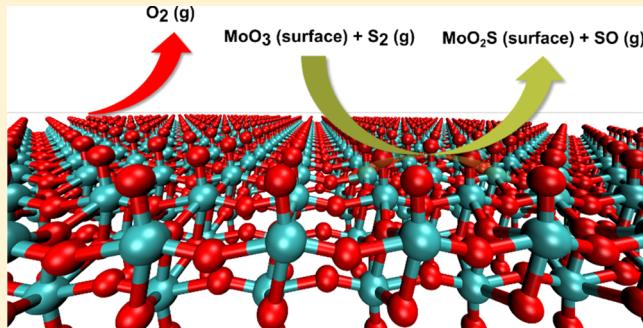
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## Supporting Information

**ABSTRACT:** Atomically thin MoS<sub>2</sub> layer, a promising transition metal dichalcogenide (TMDC) material, has great potential for application in next-generation electronic and optoelectronic devices. Chemical vapor deposition (CVD) is the most effective technique for the synthesis of high-quality MoS<sub>2</sub> layers. During CVD synthesis, monolayered MoS<sub>2</sub> is generally synthesized by sulfidation of MoO<sub>3</sub>. Although qualitative reaction mechanisms for the sulfidation of MoO<sub>3</sub> have been investigated by previous studies, the detailed reaction processes, including atomic-scale reaction pathways and growth kinetics, have yet to be fully understood. Here, we present quantum-mechanically informed and validated reactive molecular dynamics simulations of the direct sulfidation of MoO<sub>3</sub> surfaces using S<sub>2</sub> gas precursors. Our work clarifies the reaction mechanisms and kinetics of the sulfidation of MoO<sub>3</sub> surfaces as follows: the reduction and sulfidation of MoO<sub>3</sub> surfaces occur primarily at O-termination sites, followed by unsaturated Mo sites; these local reaction processes lead to nonuniform MoO<sub>x</sub>S<sub>y</sub> surface structures during the CVD process. After annealing the MoO<sub>x</sub>S<sub>y</sub> samples, the crystallized surface structures contain voids, and three different types of local surface complexes (MoO<sub>x</sub>, MoO<sub>x</sub>S<sub>y</sub>, and MoS<sub>2</sub>-like surface regions), depending on the fraction of S ingredients on the MoO<sub>x</sub>S<sub>y</sub> surface. These results, which have been validated by our reactive quantum molecular dynamics simulations and previous experimental results, provide valuable chemical insights into the CVD synthesis of large-scale and defect-free MoS<sub>2</sub> layers and other layered TMDC materials.



## 1. INTRODUCTION

Two-dimensional and layered materials such as graphene, transition metal dichalcogenide (TMDC), and hexagonal boron nitride have gained more attention for the exploration of functional nanostructures.<sup>1–3</sup> In particular, MoS<sub>2</sub> monolayer is a promising semiconducting TMDC material with great potential for electronic applications due to its outstanding physical and chemical properties, such as a layer-dependent band gap, high carrier mobility, and strong absorption in the visible frequencies.<sup>4–9</sup> Atomically thin MoS<sub>2</sub> layer has also been found to possess exceptional mechanical properties, applicable to flexible devices.<sup>10</sup> To bring such a fascinating mono/few MoS<sub>2</sub> layer into mass production, a wide range of synthesis techniques for MoS<sub>2</sub> layers and other layered TMDC materials has been proposed and developed, including mechanical exfoliation, physical vapor deposition, hydrothermal synthesis, and chemical vapor deposition (CVD).<sup>11–13</sup>

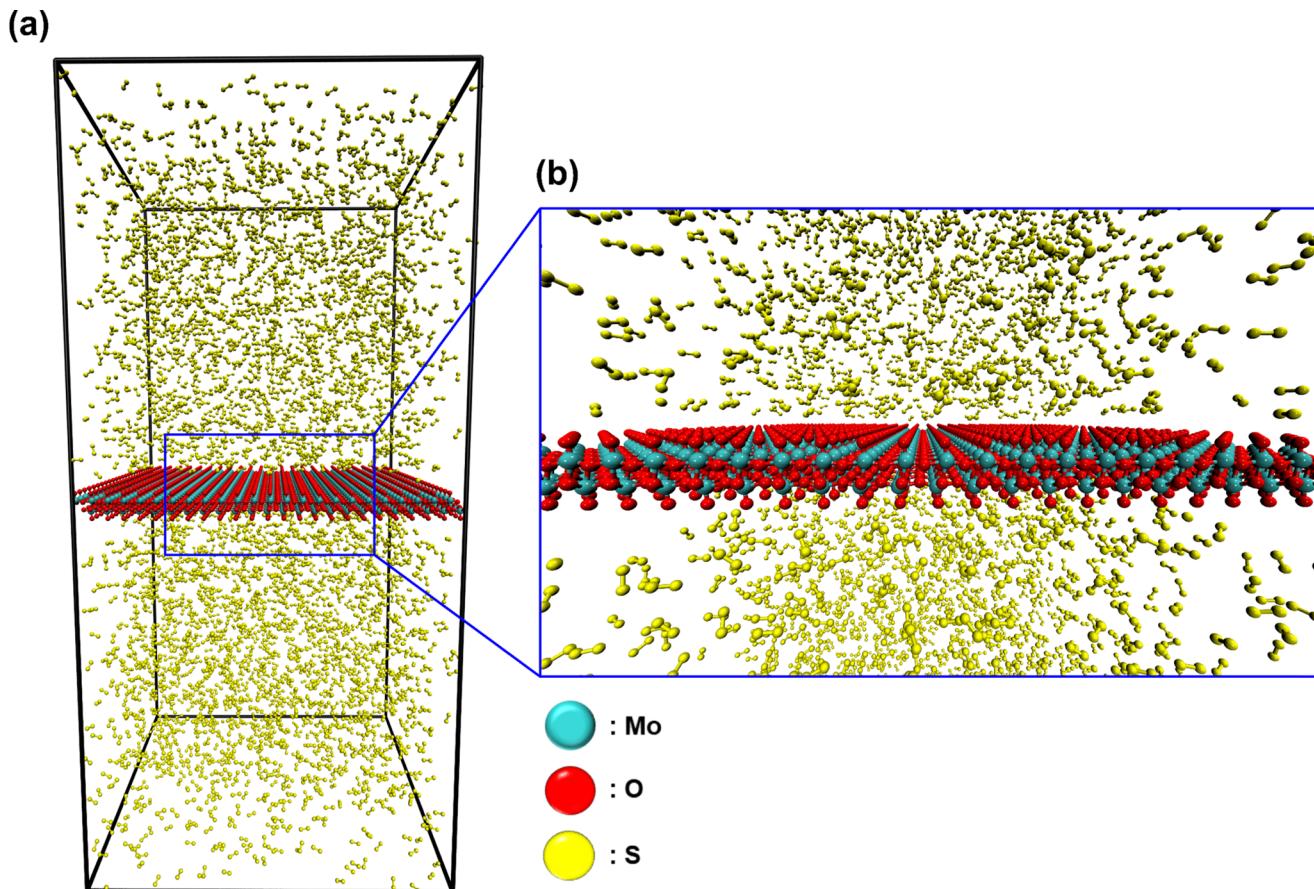
Among these techniques, CVD is the most effective method for synthesizing atomically thin MoS<sub>2</sub> layers on substrates because of its low cost, simplicity, uniformity, and scalability, compared with the other methods.<sup>13</sup> During CVD synthesis of MoS<sub>2</sub> layers, MoO<sub>3</sub> reactants and gas-phase sulfur precursors are generally used.<sup>14,15</sup> Thus, understanding the chemical reactions of MoO<sub>3</sub> reactants and gas-phase sulfur precursors is essential for the CVD synthesis of large-scale and defect-free MoS<sub>2</sub> layers. For this reason, numerous efforts have been made to investigate the reaction mechanisms during the CVD synthesis of MoS<sub>2</sub> layers.<sup>16–20</sup> Consequently, qualitative reaction mechanisms for the CVD synthesis of MoS<sub>2</sub> layers have been generally understood as follows: (a) the MoO<sub>3</sub> reactant is vaporized and interacts with gas-phase sulfur

