Adsorption Behavior of the Hydroxyl Radical and Its Effects on Monolayer MoS$_2$

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ABSTRACT: Based on first-principles density functional theory calculations, we investigated a modified routine using hydroxyl adsorption that recently demonstrated the controlled growth of MoS$_2$ monolayers. The new growth approach impedes the deposition of a second MoS$_2$ layer; however, the hydroxyl adsorption and its effects have been mostly unexplored. Through this study, we first explored the adsorption behaviors of the hydroxyl radical (OH) on monolayer MoS$_2$ and briefly discussed its effects on the stability and electronic structure. Monolayer MoS$_2$ repels charged OH$^-$, whereas the adsorption of the neutral OH radical is energetically favorable; the corresponding adsorption energies are 0.09 eV and $-1.35$ eV, respectively. The diffusion barrier of the OH radical on MoS$_2$ is 0.52 eV, indicating that the molecule can quickly diffuse. Next, the study demonstrated that for multiple OH adsorptions, a concerted reaction including OH dissociation and H$_2$O formation is more energetically favorable than the adsorption of two OH molecules by 2.50 eV, which in turn results in a mixed adsorption configuration of O and OH. In addition, we revealed that the OH adsorption creates a mid-gap state and facilitates the reconstruction of the MoS$_2$ edge.

INTRODUCTION

Transition-metal dichalcogenides (TMDs) exhibit abundant electronic and optical properties in addition to remarkable mechanical flexibility.1-3 Among TMD members, MoS$_2$ has been the most intensively studied TMD because of its tunable band gap and superior stability. MoS$_2$ has both metallic (1T) and semiconducting (2H) phases.4,5 The electronic properties of semiconducting MoS$_2$ are highly tunable, which makes it ideal for designing electronic and optoelectronic devices.6,7 For example, MoS$_2$ shows a transition from an indirect to a direct band gap when its thickness is reduced down to a single layer.1,8 This property of monolayer MoS$_2$ makes it particularly important because it can take advantage of the direct band gap, which can effectively excite electrons. Moreover, the controllable valley degree of freedom of an electron in monolayer MoS$_2$ can also be useful for manipulating information in data storage devices.5,10 MoS$_2$ layers can be grown on or inserted into van der Waals (vdW) heterolayers to provide desired properties via vdW epitaxial growth,11,12 whereas the controlled growth is highly desirable for accurate fabrication of a defined heterostructure.

Several growth approaches have been employed on various substrates for producing large-area monolayer MoS$_2$.13-15 However, the growth of MoS$_2$ has suffered from high defect densities and small domain sizes primarily because of a nucleation preference at defects on substrates.16-18 Both controlling the number and improving the quality of grown MoS$_2$ layers, therefore, become more challenging. Our previous work proposed a new controlled growth method using OH molecules to grow high-quality, large-area monolayer MoS$_2$ with a low defect density, which could be used to grow MoS$_2$ on arbitrary substrates.18 The presence of OH can enhance the binding between MoS$_2$ and the substrates, which stabilizes the grown MoS$_2$ layer. Moreover, the adsorbed OH molecules can passivate the first MoS$_2$ layer, thereby suppressing the vertical growth of a second MoS$_2$ layer. This facilitates the lateral growth of monolayer MoS$_2$. Previous studies have investigated the adsorption of OH on MoS$_2$ and other 2D materials regarding catalytic applications,19,20 However, the adsorption behaviors of OH and its effects on the properties of monolayer MoS$_2$ are mostly unexplored.

In this study, we used first-principles density functional theory (DFT) calculations to systematically investigate the adsorption behaviors of OH and its effects on monolayer MoS$_2$. Our data first revealed that the adsorption of OH is energetically favorable, with an adsorption energy $E_{\text{ads}}$ of $-1.35$ eV, in contrast to the endothermic adsorption ($E_{\text{ads}} = 0.09$ eV) of charged OH$^-$. Inclusion of an Al$_2$O$_3$ substrate lowers the $E_{\text{ads}}$ of OH by only 0.05 eV but causes the adsorption of OH$^-$ to become exothermic ($E_{\text{ads}} = -0.21$ eV). The adsorbed OH can quickly diffuse on MoS$_2$. More importantly, for multiple OH adsorptions, we predicted a concerted reaction of OH dissociation and H$_2$O formation, which stabilizes the system.
displayed the ground-state adsorption structures for OH⁻ and OH. For the charged OH⁻ ion, adsorption was an endothermic reaction and the adsorption energy $E_{ads}$ was 0.09 eV. Within the Perdew–Burke–Ernzerhof (PBE) scheme (without van der Waals correction), $E_{ads}$ was even higher (0.27 eV), indicating that OH⁻ and monolayer MoS₂ repel in a chemical reaction. The length of the O–H bond and the shortest distance between O and S atoms were 0.98 and 2.53 Å, respectively. The differences in $E_{ads}$ and the O–H bond lengths among different adsorption sites were less than 0.08 eV and 0.01 Å, respectively. On the other hand, the ground-state adsorption site for neutral OH was on top of the S atom. The numbers represent the distance between the O and S atoms.

