Adsorption of SF$_6$ Decomposed Products over ZnO(1010): Effects of O and Zn Vacancies

Dachang Chen,† Xiaoxing Zhang,*‡† Ju Tang, Hao Cui,§ Shoemiao Pi,† and Zhaolun Cui‡

†School of Electrical Engineering and Automation, Wuhan University, Wuhan 430072, China
‡State Key Laboratory of Power Transmission Equipment & System Security and New Technology, Chongqing University, Chongqing 400044, China

Supporting Information

ABSTRACT: We carried out a density functional theory study to investigate the adsorption behavior of four kinds of SF$_6$ decomposed products over the ZnO(1010) surface. The effects of O and Zn vacancies on the surface were also considered. For perfect ZnO(1010) surface, the adsorption of SO$_3$ and H$_2$S exhibits stronger chemical interactions compared to the adsorption of SOF$_2$ and SO$_2$F$_2$. For SO$_2$ and H$_2$S adsorption, there may exist new chemical bond formation between the molecule and the surface and the H$_2$S molecule experiences one H–S broken bond. The introduction of O vacancy cannot obviously enhance the chemical interactions between these four molecules and the surface. However, the Zn vacancy on the surface can significantly elevate the chemical interactions between SO$_2$/H$_2$S and the surface. The two-coordinated O atom (O$_{2c}$) on the surface plays an important role. For SO$_2$ and H$_2$S adsorption, the S atom in SO$_2$ or H$_2$S tends to bond to the O$_{2c}$ atom, bringing much larger adsorption energy compared to the adsorption over the perfect ZnO(1010) surface. This work can provide a basis for surface modification of ZnO in applications to detecting SF$_6$ decomposed products by theoretical evaluation.

1. INTRODUCTION

Semiconductor-type metal oxide nanomaterials have unique chemical and physical properties, including high specific surface area, high surface activity, and better optical properties. These excellent properties make them promising candidates in fields of catalysts, energy storage and energy conversion, gas sensor and biosensor, electrical and optical devices, and antibacterial technology. Typically, because ZnO has an approximate band gap of about 3.7 eV with exciting binding energy of about 60 meV, is low cost, and possesses chemical stability, excellent optical properties, and high activity to some typical gases, it has been widely used as gas-sensing materials. ZnO exhibits n-type semiconductor properties if no other impurity atoms are doped due to the inevitable oxygen vacancy produced during the synthetic process. Also, the introduction of highly active sites by impurity atoms can significantly promote the gas-sensing properties of some typical gases. The mechanism of ZnO based gas sensor is the changes of the conductivity if ZnO is exposed to different types of detected gases and different concentrations. After obtaining the conductivity of the sensing materials, the type and concentration of the detected gases can be evaluated. On the basis of the results of many scholars, it was found that ZnO has unique sensing properties to H$_2$S, reaching 1 ppb concentration of the detection limit. The high response to H$_2$S will make ZnO promising gas-sensing materials for hazardous gas detection and have potential value in protecting human health in some areas. The mechanism of several metal oxide gas-sensing materials has also been widely studied qualitatively, including SnO$_2$, ZnO, WO$_3$, In$_2$O$_3$, etc. The sensing properties mainly depend on the adsorption and dissociation of O$_2$ on the surface. The oxygen species can exist on the surface with multiple categories, including O$_{2c}$, O$_{2c}$, O$^-$, O$_2^-$, etc. The proportion of these species is determined by the ambient temperature, and the sensing properties rely highly on the settled temperature and the oxidation process of the detected gas molecule. However, these kinds of explanation could not be used to evaluate the adsorption process of the detected gas molecules before oxidation. As a result, theoretical evaluation by the first-principle method has been extensively adopted to assess the adsorption as well as gas-sensing properties of some popular gas-sensing materials, such as metal oxide, carbon-based materials (graphene and carbon nanotubes), transitional metal dichalcogenides, etc. To better understand the sensing mechanism of ZnO-based materials, theoretical method using the first-principle-based method is an effective and accurate way.

Received: October 25, 2018
Accepted: December 20, 2018
Published: December 28, 2018
ZnO exhibits its chemically stable hexagonal wurtzite structure. Every Zn is bonded to four ambient O atoms with a tetrahedral form. The valence state of Zn is Zn$^{2+}$, whereas that of O is O$^{2-}$. Diebold et al. systematically investigated the surfaces and interfaces of ZnO using high-resolution scanning tunneling microscopy. ZnO mainly has five typical low-index surfaces, including (1010), (1120), (0001), (0001), and (1121). The (1010) and (1120) surfaces were proved to be nonpolarized prism surfaces, whereas the (0001) and (0001) surfaces are c-oriented polarized and the (1121) surface is the pyramid face. Different surfaces have different chemical activities, and several studies have achieved gas adsorption and surface reaction on different ZnO surfaces by the first-principles method.