Received: December 6, 2017

Revised: March 8, 2018

Published: March 9, 2018





**Figure 1.** (a) Initial configuration of a monolayered  $\text{MoO}_3$  surface (4608 atoms) with 4000  $\text{S}_2$  gas molecules (8000 atoms) for RMD simulations (within an orthogonal cell of  $94.18 \text{ \AA} \times 91.14 \text{ \AA} \times 200.0 \text{ \AA}$ ). (b) Closeup of the  $\text{MoO}_3$  surface interacting with the  $\text{S}_2$  gas environment. During the RMD simulations,  $\text{S}_2$  molecules react with the  $\text{MoO}_3$  surface, leading to reduction and sulfidation steps.

precursors in CVD chambers, leading to molybdenum oxysulfide (Mo-oxysulfide) intermediates; (b) during further reaction processes, the Mo-oxysulfide intermediates convert into  $\text{MoS}_2$  entities; and (c) the  $\text{MoS}_2$  entities are finally deposited onto substrates and merged into continuous  $\text{MoS}_2$  layers. Furthermore, recent experimental studies<sup>20,21</sup> have suggested that using the as-deposited  $\text{MoO}_3$  surface on the substrates, instead of vaporized  $\text{MoO}_3$  powders, could lead to a high uniformity of  $\text{MoO}_2$  layers during CVD synthesis. During this approach, the as-deposited  $\text{MoO}_3$  surface most likely reacts with sulfur precursors on its surface, finally transforming into  $\text{MoS}_2$  layers. As such, it is expected that the direct sulfidation of  $\text{MoO}_3$  surfaces is a key reaction event during the CVD process.

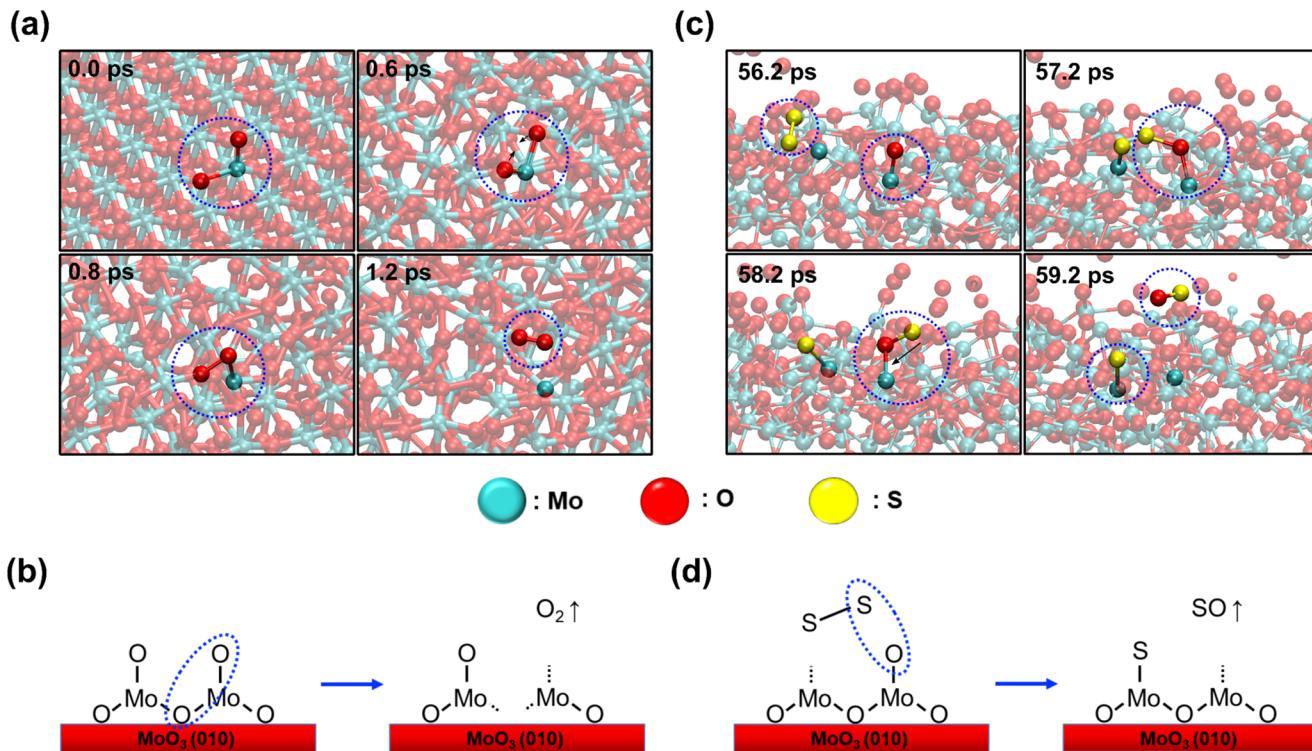
However, the detailed reaction pathways for the sulfidation of  $\text{MoO}_3$  surfaces have yet to be fully investigated. In addition, the reaction kinetics for the sulfidation of  $\text{MoO}_3$  surface remains unclear. These shortcomings are primarily due to the lack of experimental devices that capture these complex reaction events (i.e., short time scales and limited spatial resolution).<sup>22</sup> Atomistic modeling and simulations enable us to study dynamic behaviors of complex materials at the atomic level.<sup>23,24</sup> Particularly, reactive molecular dynamics (RMD) simulations allow one to describe reactive events, thus providing valuable information on the chemical and physical properties of nanoscale systems.<sup>25–27</sup>

Here, we present quantum-mechanically informed and validated ReaxFF<sup>28</sup>-RMD simulations of the direct sulfidation of  $\text{MoO}_3$  surfaces using  $\text{S}_2$  gas precursors to clarify key reaction

events during the CVD synthesis of  $\text{MoS}_2$  layers. To validate the critical reaction steps described by our RMD simulations, we also performed quantum molecular dynamics (QMD) simulations for the reactions of reduced  $\text{MoO}_3$  flakes and  $\text{S}_2$  molecules and compared the results of RMD simulations to those of previous experimental studies. Our goal is to obtain a better understanding of atomic-scale CVD synthesis processes of  $\text{MoS}_2$  monolayers and other TMDC materials. In this work, we provide new chemical insights into the mechanisms of the direct sulfidation of  $\text{MoO}_3$  surfaces and the reaction kinetics during the sulfidation and postannealing processes of the  $\text{MoO}_3$  surface.