Next, we investigated the energy profile for the diffusion reaction of the adsorbed OH on monolayer MoS₂ to understand diffusion kinetics. Here, we used the nudged elastic band method with five intermediate images constructed along the reaction pathway. Figure 2 shows the calculated energy profile together with the atomic geometries of the initial, transition, and final states. The minimum-energy diffusion occurs through a path between two neighboring S atoms. In the transition state, OH was located at the halfway point of the reaction pathway, where the distance between the O and S (Mo) atoms is 2.51 (3.77) Å. The transition state was 0.52 eV higher than the initial and final states, yielding an energy barrier of 0.52 eV against the diffusion reaction. This value is lower than or comparable with those of metal atoms on MoS₂. We estimated the diffusion rate ($D$) at 300 K to be approximately $1.9 \times 10^4$ s⁻¹, using an Arrhenius-type equation, $D = A \exp[-E_a/(k_B T)]$, and a typical pre-exponential factor ($A$) of $10^{13}$ Hz, where $k_B$ is the Boltzmann constant and $T$ is the temperature. This suggests that OH molecules quickly diffuse on MoS₂.

Next, we examined the electronic structure of the OH-adsorbed MoS₂. Figure 3a displays the calculated density of states (DOS) of clean MoS₂ and OH-adsorbed MoS₂. Based on the DOS, the band gap of monolayer MoS₂ was estimated to be 1.64 eV, which was consistent with previous DFT calculations. A comparison of the DOS of clean MoS₂ and OH-adsorbed MoS₂ shows that the adsorption of OH creates a mid-gap state within the bandgap of MoS₂. The charge density differences ($\Delta \rho$), defined as $\Delta \rho = \rho(\text{OH/MoS}_2) - \rho(\text{OH}) - \rho(\text{MoS}_2)$, show that, upon OH adsorption, electrons were primarily redistributed at the OH molecule and the adsorption site, forming an O–S bond (Figure 3b). These data demonstrate that the peak near the Fermi level in the DOS arises from the O–S bond.

Next, we investigated the adsorption of another OH molecule near the first adsorbed molecule. Here, we considered two possible scenarios: (1) the adsorption of a second OH molecule on a different adsorption site, as shown in Figure 4a, and (2) a concerted reaction of OH dissociation and H₂O formation, as shown in Figure 4b. For scenario 1, the adsorption of the second OH was also energetically favorable; the $E_{ads}$ of the second OH is ~2.05 eV, which is even higher than that of the first $E_{ads}$. The O–S bond lengths for the first and the second OH were 1.65 and 2.02 Å, respectively, which are 0.15 Å shorter and 0.22 Å longer than that of the originally adsorbed OH molecule. These results indicate that two significant. This reaction results in a mixed adsorption configuration of O and OH on MoS₂, a valuable finding for understanding the role of OH adsorption on the growth of MoS₂. Our detailed calculations further demonstrated that the OH adsorption creates a mid-gap state and makes the reconstruction of the MoS₂ zigzag edge more energetically favorable. These findings not only deepen our understanding of the adsorption behavior of OH on MoS₂ but also may prove instrumental in further improving the growth of MoS₂.