Fink et al. studied the adsorption behaviors of H$_2$, CO, and CO$_2$ over the (0001) surface considering the influence of oxygen vacancies. The (0001) surface can be stabilized by OH groups, and CO$_2$ prefers to dissociate to CO+O over the O vacancy, which can have potential application in CO$_2$ conversion reaction. Prades et al. made a comprehensive study of the gas-sensing properties of nonpolar (1010) and (1120) toward SO$_2$ and NO$_2$ by an ab initio study. NO$_2$ is easy to be adsorbed onto Zn, and two surfaces are easy to be poisoned by SO$_2$. The adsorption and dissociation processes of H$_2$S on the (1010) surface were investigated by Wang et al., and the dissociation process is easy to happen and the final product S atom can be stably adsorbed on the O vacancy. The CO$_2$ catalytic fixation process on different surfaces was studied by Tang et al., and the binding strength is the inverse of the stability of the chosen surface. Not only that, the (1010) or (0001) surface can be an effective medium for urea adsorption and decomposition, methanol reaction or other organic reaction, and small-molecule adsorption. More than the specified crystal indices, the metal oxide nanoparticles were also used to evaluate the gas-sensing properties. By doping N atom on the surface, the cohesive energy between the O$_3$/NO$_2$ molecule and the ZnO nanoparticle can be significantly increased. Not only for ZnO, the method of using nanoclusters in place of infinite specific surface structures has also been applied to other metal oxides such as TiO$_2$ and for heterojunction structures. The doping of N atom on TiO$_2$ nanoparticles can obviously improve the gas-sensing properties to NO$_2$, and the synthesis of heterojunction structures with MoS$_2$ and WS$_2$ can have high response to some specific gases such as SO$_x$, NO$_x$, or ozone. With so many theoretical studies of surface adsorption and surface interaction of typical metal oxide gas sensors, they have future potential application in many fields such as detecting SF$_6$ decomposed products.

In the field of electrical engineering, detecting SF$_6$ by application of gas-sensing materials has become an effective and low-cost way to obtain the operation status of equipment. To detect typical SF$_6$ decompositions, including SO$_2$, SOF$_2$, SO$_2$F$_{2}$, and H$_2$S, metal oxide and its composed material-based gas sensor have drawn more and more attention, such as SnO$_2$, ZnO, TiO$_2$, etc. However, the mechanism of gas-sensing properties of ZnO to SF$_6$ decomposition products has seldom been systematically studied quantitatively by theoretical approach. Although many studies have discussed the sensing properties of ZnO(0001) to several kinds of gases, we chose ZnO(1010) in this study for two typical reasons. First, the stability level of ZnO(1010) is obviously higher than that of other surfaces including ZnO(1120) and ZnO(0001) surfaces because of the lower surface formation energy. It demonstrated that the ZnO(1010) surface can be more easily obtained in experiment. Second, most of the nanowire ZnO gas sensors expose lateral nonpolar surfaces such as ZnO(1010) and ZnO(1120). Comparing the formation energies of ZnO(1010) and ZnO(1120), we chose the lower one to discuss the adsorption and gas-sensing properties in this work to investigate the chemical performance of ZnO surface to SF$_6$ decomposed products. We considered the effect of both O vacancy and Zn vacancy on the surface. First, the adsorption structures of four types of SF$_6$ decomposed products on the
Table 1. Surface Vacancy of ZnO(10\(\overline{1}0\))

| structure                   | \(E_{\text{form}}\) (eV) (considering the DFT-D2 method) | \(E_{\text{form}}\) (eV) (without the DFT-D2 method) |
|-----------------------------|--------------------------------------------------------|-----------------------------------------------------|
| ZnO with one O surface vacancy | +0.39 (Zn rich) +2.91 (O rich)                          | +0.29 (Zn rich) +2.73 (O rich)                      |
| ZnO with one Zn surface vacancy | +3.70 (Zn rich) +1.17 (O rich)                          | +3.46 (Zn rich) +1.05 (O rich)                      |

Figure 2. HOMO and LUMO of (a) (HOMO) and (d) (LUMO) perfect ZnO(10\(\overline{1}0\)) surfaces; (b) (HOMO) and (e) (LUMO) oxygen vacancy ZnO(10\(\overline{1}0\)) surfaces; and (c) (HOMO) and (f) (LUMO) zinc vacancy ZnO(10\(\overline{1}0\)) surfaces (the isosurface is 0.01 e Å\(^{-3}\)).

2. RESULTS AND DISCUSSION

2.1. Structure of ZnO(10\(\overline{1}0\)) Surface and the Formation of O and Zn Vacancies. As is mentioned in Section 2, the top layer of ZnO(10\(\overline{1}0\)) surface contains Zn\(_{3c}\), Zn\(_{4c}\), O\(_{3c}\), and O\(_{4c}\). After full geometric optimization (the two bottom layers were constrained), it can be seen in Figure 1a that the O\(_{3c}\) atoms are more protuberant compared to the Zn\(_{3c}\) atoms. When removing one O\(_{3c}\) atom out of the ZnO(10\(\overline{1}0\)) surface, one Zn\(_{3c}\) turns to two-coordinated Zn atom (Zn\(_{2c}\)) and two Zn\(_{4c}\) change to three-coordinated Zn atoms (Zn\(_{3c}\)), as shown in Figure 1b. The Zn\(_{2c}\) atom moves right to the O vacancy, and the distance between two new-formed Zn\(_{3c}\) atoms becomes smaller than the original two Zn\(_{4c}\) atoms. In summary, with the formation of one O vacancy on the ZnO(10\(\overline{1}0\)) surface, three adjacent Zn atoms are closer to each other. With respect to the formation energy of one O vacancy under different circumstances, the results are listed in Table 1. It should be noted that when considering the van der Waals (vdW) force calculated using the DFT-D2 method, all the structures used in eq 1 include the DFT-D2 correction. But without considering the vdW force, all the structures are not corrected by the DFT-D2 method. The formation of these two vacancy defects is both an endothermic process. Under a Zn-rich environment, the surface O vacancy is easy to appear. The formation energy is only +0.39 eV considering the DFT-D2 method and +0.29 eV without the DFT-D2 method. But under the O-rich environment, the O vacancy is much more difficult to form compared to the formation under Zn-rich circumstances. The formation energy elevates to +2.91 eV (including vdW force) and +2.73 eV (without vdW force). As to the formation of Zn vacancy, if the synthesis condition is Zn rich, the formation of Zn vacancy on the surface is very difficult. It exhibits +3.70 eV (considering DFT-D2) and +3.46 eV (without DFT-D2) for a Zn-rich environment, and if the environment is O rich, the formation of Zn vacancy on the surface is much easier, only +1.17 and +1.05 eV if considering DFT-D2 and not considering it, respectively. By comparing the formation energies for two kinds of vacancy defect under different environments, it can be seen that the formation of surface O vacancy under a Zn-rich environment is the easiest. Moreover, the formation of Zn vacancy is also relatively easier under an O-rich environment. This phenomenon conforms to the gas-sensing experiments of ZnO that the experimental synthesis of ZnO often contains more O vacancy compared to Zn vacancy. However, on the basis of the calculation of formation energy, because the effect of the synthesis environment is much bigger than the type of surface vacancy (the formation energy for one kind of vacancy has huge difference under different environments), the formation of vacancy can be controlled by the synthesis environment. Although the formation energy may have some deviation affected by the vdW force, the results also can provide general guidance for synthesizing ZnO gas-sensing materials with different vacancy defects.