## 2. METHODS

To describe the full dynamics of complex systems including chemical reactions, empirical reactive potentials or force fields such as COMB<sup>29,30</sup> and ReaxFF<sup>28</sup> can be effectively used and coupled with large-scale RMD simulations.<sup>31</sup> Especially, ReaxFF has shown its ability of successfully predicting not only gas-surface reactions<sup>32–34</sup> but also characteristics of two-dimensional materials.<sup>35–39</sup> A recent review paper<sup>40</sup> has provided further information on the ReaxFF potential and its applications. In this work, we used ReaxFF reactive force-field parameters for Mo/O/S elements that we previously reoptimized and validated for the CVD synthesis of  $\text{MoS}_2$  layers.<sup>41</sup> ReaxFF reactive force-field parameters used in this study can be found in the Supporting Information. To control system temperatures during RMD simulations, the NVT



**Figure 2.** Reaction mechanisms for reduction and sulfidation processes of the  $\text{MoO}_3$  surface described by RMD simulations. (a) RMD trajectories of the reduction process at 3000 K. The  $\text{MoO}_3$  surface is reduced primarily by breaking Mo–O bonds: one from the O-termination site and the other from the Mo–O–Mo bridge, liberating an  $\text{O}_2$  molecule. (b) Schematics of the reaction mechanism for the reduction process in (a). (c) RMD trajectories of the sulfidation process at 3000 K.  $\text{S}_2$  molecule reacts preferably with an O-termination site, along with a neighboring Mo-dangling bond, resulting in the formation of Mo–S bond and  $\text{SO}$  gas molecule. (d) Schematics of the reaction mechanism of the sulfidation process in (c). Note that the blue dotted circles and black arrows in (a, c) highlight local surface composition/molecules and critical reaction steps (i.e., bond breakage or formation), respectively. The blue dotted ellipses in (b, d) represent atoms in the surface structure and/or gas molecules participating in the key reaction steps.

ensemble with the Nosé–Hoover<sup>42,43</sup> thermostat was applied to the whole systems; a relatively small time step of 0.20 fs along with a temperature damping constant of 20.0 fs was used to properly describe chemical reactions for our RMD simulations. During the sulfidation process, we used an orthogonal cell of  $94.18 \text{ \AA} \times 91.14 \text{ \AA} \times 200.0 \text{ \AA}$ , which included a monolayered  $\text{MoO}_3$  surface ( $94.18 \text{ \AA} \times 91.14 \text{ \AA} \times 6.0 \text{ \AA}$ ) in the middle of the cell and 4000  $\text{S}_2$  gas molecules (system density:  $0.42 \text{ g/cm}^3$ ). In addition, a periodic boundary condition was applied to all of the directions. Then, the entire system was exposed to 3000 K for 2.0 ns, followed by 4000 K for 1.8 ns and 5000 K for 2.0 ns. Note that our simulated temperatures (3000–5000 K) were much higher than the experimental temperatures ( $\sim 1200 \text{ K}$ )<sup>13,15</sup> so that the  $\text{MoO}_3$  surface was easily vaporized, thus not holding solid-phase  $\text{MoO}_{x,y}$  surface structures during the RMD simulations. For this reason, one-body spring forces were independently applied to all of the Mo atoms in the  $\text{MoO}_3$  surface. In doing so, we could successfully describe key reaction events during our RMD simulations (such as  $\text{O}_2/\text{SO}$  gas and Mo–S bond formation) while preventing diffusion of Mo atoms into vacuum layers (i.e., the system kept maintaining solid-phase  $\text{MoO}_{x,y}$  surface structures during the entire RMD simulations up to 5000 K). After that, we performed the annealing process of the reduced/sulfidized  $\text{MoO}_{x,y}$  surfaces. For comparison, two different surface structures— $\text{MoO}_{0.69}\text{S}_{1.52}$  and  $\text{MoO}_{0.42}\text{S}_{1.95}$  surfaces—were taken from the previous sulfidation processes at 3.8 and 5.8 ns, respectively. All of the gas-phase molecules in

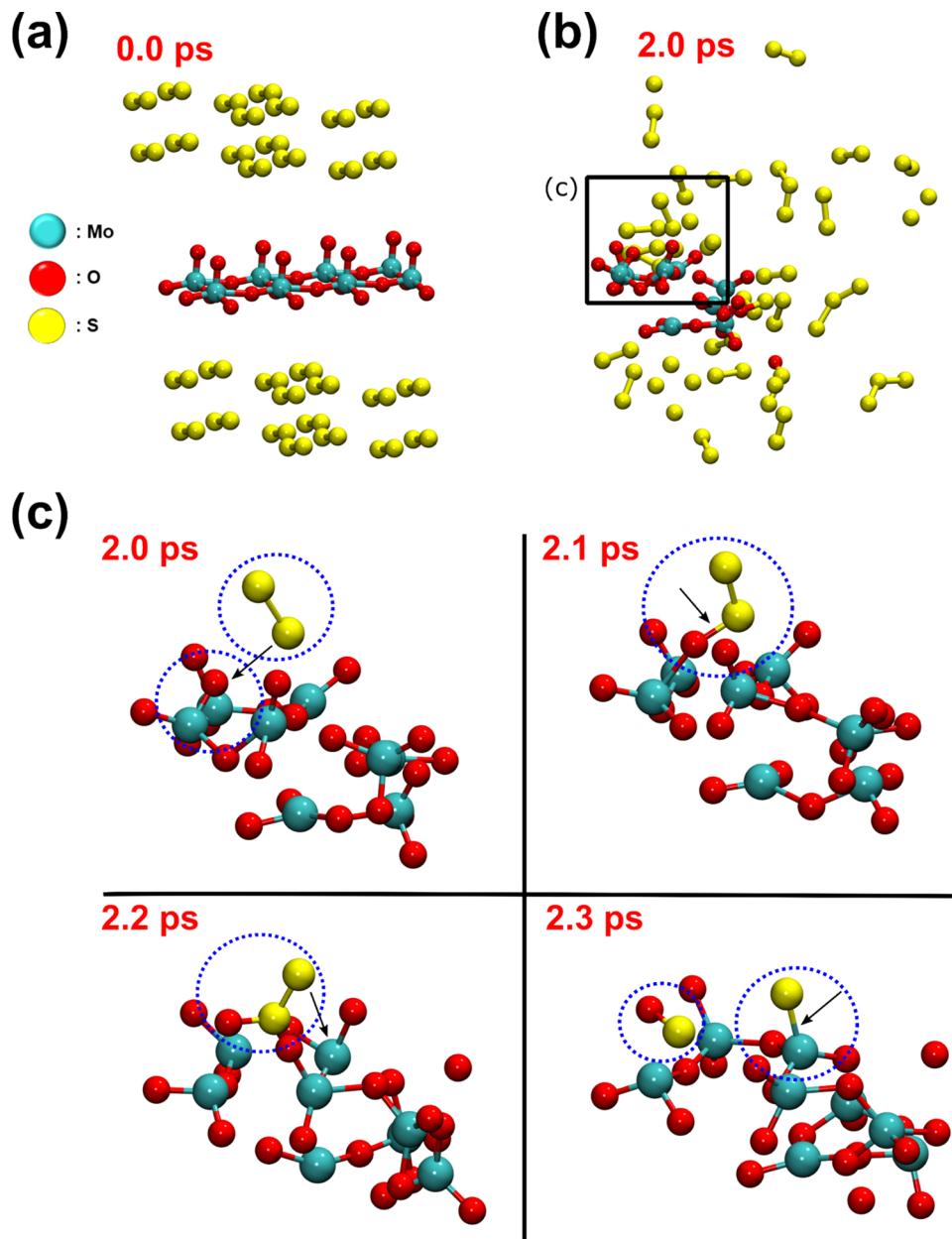
the vacuum layers were removed from these two simulation domains, and then, the surface structures were heated at a constant temperature of 1500 K up to 0.25 ns and cooled to 300 K for an additional 0.25 ns.