### RESULTS AND DISCUSSION

We first determined the favorable atomic configurations of OH⁻ and OH adsorbed on monolayer MoS₂. Here, we considered several possible adsorption sites, and Figure 1 displays the ground-state adsorption structures for OH⁻ and OH. For the charged OH⁻ ion, adsorption was an endothermic reaction and the adsorption energy $E_{ads}$ was 0.09 eV. Within the Perdew–Burke–Ernzerhof (PBE) scheme (without van der Waals correction), $E_{ads}$ was even higher (0.27 eV), indicating that OH⁻ and monolayer MoS₂ repel in a chemical reaction. The length of the O–H bond and the shortest distance between O and S atoms were 0.98 and 2.53 Å, respectively. The differences in $E_{ads}$ and the O–H bond lengths among different adsorption sites were less than 0.08 eV and 0.01 Å, respectively. On the other hand, the ground-state adsorption site for neutral OH was on top of the S atom (Figure 1b) and the corresponding $E_{ads}$ was ~1.35 eV, which was in good agreement with a previous DFT study. These results show that the adsorption of neutral OH is spontaneous and therefore energetically favorable. Consequently, we focused on the adsorption of neutral OH rather than charged OH⁻ hereafter. $E_{ads}$ without the van der Waals correction was also slightly higher (~1.16 eV), showing that the adsorbed OH molecule was chemically bound to MoS₂. The lengths of the O–H and O–S bonds were 0.98 and 1.80 Å, respectively. We considered different orientations of OH molecules adsorbed on the S site. $E_{ads}$ for the different OH orientations was slightly higher (~0.02 eV) than that of the ground state, showing that the effects of molecular orientation on $E_{ads}$ are negligible.

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adsorbed OH molecules are attractive. The resulting configuration of the second scenario included the adsorption of atomic O on top of the S site, forming a hydrogen bond with an H$_2$O molecule. The distances between the O and H (S) atoms were 1.93 (1.49) Å. The corresponding $E_{ads}$ was $-4.63$ eV, which is lower than that of scenario 1 by 2.58 eV. The concerted reaction of scenario 2 can be initiated from the resulting state of scenario 1, and our transition state calculations reveal that the process is a barrier-less reaction (Figure S2). This indicates that two neighboring adsorbed OH can spontaneously initiate the concerted reaction, while two separate OH should overcome the diffusion barrier. Thus, we can conclude that the concerted reaction is energetically favorable on MoS$_2$.

Many 2D materials have been grown on substrates, and the substrate can affect the chemistry of the adsorbate. To examine the effects of a substrate, we investigated the adsorption of OH (OH$^-$) on monolayer MoS$_2$ deposited on a sapphire [$\alpha$-Al$_2$O$_3$(001)] substrate, considering the fact that monolayer MoS$_2$ growth was successfully achieved on this substrate in our previous experiment. For the adsorption of OH$^-$, $E_{ads}$ was $-0.21$ eV, which indicates that the adsorption was exothermic, whereas the length of the OH bond was unchanged, the shortest distance between O and S atoms was 2.28 Å, which is shorter than the value (2.53 Å) without the substrate. On the other hand, $E_{ads}$, O–H, and O–S bond lengths for a neutral OH were $-1.40$ eV, 0.98, and 1.80 Å, respectively, which are almost the same compared to those without the substrate. For both charged and neutral cases, changes in the structure of the MoS$_2$ layer are negligible. Our Bader charge analysis reveals that the total number of transferred charges from the Al$_2$O$_3$ substrate to the OH-adsorbed MoS$_2$ is $\sim 0.2$ e per unit cell. These charges are mostly transferred to the adsorbed OH (OH$^-$), which also modifies the electronic structure (see DOS in Figure S1). Overall, the adsorption on MoS$_2$/$\alpha$-Al$_2$O$_3$(001) is energetically favorable for both OH$^-$ and OH.

To further investigate the high-coverage adsorption of OH, we performed ab initio molecular dynamics (AIMD) simulations at 300 K and included the sapphire substrate. Figure S displays the final structures after 0.1 ps simulations together with the energy profiles of the OH molecules on monolayer MoS$_2$. During the AIMD simulations, monolayer MoS$_2$ remained nearly intact with slight changes in the Mo–S bond lengths (at most 0.18 Å), indicating that the MoS$_2$ layer was stable even over multiple OH adsorptions. Similar to the case with two OH molecules adsorbing, H$_2$O molecules were formed and the remaining O atoms were adsorbed on S atoms, which in turn created the O–S bonds. The calculated energy profile shows that these concerted reactions significantly lowered the total energies of the systems. A previous DFT study suggested that H$_2$O also prefers chemisorption and...
dissociation into OH and H on MoS$_2$. This fact implies that the H$_2$O molecules formed by the concerted reaction can also undergo separation into OH and H again, eventually leaving a mixed adsorption configuration of OH and O.