To assess the active site of perfect and defective ZnO(10\(\overline{1}0\)) surfaces, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) isosurfaces were calculated, as shown in Figure 2. The morphology of HOMO---LUMO has great influence on the adsorption properties. The HOMO of the perfect ZnO(10\(\overline{1}0\)) surface mainly locates near the O\(_{3c}\) atoms, whereas the LUMO is mainly around both the O\(_{3c}\) atoms and the Zn\(_{3c}\) atoms. As a result, the active sites of the ZnO(10\(\overline{1}0\)) surface are both the O\(_{3c}\) atoms and the Zn\(_{3c}\) atoms. For ZnO(10\(\overline{1}0\)) surface containing one O vacancy, it can be seen that beside the same active sites as the perfect ZnO(10\(\overline{1}0\)) surface, the LUMO appears around the Zn\(_{3c}\) atom. Also, the O vacancy can weaken the activity of other O\(_{3c}\) atoms because of the smaller isosurface. As to the Zn vacancy, the HOMO---LUMO nearly
SOF₂, there exists totally 21 bonding molecular orbitals (42 electrons). SO₂ totally has 32 electrons, forming 16 bonding orbitals. The molecular orbitals, as shown in Figure 8g. There are four separated molecular orbitals in the range from −13 to 0 eV. By comparing the DOS of the isolated molecule and adsorbed molecule, the chemical interactions can be evaluated to some extent. When carrying out the adsorption process, the initial adsorption position and adsorption direction were first set. The adsorption position for the gas molecule over the perfect ZnO(1010) surface is mainly two sites (the top of Zn₃c (T₂Zn) and the top of O₃c (T₀)). The different directions of the adsorbed gas molecule are also considered. There are three directions for SO₂ and H₂S (parallel to the surface and vertical to the surface with S downward and S upward) and two directions for SOF₂ (S upward and S downward) and SO₂F₂ (one O upward and one F upward). After obtaining several adsorption structures with the local minimum total energy, only the adsorption structures with the maximum adsorption energy for every gas molecule were considered to further discuss the structure parameters, adsorption parameters, electronic properties, and chemical interactions. The DFT-D2 method was considered in all adsorption structures. All the obtained adsorption structures with the local minimum total energy are shown in Figure S1 with adsorption energy comparison.

The adsorption structures with the maximum adsorption energy for the gas molecule over the perfect ZnO(1010) surface are shown in Figure 3. The SO₂ prefers to be adsorbed on the T₀ site with the molecule nearly parallel to the surface. The distance between the gas molecule is 1.96 Å (S–O₃c), much larger than the bond length of S–O in the isolated SO₂ molecule (about 1.48 Å). The interaction between the S (in SO₂) and O₃c is weaker than the S–O bonding interaction in SO₂. For SOF₂, the adsorption site is the same as the adsorption of SO₂ (T₀ site), but the distance is much longer (2.29 Å between S and O₃c). As to the adsorption of SO₂F₂, the adsorption distance is even longer. The distance between the S atom (in SO₂F₂) and the O₃c atom reaches 2.81 Å, much larger than that of the adsorption of SO₂ and SOF₂. The adsorption of the above three molecules does not show much morphology change of the gas molecule, and there is no obvious bond breakage in the gas molecule. However, the adsorption of H₂S has some differences. One H atom in H₂S moves very close to one O₃c atom, and one H–S bond is significantly longer, from about 1.36 to 2.03 Å. The adsorption distance is much smaller than the above three gas molecules, only 1.03 Å between the H atom and the O₃c atom. This phenomenon in this study is in accordance with the former report by other scholars. The bond broken process does not show obvious energy barrier, and the adsorption process of H₂S is a spontaneous process. The adsorption parameters of these four gas molecules adsorbed over the perfect ZnO(1010) surface are shown in Table 2. It can be seen that the adsorption of H₂S exhibits the largest adsorption energy, reaching −1.64 eV. This phenomenon may be attributed to the released energy from the possible formation of the new H–O bond. The adsorption energy for SO₂ is smaller compared to H₂S but larger than that of SOF₂ and SO₂F₂. We estimated that the strength of the chemical interaction between the surface and the molecule may be partially relevant to the adsorption distance, so the shorter distance may bring larger adsorption energy. As to the electron transfer, four molecules all accept...
electrons, and the value of electron transfer for SO₂ is the largest. We estimate that although H₂S shows the largest adsorption energy and new bond formation, the formation bond may not bring much electron transfer. However, for SOF₂ and SO₂F₂, the distance is much longer and the interactions are much weaker, so the adsorption does not bring much electron transfer.