### 3. RESULTS AND DISCUSSION

Our work elucidates the detailed reaction pathways and kinetics for the sulfidation of  $\text{MoO}_3$  surfaces. In this section, we report the results of our RMD and QMD simulations and their analyses.

**3.1. Reaction Mechanisms for the Sulfidation of  $\text{MoO}_3$  Surfaces.** To clarify the reaction mechanisms associated with CVD synthesis of  $\text{MoS}_2$  layers, we performed RMD simulations of the sulfidation process with a gas-surface system, including a monolayered  $\text{MoO}_3$  surface ( $94.18 \text{ \AA} \times 91.14 \text{ \AA} \times 6.00 \text{ \AA}$ ) and  $\text{S}_2$  gas molecules (see Figure 1a,b).

Note that the system configuration is a simplified experimental model that uses as-deposited  $\text{MoO}_3$  surfaces on substrates and vaporized sulfur precursors during the CVD process,<sup>20,44</sup> and we assumed that the reactions in the interface between as-deposited  $\text{MoO}_3$ /substrates do not play a critical role in the sulfidation of the  $\text{MoO}_3$  surface. That is, our system only includes monolayered  $\text{MoO}_3$  without supported substrates, interacting directly with  $\text{S}_2$  gas molecules on the top and bottom surfaces. In doing so, we primarily simulated and investigated reaction events between the  $\text{MoO}_3$  surface and  $\text{S}_2$  gas molecules, leading to reduction and sulfidation steps efficiently. The system was then exposed to 3000 K for up to

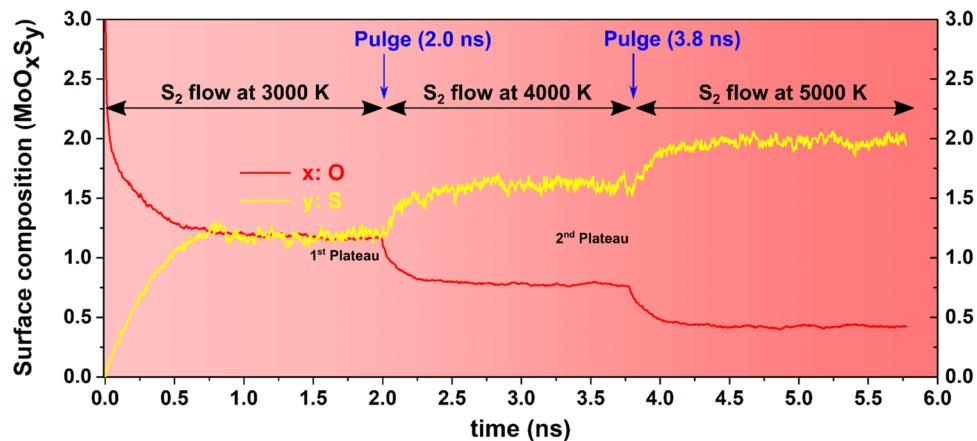


**Figure 3.** QMD simulations of the sulfidation of a reduced  $\text{MoO}_3$  flake. System configurations (a) at 0.0 ps and (b) 2.0 ps. Note that the reduced  $\text{MoO}_x$  slab was vaporized at high temperature, thus accelerating the chemical reactions of the  $\text{MoO}_x$  and  $\text{S}_2$  molecules. (c) Closeups of the black rectangle in (b) up to 2.3 ps, showing the reaction pathways for the sulfidation of the  $\text{MoO}_x$  cluster. The reaction mechanism by QMD simulation, leading to Mo–S bond and SO gas molecules, is in excellent agreement with our RMD simulations (see Figure 2c,d), thus validating our ReaxFF reactive force field for CVD simulations. The blue dotted circles and black arrows indicate critical reaction steps for the Mo–S bond and SO gas formation.

2.0 ns during our RMD simulations. It should also be noted that in our recently published work,<sup>41</sup> we suggested reaction mechanisms that are validated by the experimental literature,<sup>16,45</sup> for the reduction and sulfidation processes of  $\text{MoO}_3$  surfaces involving (1)  $\text{O}_2$  evolution, (2)  $\text{SO}/\text{SO}_2$  formation, and (3) Mo–S bond formation. To further clarify our proposed reaction mechanisms, we investigated detailed RMD trajectories and the corresponding schematics of the reaction mechanisms that clearly show stepwise  $\text{O}_2$  evolution.

Figure 2a–d demonstrates the reaction mechanisms for the reduction and sulfidation processes described above by taking into account detailed RMD trajectories. In Figure 2a, our RMD trajectories elucidate the reaction mechanism for the reduction

process of the  $\text{MoO}_3$  surface as follows: at 0.6 ps, the O atom in an O-termination site reacted preferably with a neighboring O atom in the Mo–O–Mo bridge; at 0.8 ps, the Mo–O bond in the Mo–O–Mo bridge broke, forming an O–O bond; at 1.2 ps,  $\text{O}_2$  molecules desorbed from the  $\text{MoO}_3$  surface, and thus, the surface was reduced. Figure 2b provides the schematics of this reaction mechanism, corresponding to the reduction step of the  $\text{MoO}_3$  surface. It is worth noting that the reduction process described by our RMD simulation is in excellent agreement with X-ray photoemission spectroscopy experiments by Salazar et al.,<sup>44</sup> who confirmed that during the annealing process, the as-deposited  $\text{MoO}_3$  surface was gradually reduced by Mo–O bond ruptures (i.e., the as-deposited  $\text{MoO}_3$  surface lost O

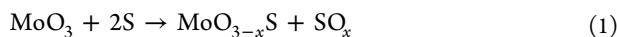


**Figure 4.** Rate of the reduction/sulfidation processes. Red and yellow curves represent a decrease in O atoms (i.e., reduction) and an increase in S atoms (i.e., sulfidation) on the  $\text{MoO}_x\text{S}_y$  surface composition, respectively, as a function of time. To increase the reaction rate, RMD simulations were performed at 3000 K for 2.0 ns, followed by 4000 K for 1.8 ns and then 5000 K for an additional 2.0 ns, and purging processes were performed at 2.0 and 3.8 ns.

atoms), thus validating our proposed reaction mechanism for the reduction step.

Subsequently, as shown in Figure 2c,  $\text{S}_2$  gas molecule interacted with both the O-termination and O-vacancy site (at 56.2 and 57.2 ps), thus breaking the S–S bond and leading to Mo–S bond and SO gas molecule (at 58.2 and 59.2 ps); the reaction mechanisms for this sulfidation process are also summarized in Figure 2d. To validate the full dynamics of our RMD simulations for the Mo–S bond and SO gas formation at high temperatures, we performed QMD simulations of the sulfidation of a reduced  $\text{MoO}_3$  flake using  $\text{S}_2$  gas molecules at 4500 K (Figure 3a). Detailed information on QMD methods and simulation schedules can be found in the Supporting Information. Our RMD simulations using reactive force fields for CVD process confirm the reaction mechanism for Mo–S bond formation and the evolution of SO molecular fragments deduced from QMD simulations, thus validating our ReaxFF reactive force-field-based RMD simulations.