The reconstruction of the TMD edges plays a crucial role in the growth of TMD layers, and the adsorption of OH may affect the energies of such a reconstruction. To examine this possibility for MoS$_2$, we compared the relative energies of reconstructed and unreconstructed MoS$_2$ edges in the presence of OH. It is notable that the zigzag edge of MoSe$_2$, which is Mo-terminated, showed a $2 \times 1$ reconstruction that substantially lowered the energy.

Similarly, the $2 \times 1$ reconstruction of the MoS$_2$ zigzag edge (Figure 6) reduced the adsorption energy ranging from 0.09 to 1.49 eV, respectively. This indicates that the edge is an active site for both OH$^{-}$ and O. After the OH adsorption, the $2 \times 1$ reconstructed edge is much lower in energy than the unreconstructed edge, by 1.35 eV per supercell. This indicates that the edge reconstruction is energetically favorable in the presence of OH. For comparison, the effects of O adsorption on the energies of the MoS$_2$ edge were also investigated. As an O atom adsorbed at the edge, the reconstructed edge was 0.31 eV lower in energy than the unreconstructed edge, which was nearly the same as the clean edge. Overall, these data imply that the OH (OH$^{-}$) adsorption facilitates the $2 \times 1$ reconstruction of the zigzag edge.

**CONCLUSIONS**

In conclusion, we have investigated the adsorption of OH$^{-}$ and OH on monolayer MoS$_2$. The adsorption of OH$^{-}$ is weak, with an adsorption energy ranging from 0.09 to $-0.21$ eV, while that of OH is much stronger, with the adsorption energy of $-1.35$ eV. We further revealed that the concerted reaction, involving OH dissociation and H$_2$O formation, dramatically lowers the total energy and, therefore, a mixed adsorption configuration of O and OH is energetically preferred. This is also confirmed by our molecular dynamics simulations. Finally, we demonstrated that the adsorption of OH could modify the energies of MoS$_2$ edge reconstructions, an essential factor that can affect the properties of MoS$_2$. These central findings may prove instrumental in further improving the growth of MoS$_2$ and, therefore, are expected to stimulate future studies in this research field. In particular, the delicate chemical reactions of OH on MoS$_2$ and its effects on the growth of MoS$_2$ are still an open question.

**COMPUTATIONAL METHODS**

The first-principles DFT calculations were performed using the Vienna Ab-initio Simulation Package (VASP). The projector-augmented wave method and the PBE exchange–correlation functional were used for the calculations. A semiclasical dispersion correction scheme (DFT-D3) was employed to include the effects of long-range vdW interactions, within which the optimized lattice parameters for bulk MoS$_2$ are $a = b = 3.15$ Å and $c = 17.95$ Å. An MoS$_2$ monolayer grown on a sapphire substrate was simulated by a supercell of 12-layer $p(2 \times 2)$ α-Al$_2$O$_3$(001) and $a(3 \times 3)$ MoS$_2$ monolayer. MoS$_2$ nanoribbons were simulated using a periodic supercell with a ribbon width of approximately 20 Å and a vacuum space of approximately 20 Å. All the simulated structures included a vacuum space of approximately 20 Å in the out-of-plane direction. During structural optimization, the charged systems were simulated by using homogeneous background charges, and the cutoff energy used for the plane-wave basis set was 500 eV. A canonical ensemble was adopted for the AIMD simulation using the algorithm of Nosé, and the time interval for the ionic motion was 0.1 fs. For neutral systems, the adsorption energy ($E_{\text{ads}}$) was defined as

$$E_{\text{ads}} = E_{\text{tot}}(\text{adsorbate/MoS}_2) - E_{\text{tot}}(\text{MoS}_2) - E_{\text{tot}}(\text{adsorbate})$$

where $E_{\text{tot}}(\text{MoS}_2)$, $E_{\text{tot}}(\text{adsorbate})$, and $E_{\text{tot}}(\text{adsorbate/MoS}_2)$ represent the total energy for the MoS$_2$, adsorbate, and OH (O or H$_2$O)-adsorbed MoS$_2$, respectively. The charged systems were simulated by using homogeneous background charges, and $E_{\text{ads}}$ was calculated in the same way as described in a previous DFT study.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03837.

Projected densities of states of OH-adsorbed MoS$_2$ and calculated energy profile for the concerted reaction (PDF)

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**Notes**

The authors declare no competing financial interest.

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