The CDD and ELF configurations are also discussed, as shown in Figure 4. There exists a charge depletion region between the O₃c and the S atom but an obvious charge accumulation region above S and around O atoms in SO₂. A large charge depletion region can also be found around the O₃c atom. It can be seen that the electron accumulation region mainly exists around SO₂, whereas electron depletion mainly happens around the O₃c atom, resulting in the electron acceptor role of the SO₂ molecule. For SOF₂ and SO₂F₂, there exists a small accumulation region between the S atom and the O₃c atom. However, the accumulation and depletion mainly appear around the molecule, indicating that although the adsorption does not bring obvious electron transfer between the molecule and the surface, it exactly changes the electron distribution and molecular orbitals of the molecule itself. For H₂S adsorption, large accumulation appears around the S atom and the depletion region is around the O₃c atom, reflecting the obvious electron-accepting behavior of the S atom in H₂S. As to the ELF configurations in Figure 4e–h, there exists a yellow region between the O₃c and the S atom, and the value of the yellow region is about 0.5–0.6. This phenomenon demonstrates that electron pairs may exist between these two atoms, resulting in a possible new-formed chemical bond between the SO₂ and the surface. However, for SOF₂ and SO₂F₂, a green or blue region occurs between the adsorbed molecule and the surface, indicating much lower possible new bond formation compared to the adsorption of SO₂. For H₂S adsorption, the H atom moves to the strong electron localization region of the O₃c atom, indicating strong interactions between the H atom and the O₃c atom. In summary, the interactions between the surface and SO₂/H₂S are much stronger than the interactions between the surface and SOF₂/SO₂F₂. To discuss the influence on the molecular orbitals by adsorption, DOS analysis was also carried out.

The molecular orbitals of SO₂ exhibit new hybridization and may form new orbitals among the previous 11th–16th orbitals, as seen in Figure 9a, demonstrating significant redistribution of the electron structure of the SO₂ molecule. Moreover, in Figure 9b, obvious hybridization of S 3s, S 3p, O 2s, and O 2p orbitals near −10 eV and S 3p and O 2p orbitals near −5, +3 eV can be found, indicating apparent chemical interactions between the S and the O₃c atom. As to the adsorbed SOF₂ molecule, the redistribution of the 16th–21st orbitals can be found. This phenomenon is in accordance with the electron accumulation and depletion regions in the SOF₂ molecule itself. The hybridization of S 3p and O 2p orbitals near −8, +3 eV can also be found, but the degree is weaker than that of the adsorption of SO₂. In Figure 9e, the height and the width of the 22nd–25th peaks experience obvious change, but these peaks are still detached with very little hybridization.

| gas molecule | $E_a$ (eV) | $Q_t$ (e) | $D$ (Å) |
|--------------|-----------|-----------|---------|
| SO₂          | −1.27     | −0.19     | 1.96 (S–O₃c) |
| SOF₂         | −0.86     | −0.05     | 2.29 (S–O₃c) |
| SO₂F₂        | −0.57     | −0.04     | 2.81 (F–O₃c) |
| H₂S          | −1.64     | −0.10     | 1.03 (H–O₃c) |

Figure 4. (a)–(d) CDD configurations (the isosurface is 0.01 e Å⁻³) and (e)–(h) ELF configurations of SF₆ decomposed products adsorbed over the perfect ZnO(1010) surface.
Moreover, a little hybridization of S 3p and O 2p orbitals is near −7, +2.5 eV. For H₂S adsorption, because the H₂S molecule loses its former molecular structure, the 7th−9th orbitals have tremendous changes with many new-formed orbitals, and significant hybridization of H 1s, O 2s, and O 2p orbitals happens near −8 eV. On the basis of the above analysis, for different gas adsorptions, the adsorption brings different degrees of redistribution of molecular orbitals to the adsorbed gas molecule and different orbital hybridizations between the molecule and the O₃c atom. One thing that should be noted is that the DOS configurations of the gas molecule often exhibit left shift, and this phenomenon is even more obvious for SO₂, SOF₂, and SO₂F₂. The reason is that the Fermi level in the Dmol³ package is defined as the highest occupied molecular orbital (HOMO) for the isolated gas molecule and the highest valence band for periodic structure. The left shift can be attributed to the different energy value of the HOMO of the molecule and the valence band of the ZnO surface. The energy value of the HOMO of the gas molecule (especially for SO₂, SOF₂, and SO₂F₂) is lower than that of the valence band of the ZnO surface. After the adsorption, the Fermi level is defined as the highest valence band of the new adsorption structure, which is very different from the HOMO of the isolated molecule. In brief, the absolute energy value of the "0 eV" of the isolated gas molecule and the adsorbed gas molecule is different, resulting in the visual left shift.