The reduced  $\text{MoO}_3$  flake was vaporized and interacted actively with  $\text{S}_2$  gas molecules at 2.0 ps (Figure 3b). Then, the atomistic reaction pathways were investigated using further QMD trajectories up to 2.3 ps (Figure 3c): at 2.0 ps, the  $\text{S}_2$  molecule diffused to an O-termination site of the reduced  $\text{MoO}_3$  cluster; at 2.1 ps, one of the S atoms in the  $\text{S}_2$  molecule chemisorbed nondissociatively onto the O-termination site; at 2.2 ps, the other S atom in the  $\text{S}_2$  molecule bound to an undercoordinated Mo atom that was available; at 2.3 ps, finally, the S–S bond broke, resulting in the formation of an SO molecule and Mo–S bond. Comparing the RMD simulations with the QMD trajectories, we confirmed that the reaction mechanism for the sulfidation step of the reduced  $\text{MoO}_3$  surface by the RMD simulations was qualitatively consistent with that of our QMD simulations. Furthermore, our proposed reaction mechanism agrees with that of a previous study<sup>18</sup> as follows



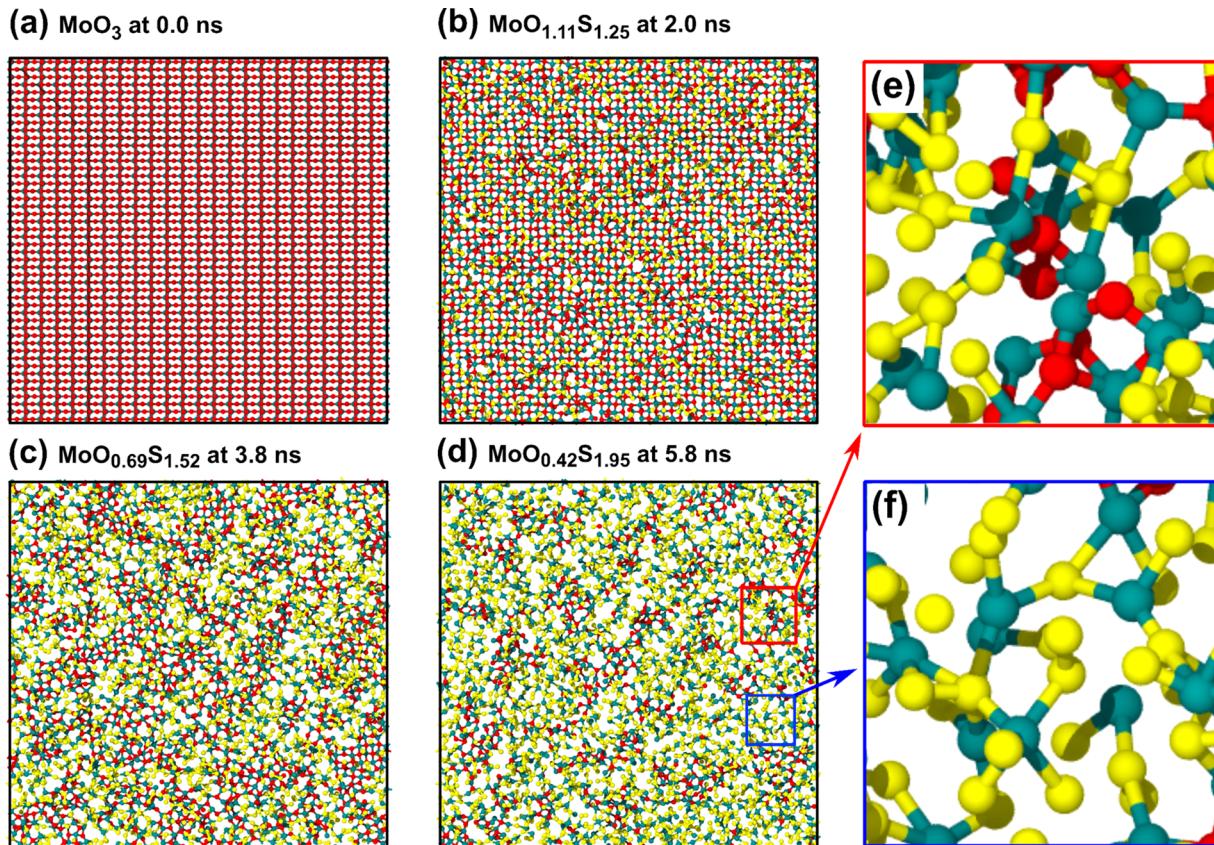
Given the results and observations above, we suggest that CVD synthesis of  $\text{MoS}_2$  layers from the direct sulfidation of  $\text{MoO}_3$  surface can be achieved by combined reduction and sulfidation steps, forming  $\text{O}_2$  and  $\text{SO}_x$  products and eventually leading to Mo–S bond formation.

### 3.2. Reduction and Sulfidation Rates of the $\text{MoO}_3$ Surface.

To understand reaction kinetics for CVD synthesis of  $\text{MoS}_2$  layers, we evaluated the reduction and sulfidation rates of the initial  $\text{MoO}_3$  surface up to 5.8 ns (Figure 4). For this analysis, RMD simulations of the sulfidation processes ( $\text{S}_2$  flow on the  $\text{MoO}_3$  surface) were performed at 3000 K for 2.0 ns, followed by 4000 K for 1.8 ns and 5000 K for 2.0 ns. All gas-phase molecules were purged, and then, 4000  $\text{S}_2$  gas molecules were redistributed at 2.0 and 3.8 ns. By using the two simulation procedures described above (i.e., elevating temperatures and purging gas molecules), we were able to efficiently increase the reaction rates for the reduction and sulfidation processes within a limited time scale (~5.8 ns).

These simulation schedules also allowed us to further describe the reaction events after the system reached the first and second plateaus, corresponding to times  $t = 1.5$ –2.0 ns and  $t = 3.5$ –3.8 ns, respectively. To validate our simulated models with such a high temperature, we provide some simulation details as follows:

1. To support our proposed reaction mechanisms from high-temperature simulations, we performed additional RMD simulations using the same surface model with lower temperatures in the range of 270–1900 K to clearly determine the initiation temperature for the reactions of the  $\text{SO}/\text{SO}_2$  and Mo–S bond formation. On the basis of the results in Figure S1, we conclude that the number of S–O bonds rapidly increases around 400 K mainly due to  $\text{S}_2$  physisorption on the  $\text{MoO}_3$  surface, and then  $\text{SO}_x$  gas molecules start evolving at 1000 K, leading to Mo–S bonds. Moreover, we observed that essential reaction steps at low temperatures are consistent with those in high-temperature simulations, suggesting that it is feasible to simulate critical reactions associated with CVD synthesis at low temperatures although this requires a significant amount of computational costs.
2. To stabilize the  $\text{MoO}_3$  surface at 5000 K in our RMD simulations, we have used a one-body spring force on Mo atoms, thus allowing for stable initial and intermediate surface structures.
3.  $\text{S}_2$  gas molecules reacting with both sides of  $\text{MoO}_3$  are different from the case of experimentally predeposited  $\text{MoO}_3$  on the substrate. However, in our previous work



**Figure 5.** (a–d) Top views of the transformation of  $\text{MoO}_x\text{S}_y$  surface structures in the  $x$ – $y$  plane at 0.0, 2.0, 3.8, and 5.8 ns, respectively, corresponding to the time steps in Figure 4. All gas-phase molecules are not shown for clarity. (e, f) Closeups of local surface regions in (d), corresponding to Mo-oxysulfide and  $\text{MoS}_x$  surface regions, respectively. Note that the initial  $\text{MoO}_3$  surface was locally reduced and sulfidized as the simulation time elapsed, thus forming the two local surface regions nonuniformly (red balls and sticks: O; yellow balls and sticks: S; cyan balls and sticks: Mo).