### 2.3. SF₆ Decomposed Products Adsorbed on the ZnO(1010) Surface with O Vacancy

In this section, we consider the effect of surface O vacancy on the adsorption of SF₆ decomposition products. The initial adsorption directions for the gas molecule were set the same as the adsorption over the perfect ZnO(1010) surface. The initial adsorption sites were set as only the top of the vacancy site (TV) to compare the difference with the adsorption on the perfect ZnO(1010) surface. All the adsorption structures with the local minimum total energy are shown in Figure S2. As is mentioned above, the adsorption structures with the maximum adsorption energy of every molecule were chosen for detailed discussion (as listed in Table 3). For SO₂ adsorption, it can be seen in Figure 5a and electron transfer, the introduction of O vacancy does not elevate the adsorption energy for all gas molecules. On the contrary, the adsorption energies for SOF₂ and SO₂F₂ decrease a little. As a result, the surface O vacancy does not obviously enhance the interactions between the surface and the SF₆ decompositions. But the electron transfer is a little larger than the adsorption on the perfect surface for SO₂, which may bring better response.

On comparing the CDD and ELF configurations for SO₂, SOF₂, and SO₂F₂ adsorptions on the perfect surface and the O vacancy surface in Figures 4 and 6, they show nearly the same configuration. As to the DOS configurations of molecular orbitals and atomic orbitals in Figure 10, the morphology of the adsorbed molecules and the hybridization of the atomic orbitals are also nearly the same, so we do not repeatedly discuss them again. In summary, the introduction of O vacancy does not obviously enhance the interactions between the surface and the SF₆ decomposed molecules. Only a little larger electron transfer can be found.

### 2.4. SF₆ Decomposed Products Adsorbed on the ZnO(1010) Surface with Zn Vacancy

By introducing one Zn vacancy on the surface, one O₃c atom changes to O₂c atom and two O₄c atoms become O₃c atoms. After full geometric optimization, the O₂c atom is out of its initial position. It moves away from the vacancy, as shown in Figure 1c. The initial adsorption distances of the gas molecule are the same as mentioned in Sections 2.2 and 2.3. The adsorption sites are set as the top of the vacancy site (TV) and the top of the O₂c atom (TO). Moreover, the final adsorption structures are chosen with the minimum total energy (maximum adsorption energy), as shown in Figure 7 and Table 4. Other adsorption structures are shown in Figure S3.

The SO₂ is prone to be adsorbed over the TO site with smaller adsorption distance (1.63 Å) compared to the adsorption on the perfect and O vacancy surfaces. More important, the adsorption energy is much larger than the adsorption on other surfaces. Thus, the SO₂ molecule has larger chemical interactions with the O₂c atom compared to the O₃c atom. The electron transfer exhibits little change compared to the adsorption on the perfect surface. As to the adsorption of SOF₂ and SO₂F₂, both of them are not likely to be adsorbed on the TO site; instead, the adsorption on the TV site brings larger adsorption energies for SOF₂ and SO₂F₂—it locates nearly right above one O₃c atom. Compared to the adsorption energy and electron transfer for SOF₂ and SO₂F₂ adsorption, it can be seen that the Zn vacancy also cannot lead to the obvious elevation of the adsorption energy, only bringing small increases of electron transfer for SOF₂ adsorption. However, the Zn vacancy can bring significant different phenomenon to H₂S adsorption. In Figure 7d, one H–S bond is possibly broken with much larger H–S distance (2.38 Å). The S atom in H₂S also moves close to the O₂c atom. Like the adsorption of H₂S on the perfect surface, the adsorption on the Zn vacancy surface does not show obvious energy barrier and exhibits spontaneous H–S bond breakage with exothermic process. The adsorption of H₂S exhibits a much larger adsorption energy compared to the adsorption over the perfect surface (−2.98 eV compared to −1.64 eV). This significant elevation of adsorption energy is attributed not only to the broken bond of H–S, but also to the chemical interactions between the S atom in H₂S and the O₂c atom. The CDD and ELF configurations of the gas molecule adsorbed on the Zn vacancy surface are shown in Figure 8. There exists obvious

| gas molecule | E_f (eV) | Q_e (e) | D (Å) |
|--------------|---------|---------|-------|
| SO₂         | −1.29   | −0.26   | 1.72 (S–O₃c) |
| SOF₂        | −0.81   | −0.08   | 2.26 (S–O₃c) |
| SO₂F₂       | −0.53   | −0.03   | 2.83 (F–O₃c) |
| H₂S         | −1.65   | −0.12   | 1.02 (H–O₃c) |
charge depletion between the S atom and the O$_{2c}$ atom, whereas charge accumulation happens around two O atoms in SO$_2$ from the ELF configuration of SO$_2$ adsorption, an apparent yellow region can be found between the S atom and the O$_{2c}$ atom, indicating possible new bond formation. For SOF$_2$, the depletion region mainly locates below the S atom and the accumulation is mainly around other atoms in the molecule, demonstrating that the electron transfer between the molecule and the surface is relatively weaker, but the adsorption process brings intramolecular electron transfer in SOF$_2$ like the adsorption on the perfect surface. In Figure 8c, the charge accumulation region is mainly between the SOF$_2$ molecule and the surface. Figure 8f,g shows an obvious blue region between SOF$_2$ and O$_{3c}$ and between SO$_2$F$_2$ and the surface, indicating little possibility of bond formation for SOF$_2$ and SO$_2$F$_2$ adsorption over the Zn vacancy surface. For H$_2$S adsorption, the CDD configuration exhibits apparent charge depletion around the new-formed O–H bond with charge accumulation around the S atom. The ELF configuration shows that there exists a yellow region between the S atom and
the O$_{\text{2c}}$ atom, indicating a possible new-formed S–O chemical bond. To assess the chemical interactions, the DOS as well as the molecular orbitals are analyzed and compared with the adsorption on the perfect surface (Figure 9) and on the surface with one O vacancy (Figure 10).