(ref 41), we sulfidized predeposited  $\text{MoO}_3$  on the alumina substrate and we still observed the reactions occurring on the  $\text{MoO}_3$  surface.

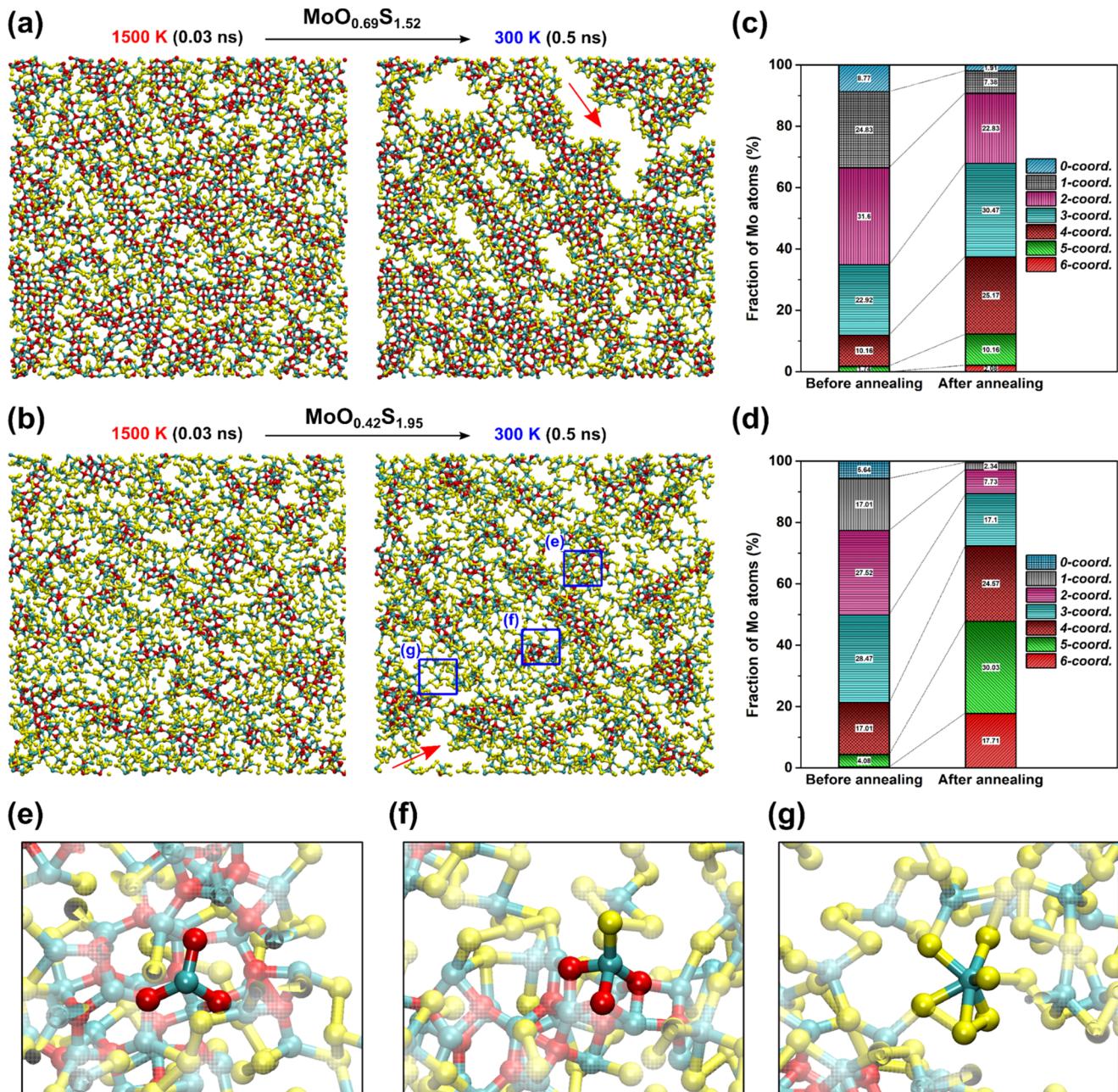
As shown in Figure 4, at the first stage ( $T = 3,000$  K), a fraction of O atoms (red curve) decreased, whereas a fraction of S atoms (yellow curve) increased, after which the system reached the first plateau, indicating that the reduction and sulfidation processes began simultaneously. However, the rate of the reduction process was faster than that of the sulfidation process (e.g., the initial  $\text{MoO}_3$  surface converted to  $\text{MoO}_{1.11}\text{S}_{1.25}$  at 2.0 ns). These results reveal that during this stage, the as-deposited  $\text{MoO}_3$  surface primarily lost O atoms through the formation of  $\text{O}_2$  and  $\text{SO}$ , leaving unsaturated Mo sites, and the reduced  $\text{MoO}_x$  surface gained S atoms through reactions of the unsaturated Mo sites and  $\text{S}_2$  gas correspondingly (see the previous section for the reaction mechanisms in detail). Movie S1 in the Supporting Information provides full dynamics of the reduction and sulfidation processes up to 2.0 ns.

During the second stage ( $T = 4,000$  K), the reduced  $\text{MoO}_{1.11}\text{S}_{1.25}$  surface (2.0 ns) further transformed into an  $\text{MoO}_{0.69}\text{S}_{1.52}$  surface at 3.8 ns, indicating that the loss of O atoms was still greater than the gain of S atoms, but the reduction and sulfidation rates decreased compared to those in the previous stage up to 2.0 ns. On the basis of these observations, one can expect that as the CVD process proceeded, the O-termination sites that were available on the

$\text{MoO}_x\text{S}_y$  surface gradually decreased because of  $\text{O}_2/\text{SO}$  gas formation (as discussed in the previous section), thus lowering the reduction and sulfidation rates accordingly. These results validate an experimental study<sup>16</sup> reporting that the O-termination site on the  $\text{MoO}_3$  surface was the most reactive site for the general sulfidation process.

The  $\text{MoO}_{0.69}\text{S}_{1.52}$  surface (3.8 ns) finally transformed into the  $\text{MoO}_{0.42}\text{S}_{1.95}$  surface at 5.8 ns ( $T = 5,000$  K). During this stage, the reduction and sulfidation rates dropped further, but interestingly, the sulfidation rate was faster than the reduction rate. This can be explained by the fact that more sulfur precursors could actively react with the  $\text{MoO}_x\text{S}_y$  surface because the initial  $\text{MoO}_3$  surface was almost reduced ( $\text{MoO}_{0.69}\text{S}_{1.52}$ ) during the first two stages, and thus, the sulfidation process could predominate as the unsaturated Mo sites provided preferable binding sites for  $\text{S}_2$  molecules. In summary, our RMD simulations clarify the reduction and sulfidation kinetics on the  $\text{MoO}_3$  surface as follows.