The DOS configurations are all shown in Figure 11. The 17th antibonding orbital of SO$_2$ partially moves near the Fermi level, and the 11th–16th bonding orbitals also experience significant hybridization and new bond formation. As to the chemical interactions between the S atom and the O$_{\text{2c}}$ atom in

| gas molecule | $E_a$ (eV) | $Q_t$ (e) | $D$ (Å)  |
|--------------|-----------|----------|--------|
| SO$_2$       | −1.72     | −0.15    | 1.63 (S–O$_{\text{2c}}$) |
| SOF$_2$      | −0.62     | −0.06    | 2.77 (S–O$_{\text{2c}}$) |
| SO$_2$F$_2$  | −0.52     | −0.10    | 2.42 (O–Zn$_{\text{3c}}$) |
| H$_2$S       | −2.98     | −0.14    | 0.99 (H–O$_{\text{3c}}$) |

Figure 7. Adsorption structures of SF$_6$ decomposed products over the Zn vacancy ZnO(10$\overline{1}0$) surface: (a) SO$_2$, (b) SOF$_2$, (c) SO$_2$F$_2$ and (d) H$_2$S.

Table 4. Adsorption Energy ($E_a$), Electron Transfer ($Q_t$), and Adsorption Distance ($D$) of the Gas Molecule Adsorbed over the ZnO(10$\overline{1}0$) Surface with Zn Vacancy

Figure 8. (a)–(d) CDD configurations (the isosurface is 0.01 e Å$^{-3}$) and (e)–(h) ELF configurations of SF$_6$ decomposed products adsorbed over the Zn vacancy ZnO(10$\overline{1}0$) surface.

Figure 8. (a)–(d) CDD configurations (the isosurface is 0.01 e Å$^{-3}$) and (e)–(h) ELF configurations of SF$_6$ decomposed products adsorbed over the Zn vacancy ZnO(10$\overline{1}0$) surface.

18746
Figure 9. DOS of the gas molecule adsorbed over the perfect ZnO(10$ar{1}0$) surface: (a) and (b), SO$_2$ adsorption; (c) and (d), SOF$_2$ adsorption; (e) and (f), SO$_2$F$_2$ adsorption; and (g) and (h), H$_2$S adsorption (corresponding to Figure 3).

Figure 11b, there is obvious hybridization of S 3p and O 2p near $-10$, $-7.5$, and $+3$ eV. The hybridization demonstrates strong chemical interactions between the S atom and the O$_{2c}$ atom, which conforms to the possible new bonding in ELF configuration. The molecular orbitals of SOF$_2$ and SO$_2$F$_2$ also have some changes to some extent, such as the 16th$-$21st...
orbits of SOF₂ and the 22nd–25th orbitals of SO₂F₂. However, very little hybridization between the atom in the gas molecule and the atom on the surface can be found in Figure 11d,f. As a result, there is low possibility for new bond formation between the surface and the gas molecule (SOF₂ or SO₂F₂), but there still exists some chemical interactions.

Figure 10. DOS of the gas molecule adsorbed over the O vacancy ZnO(1010) surface: (a) and (b), SO₂ adsorption; (c) and (d), SOF₂ adsorption; (e) and (f), SO₂F₂ adsorption; and (g) and (h), H₂S adsorption (corresponding to Figure S).
bringing a degree of change of molecular orbitals. For H$_2$S adsorption, the molecular orbitals of H$_2$S exhibit tremendous changes as it can be seen in Figure 11g. This phenomenon is mainly due to the bond breaking. Also, large area of hybridization between the S atom and the O$_{2c}$ atom can be seen near $-12$, $-7$ to $-6$, 0, and $+3$ eV. The hybridization
illustrates strong chemical interactions between these two atoms, and thus strong chemical interactions happen for H$_2$S adsorbed on the T$_0$ site, resulting in the H$-\overline{S}$ bond being broken and much larger adsorption energy.

2.5. Diffusion Behavior of Gas Molecule over the Surface. The diffusion behavior is important for determining the sensing performance of nanomaterials toward gas detection. For H$_2$S adsorption over the perfect ZnO(1010) surface, because it showed obvious decomposition with no energy barrier, the diffusion of both pieces will be very difficult, so we did not take it into consideration. And of course, the adsorption over the O or Zn vacancy mainly happens if the vacancy exists, so we also did not consider them. As a result, we mainly discussed the diffusion behaviors of SO$_2$, SOF$_2$, and SO$_2$F$_2$ over the ZnO(1010) surface by calculating energy barriers and comparing them with the adsorption energies to evaluate the difficult level of the diffusion process, as shown in Figure 12. The diffusion of SO$_2$ from one O$_{3c}$ site to another O$_{3c}$ site exhibits 0.91 eV energy barrier, much smaller than the adsorption energy (1.27 eV), so we estimate that the diffusion process is very easy for SO$_2$. Also, nearly the same phenomenon can be observed for SOF$_2$ and SO$_2$F$_2$, that is, the energy barrier is much smaller than the adsorption energy. As a result, the diffusion process is relatively easy for these three kinds of SF$_6$ decomposed products, and this phenomenon can bring benefits to the desorption process.

3. CONCLUSIONS

This work discussed the adsorption behaviors of four kinds of SF$_6$ decomposed products on the perfect, O vacancy, and Zn vacancy ZnO(1010) surfaces. The perfect ZnO(1010) exhibits considerable chemical interactions to SO$_2$ and H$_2$S with possible new bond formation. In spite of this, the H$_2$S can be easily dissociated to H and H$-\overline{S}$ species with no energy barrier. Four kinds of molecules all act as the electron acceptor. The introduction of one O vacancy on the surface does not bring obvious enhancement for chemical interactions between these four molecules and the surface. The O vacancy can only slightly increase the electron transfer between the adsorbed molecule and the surface. However, when introducing one Zn vacancy on the surface, the O$_{3c}$ atom exhibits high chemical activity to SO$_2$ and H$_2$S, bringing much larger adsorption energy. The chemical interactions can also be reflected by the changes of molecular orbitals of the adsorbed molecule and the hybridization between the atom in the molecule and the atom in ZnO. To enhance the surface interactions to SO$_2$ or H$_2$S to improve the gas-sensing properties, it is feasible to introduce more Zn vacancies on the surface. This study provides a theoretical basis surface modification of ZnO-based gas-sensing materials applied in detecting SF$_6$ decomposition products.

4. COMPUTATIONAL METHODS

The first-principle calculations using the density functional theory (DFT) method were achieved by linear combination of atomic orbitals in the Dmol$^3$ package. The Perdew–Burke–Ernzerhof function approached by the generalized gradient approximation was adopted in consideration of the approximation of the exchange-correlation functional. The double numerical polarization basis set combined with the DFT semicore pseudopotential was chosen with a global cutoff radius of 4.5 Å. When considering long-range van der Waals force for gas adsorption, the DFT-D2 method proposed by Grimme was adopted. When carrying out geometric optimization process, $1.0 \times 10^{-6}$ Ha, 0.001 Ha Å$^{-1}$, and
0.005 Å (1 Ha = 27.21 eV) for energy tolerance, maximum force, and displacement were set for convergence, respectively.

The hexagonal wurtzite structure of bulk ZnO has lattice cell parameters of \(a = 3.24\) Å, \(c = 5.21\) Å.\(^{13}\) The ZnO(10\(\bar{1}\)) surface was cleaved with three layers, as shown in Figure 1a. The bottom two layers were constrained before proceeding with geometric optimization, and only the first top layer was fully relaxed. The first top layer of the ZnO(10\(\bar{1}\)) surface contains two different types of Zn and O atoms, including three-coordinated Zn atom (Zn\(_{3c}\)), four-coordinated Zn atom (Zn\(_{4c}\)), three-coordinated O atom (O\(_{3c}\)), and four-coordinated O atom (O\(_{4c}\)). To consider the role of one O vacancy or one Zn vacancy in the adsorption process, one Zn or one O atom was removed from the surface, and after full geometric optimization, the final perfect ZnO(10\(\bar{1}\)) surface and the surface with one Zn or O vacancy were obtained, as shown in Figure 1.

A \(4 \times 4 \times 1\) and a \(6 \times 6 \times 1\) \(k\)-point were set when carrying out geometric optimization and electronic property calculations.\(^{31}\) Considering the difficulty of defect formation, we calculated the formation energy of one O vacancy and Zn vacancy with and without vDW force. The formation energy of one O or Zn vacancy on the surface in different environments (Zn rich and O rich) was obtained as follows\(^{42}\)

\[
E_{\text{form}} = E_{\text{defect ZnO surface}} - E_{\text{perfect ZnO surface}} + \sum n_{\text{Zn}} \mu_{\text{Zn}} + \sum n_{\text{O}} \mu_{\text{O}}
\]  

(1)

where \(E_{\text{defect ZnO surface}}\) and \(E_{\text{perfect ZnO surface}}\) are the total calculated energy of ZnO(10\(\bar{1}\)) surface with one vacancy, perfect ZnO(10\(\bar{1}\)) surface, the number of Zn vacancy, the chemical potential of one Zn atom, and the number of O vacancy, and the chemical potential of one O atom, respectively. In this work, for one Zn vacancy on the surface, \(n_{\text{Zn}} = 1\) and \(n_{\text{O}} = 0\), and for one O vacancy on the surface, \(n_{\text{Zn}} = 0\) and \(n_{\text{O}} = 1\). The chemical potentials of one Zn and one O atom were calculated using the bulk phase of the Zn crystal and the oxygen molecule. This method proved to be accurate and efficient for calculating defective structure of ZnO.\(^{43}\)

After obtaining the structures of perfect and defect ZnO(10\(\bar{1}\)) surfaces, one gas molecule of SF\(_6\) decomposed products was put upon the surface with a different initial position. After full geometric optimization, the adsorption energy of every gas molecule adsorbed on the ZnO(10\(\bar{1}\)) surface can be defined as

\[
E_a = E_{\text{ZnO surface/gas}} - E_{\text{ZnO surface}} - E_{\text{gas}}
\]  

(2)

where \(E_{\text{ZnO surface/gas}}\) is the total energy of one molecule adsorbed on the perfect or defect ZnO(10\(\bar{1}\)) surface. \(E_{\text{ZnO surface}}\) and \(E_{\text{gas}}\) are the total energies of the perfect or defect ZnO(10\(\bar{1}\)) surface and one gas molecule before adsorption, respectively. To understand the physical and chemical interactions between the adsorbed gas molecule and the ZnO(10\(\bar{1}\)) surface, the charge density, electron localization function (ELF), and density of states (DOS) were calculated and analyzed.