The reduction process is more active than the sulfidation process at the early stage, whereas this trend reverses at the later stage of the CVD process as a result of changes in the reactive sites that are available (the O-termination sites or unsaturated Mo sites) for  $\text{S}_2$  precursors. Transformation of the  $\text{MoO}_3$  surface to the  $\text{MoO}_x\text{S}_y$  surface was further investigated during the entire CVD process up to 5.8 ps. Figure 5a–d shows the top views (in the  $x$ – $y$  plane) of the  $\text{MoO}_x\text{S}_y$  surfaces at 0.0, 2.0, 3.8, and 5.8 ns, respectively, corresponding to the time steps in Figure 4. It is interesting to note that the initial  $\text{MoO}_3$



**Figure 6.** (a, b) Top views of the time evolution of  $\text{MoO}_{0.69}\text{S}_{1.52}$  and  $\text{MoO}_{0.42}\text{S}_{1.95}$  surface morphologies, respectively, during the annealing process. During this process, relatively significant surface voids in the  $\text{MoO}_{0.69}\text{S}_{1.52}$  surface structure were observed, compared to those in the  $\text{MoO}_{0.42}\text{S}_{1.95}$  surface structure. The red arrows in (a, b) point to the largest voids formed during the annealing process. (c, d) Corresponding changes in Mo-coordination numbers, only counted by S atoms, for the  $\text{MoO}_{0.69}\text{S}_{1.52}$  and  $\text{MoO}_{0.42}\text{S}_{1.95}$  surface structures. Note that portions of high Mo-coordination numbers (e.g., 4–6 coordination) increased as the surface structures were locally crystallized. (e–g) Closeups of local surface complexes in the blue rectangles in (b), corresponding to local  $\text{MoO}_x$ ,  $\text{MoO}_x\text{S}_y$ , and  $\text{MoS}_2$ -like regions, respectively.

surface (Figure 5a) was selectively sulfidized as the simulation time elapsed (Figure 5b–d), and the surface structures were divided primarily into two local regions: Mo-oxysulfide (Figure 5e) and  $\text{MoS}_x$  (Figure 5f), which were qualitatively consistent with experimental observations.<sup>46</sup> On the basis of our RMD simulations, the characteristics of the local sulfidation can be understood as follows: the reduction process occurred locally on the initial  $\text{MoO}_3$  surface, resulting in a wide range of Mo-coordination numbers on the  $\text{MoO}_x\text{S}_y$  surface. This result yielded different sulfidation behaviors on the local  $\text{MoO}_x\text{S}_y$  surface, that is,  $\text{S}_2$  molecules reacted preferably with the local

$\text{MoO}_x\text{S}_y$  surface, where a number of Mo-dangling bonds existed.

This trend was also experimentally confirmed by Salazar et al.,<sup>44</sup> reporting that the annealing process for the as-deposited  $\text{MoO}_3$  surface generated a wide range of Mo oxidation states, each of which led to different sulfidation rates. Thus, our RMD simulations demonstrated that during the CVD process, the initial  $\text{MoO}_3$  surfaces nonuniformly convert into  $\text{MoO}_x\text{S}_y$  surface structures as the surfaces are locally reduced and sulfidized.

**3.3. Annealing Process of  $\text{MoO}_x\text{S}_y$  Surfaces.** In a typical CVD process, samples are heated and cooled down to room

temperature after the sulfidation process.<sup>47,48</sup> To elucidate the evolution of surface morphologies during this annealing process, we performed RMD simulations of the annealing processes using the  $\text{MoO}_{0.69}\text{S}_{1.52}$  (Figure 5c) and  $\text{MoO}_{0.42}\text{S}_{1.95}$  (Figure 5d) surface structures; all gas-phase molecules were removed from each system, and then, the surface structures were exposed to 1500 K up for 0.25 ns, followed by cooling steps from 1500 to 300 K for 0.25 ns. Figure 6a,b shows the top views of the time evolution of the  $\text{MoO}_{0.69}\text{S}_{1.52}$  and  $\text{MoO}_{0.42}\text{S}_{1.95}$  surface morphologies during the annealing process, respectively. Interestingly, we found that the fractions of O and S atoms on the  $\text{MoO}_x\text{S}_y$  surfaces affected the crystallization behaviors of the surface structures further. Namely, local surface voids were increasingly formed on both surface structures during the annealing process, but relatively large voids were created on the  $\text{MoO}_{0.69}\text{S}_{1.52}$  surface, compared to that on the  $\text{MoO}_{0.42}\text{S}_{1.95}$  surface (see red arrows in Figure 6a,b pointing at the largest surface void on each surface). These results imply that the  $\text{MoO}_x\text{S}_y$  surface with sulfur deficiency ( $\text{MoO}_{0.69}\text{S}_{1.52}$ ) induces Mo atoms to further diffuse into neighboring S atoms that are available during the crystallization stage. In contrast, the  $\text{MoO}_x\text{S}_y$  surface with sufficient sulfur ( $\text{MoO}_{0.42}\text{S}_{1.95}$ ) allowed relatively little diffusion of Mo atoms on the surface, resulting in reduced surface voids on its surface structure accordingly. Such void formation, depending on the amount of gas-phase sulfur precursors, was also observed experimentally by Taheri et al.<sup>20</sup> using optical microscope images. Thus, it is expected that the degree to which Mo atoms diffuse, affected by the fraction of S atoms on the surface, is responsible for the size of surface voids that are formed on the  $\text{MoO}_x\text{S}_y$  samples during the local crystallization step. Full dynamics of the local void formation on the  $\text{MoO}_{0.69}\text{S}_{1.52}$  and  $\text{MoO}_{0.42}\text{S}_{1.95}$  surface structures are available in Movies S2 and S3 (the Supporting Information), respectively. The initial thickness of the  $\text{MoO}_3$  surface (i.e., O–O distance within a single  $\text{MoO}_3$  layer) was 6.74 Å. The single  $\text{MoO}_3$  layer was cleaved from the bulk  $\alpha\text{-MoO}_3$  crystal in the z-direction. After sulfidation and annealing processes (the right snapshot in Figure 6a), the average thickness was between 4.2 and 4.8 Å (see Figure S2 in the Supporting Information for the side views of the surface models during RMD simulations). The thickness of the intermediate  $\text{MoO}_x\text{S}_y$  surface was measured from S–S bond distances in the local  $\text{MoS}_2$ -like complexes, which can be primarily considered as real hexagonal  $\text{MoS}_2$  structures. As the surface becomes sulfidized, the thickness of the initial single layer decreases. Such a thickness change could be understood by the fact that the initial  $\text{MoO}_3$  surface has double sheets of Mo planes with O-termination sites on the top and bottom surfaces,<sup>49</sup> whereas the  $\text{MoS}_2$  monolayer consists of a single Mo plane with S atoms on the top and bottom surfaces.<sup>50</sup> Our RMD simulations reveal that as the O atoms in the  $\text{MoO}_3$  surface were replaced by S atoms, the Mo atoms get redistributed (i.e., they form a single plane), and thus, the intermediate structures became thinner during sulfidation.

Additionally, changes in Mo-coordination numbers (only counted by the surrounding S atoms) were measured to study local coordination complexes on the  $\text{MoO}_x\text{S}_y$  surface. Figure 6c,d compares the changes in Mo-coordination numbers of the  $\text{MoO}_{0.69}\text{S}_{1.52}$  surface to that on the  $\text{MoO}_{0.42}\text{S}_{1.95}$  surface. It is worth noting that after the annealing process, the  $\text{MoO}_x\text{S}_y$  surface with sufficient sulfur led to an increased portion of highly coordinated (4-, 5-, and 6-coordination) local complexes (72.3%), whereas a relatively small portion of high Mo-

coordination numbers (38.4%) was found on the  $\text{MoO}_x\text{S}_y$  surface with sulfur deficiency. These results suggest that sufficient sulfur ingredients are required to form highly crystallized  $\text{MoS}_2$  layers.

Subsequently, three types of local surface complexes were found:  $\text{MoO}_x$ ,  $\text{MoO}_x\text{S}_y$ , and  $\text{MoS}_2$ -like surface complexes, as shown in Figure 6e–g, respectively. The observations of these three clusters were qualitatively consistent with those of Salazar et al.<sup>44</sup> They also reported that after CVD growth, a stable  $\text{MoS}_2$  structure contained a small amount of Mo-oxide and Mo-oxysulfide intermediates, which could render the  $\text{MoS}_2$  layers nonuniform. We further elucidate in this work that these structures can be controlled by altering the duration of sulfur exposure to the  $\text{MoO}_x\text{S}_y$  surface. As such, it can be assumed that a large portion of local  $\text{MoS}_2$ -like clusters and small portions of local  $\text{MoO}_x$  or  $\text{MoO}_x\text{S}_y$  clusters are responsible for high-quality  $\text{MoS}_2$  samples. To confirm this prediction, the percentage of local surface complexes on the  $\text{MoO}_{0.69}\text{S}_{1.52}$  and  $\text{MoO}_{0.42}\text{S}_{1.95}$  surfaces was measured after the annealing process (Table 1).

**Table 1. Comparison of Local Surface Complexes ( $\text{MoO}_x$ ,  $\text{MoO}_x\text{S}_y$ , and  $\text{MoS}_2$ -like Surface Complexes, Indicated in Figure 6e–g) in the Annealed  $\text{MoO}_{0.69}\text{S}_{1.52}$  and  $\text{MoO}_{0.42}\text{S}_{1.95}$  Surface Structures<sup>a</sup>**

annealed surface composition	percentage of local surface compounds		
	$\text{MoO}_x$ cluster (%)	$\text{MoO}_x\text{S}_y$ cluster (%)	$\text{MoS}_2$ -like cluster (%)
$\text{MoO}_{0.69}\text{S}_{1.52}$	1.91	96.35	1.74
$\text{MoO}_{0.42}\text{S}_{1.95}$	0.52	77.78	21.70

<sup>a</sup>Note that the lower oxygen and higher sulfur components in the surface structures lead to a higher portion of local  $\text{MoS}_2$ -like clusters and smaller surface voids, as shown in Figure 6b.

As expected, the  $\text{MoO}_{0.42}\text{S}_{1.95}$  (sulfur-sufficient) surface structures, corresponding to Figure 6b, contained a relatively large fraction of  $\text{MoS}_2$ -like surface complexes (21.70%) and smaller fractions of  $\text{MoO}_x\text{S}_y$  (77.78%) and  $\text{MoO}_x$  (0.52%) surface complexes, when compared to those on the  $\text{MoO}_{0.69}\text{S}_{1.52}$  (sulfur-deficient) surface structure (i.e.,  $\text{MoS}_2$ -like: 1.74%;  $\text{MoO}_x\text{S}_y$ : 96.35%;  $\text{MoO}_x$ : 1.91%). The structure of  $\text{MoS}_2$  monolayer consists of a single sheet of Mo plane sandwiched between two planes of S atoms, thus forming a hexagonal crystal structure. During our simulations,  $\text{MoS}_2$ -like structures in Figure 6g were found to be qualitatively consistent with the local hexagonal structures in  $\text{MoS}_2$  monolayers as each Mo atom in the  $\text{MoS}_2$  structure possesses six neighboring S atoms on it. This can be supported by changes in the number of neighboring S atoms on Mo elements in Figure 6c,d. On the basis of this structural information, the intermediate surface structure, derived by our RMD simulations, could be further converted into local hexagonal  $\text{MoS}_2$  structures, and they are expected to be merged into a single crystalline  $\text{MoS}_2$  layer during the long-time introduction of sulfur precursors, which has been postponed for a future work.

#### 4. CONCLUSIONS

In conclusion, we performed RMD simulations of the direct sulfidation of monolayered  $\text{MoO}_3$  surface using gas-phase  $\text{S}_2$  precursors to investigate atomic-scale reaction processes for CVD synthesis of  $\text{MoS}_2$  layers. Our RMD simulations, validated by our QMD simulations and data from the experimental

literature, revealed the detailed reaction mechanisms and growth kinetics for the direct sulfidation of the  $\text{MoO}_3$  surface as follows: (1) the reduction and sulfidation processes primarily begin from the O-termination sites, forming  $\text{O}_2/\text{SO}$  gas molecules and consequently Mo–S bond; (2) the initial  $\text{MoO}_3$  surface is locally (nonuniformly) reduced and sulfidized, depending on the available reactive sites, like the O-termination and unsaturated Mo sites; and (3) the fraction of S atoms on the  $\text{MoO}_{x,y}\text{S}_y$  surface influences the degree of void formation and Mo-coordination changes, as well as the portion of the local coordination complexes. Owing to the limited length of molecular dynamics trajectories, we were unable to simulate the full dynamics of conversion of  $\text{MoO}_3$  to  $\text{MoS}_2$  structure in this work. Therefore, the initial  $\text{MoO}_3$  surface structures were not completely converted to  $\text{MoS}_2$  stoichiometric structures at the end of our RMD simulations. We plan to perform long-time RMD simulations (e.g.,  $t > 100$  ns) to further clarify the formation of crystalline hexagonal  $\text{MoS}_2$  structures during CVD synthesis of  $\text{MoS}_2$  layers. To implement these long reactive simulations for times that are in  $\sim 100$  ns time regime and beyond, we have developed new time-to-solution algorithms that allow us to distribute our simulations on a much larger number of cores than is possible in conventional domain decomposition algorithms.

Our new chemical insights allow us to further clarify key reaction events during the CVD process, including the role of O-termination in the reduction/sulfidation steps and the origin of experimentally observed discontinuities and nonuniformities on the  $\text{MoO}_{x,y}$  samples.<sup>20,51,52</sup> We believe that our work will help guide scalable CVD techniques for the synthesis of large-scale and defect-free  $\text{MoS}_2$  layers and other layered TMDC materials for future applications.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.jpcc.7b12035](https://doi.org/10.1021/acs.jpcc.7b12035).

Details of QMD methods and simulations schedules; validation of RMD simulations; changes in the thickness of surface structures during the sulfidation process ([PDF](#))

ReaxFF reactive force-field parameters for Mo/O/S elements ([PDF](#))

RMD trajectories of the reduction and sulfidation processes up to 2.0 ns (Movie S1); RMD trajectories of the local void formation on the  $\text{MoO}_{0.69}\text{S}_{1.52}$  surface during the annealing process (Movie S2); RMD trajectories of the local void formation on the  $\text{MoO}_{0.42}\text{S}_{1.95}$  surface during the annealing process (Movie S3) ([ZIP](#))

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was supported as part of the Computational Materials Sciences Program funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Award Number DE-SC00014607. The simulations were performed at the Argonne Leadership Computing Facility under the DOE INCITE program and at the Center for High Performance Computing of the University of Southern California.

## ■ ABBREVIATIONS

TMDC, Transition metal dichalcogenide; RMD, Reactive molecular dynamics; QMD, Quantum molecular dynamics; CVD, Chemical vapor deposition

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