After calculating the charge density, the three-dimensional charge density difference (CDD) can be calculated using the following equation

\[
\Delta \rho = \rho_{\text{ZnO surface/gas}} - (\rho_{\text{ZnO surface}} + \rho_{\text{gas}})
\]  

(3)

where \(\rho_{\text{ZnO surface/gas}}\), \(\rho_{\text{ZnO surface}}\), and \(\rho_{\text{gas}}\) are the total charge density of the optimized adsorption structure, perfect or defect ZnO(10\(\bar{1}\)) surface, and isolated gas molecule, respectively. The electron accumulation region was colored as purple, and the electron depletion region was marked as green. The total charge density result can also deduce the electron transfer between the adsorbed gas molecule and the ZnO(10\(\bar{1}\)) surface using the charge analysis method proposed by Hirshfeld as\(^{44}\)

\[
Q = -\int \left( \sum \rho_0(r) \rho(r) - \sum \rho_0'(r) \rho'(r) \right) dr
\]  

(4)

where \(\rho_0(r)\) is the charge density of one selected isolated atom. By adding up all \(\rho_0(r)\) of every atom, \(\sum \rho_0(r)\) can be obtained. \(\rho(r)\) represents the total electron density of the calculated structure.

To evaluate the chemical bond formation between the adsorbed gas molecule and the ZnO(10\(\bar{1}\)) surface, the ELF configurations were calculated. The region where the value was close to 1/2 demonstrated high probability of bonded electron pair, indicating the possible new-formed chemical bonds between the adsorbed gas molecule and the ZnO(10\(\bar{1}\)) surface.\(^{45}\) To further investigate the chemical interactions, the molecular orbitals of the gas molecule and the DOS were also taken into consideration.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02933.

Adsorption structure with the local minimum total energy and adsorption energy comparison for SF\(_6\) decomposed products over perfect ZnO surface, O vacancy ZnO surface, and Zn vacancy ZnO surface (PDF)

**AUTHOR INFORMATION**

Corresponding Author

*E-mail: xiaoxing.zhang@outlook.com. Tel: +86-136-2727-5072.

ORCID

Xiaoxing Zhang: 0000-0001-5872-2039
Hao Cui: 0000-0002-9410-6345

Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

We gratefully acknowledge the financial support from National Natural Science Foundation of P. R. China (Project No. 51777144).

**REFERENCES**

(1) Wenderich, K.; Mul, G. Methods, mechanism, and applications of photodeposition in photocatalysis: a review. *Chem. Rev.* 2016, 116, 14587–14619.
(2) Kattel, S.; Liu, P.; Chen, J. G. Tuning selectivity of CO\(_2\) and H\(_2\)O hydrogenation reactions at the metal/oxide interface. *J. Am. Chem. Soc.* 2017, 139, 9739–9754.
(3) Acar, C.; Dincer, I.; Naterer, G. F. Review of photocatalytic water-splitting methods for sustainable hydrogen production. *Int. J. Energy Res.* 2016, 40, 1449–1473.
(4) Zhang, P.; Wu, J.; Zhang, T.; Wang, Y.; Liu, D.; Chen, H.; Li, S. Perovskite Solar Cells with ZnO Electron-Transporting Materials. Adv. Mater. 2018, 30, No. 1703737.

(5) Liu, X.; Ioccozia, J.; Wang, Y.; Cui, X.; Chen, Y.; Zhao, S.; Lin, Z. Noble metal-metal oxide nanohybrids with tailored nanostructures for efficient solar energy conversion, photocatalysis and environmental remediation. Energy Environ. Sci. 2017, 10, 403–443.

(6) Ong, C. B.; Ng, L. Y.; Mohammad, A. A. W. A review of ZnO nanoparticles as solar photocatalysts: synthesis, mechanisms and applications. Renewable Sustainable Energy Rev. 2018, 81, 536–551.

(7) Dral, A. P.; Johari, E. 2D metal oxide nanoflakes for sensing applications: Review and perspective. Sens. Actuators, B 2018, 272, 369–372.

(8) Zhu, L.; Zeng, W. Room-temperature gas sensing of ZnO-based gas sensor: A review. Sens. Actuators, A 2017, 267, 242–261.

(9) Miller, D. R.; Akbar, S. A.; Morris, P. A. Nanoscale metal oxide-based heterojunctions for gas sensing: a review. Sens. Actuators, B 2014, 204, 250–272.

(10) Kumar, S.; Alhalawat, W.; Kumar, R.; Dibbaghi, N. Graphene, carbon nanotubes, zinc oxide and gold as elite nanomaterials for fabrication of biosensors for healthcare. Biosens. Bioelectron. 2015, 70, 498–503.

(11) Petti, L.; Münzenrieder, N.; Vogt, C.; Faber, H.; Büthe, L.; Cantarella, G.; Tröster, G. Metal oxide semiconductor thin-film transistors for flexible electronics. Appl. Phys. Rev. 2016, 3, 011305.

(12) Sirelkhatim, A.; Mahmud, S.; Seen, A.; Kau, N. H. M.; Ann, L. C.; Bakhori, S. K. M.; Mohamad, D. Review on zinc oxide nanoparticles: antibacterial activity and toxicity mechanism. Nano-Micro Lett. 2015, 7, 219–242.

(13) Wang, C.; Chu, X.; Wu, M. Detection of H2S down to ppb levels at room temperature using sensors based on ZnO nanorods. Sens. Actuators, B 2006, 113, 320–323.

(14) Hosseini, Z. S.; Mortezaii, A. Room temperature H2S gas sensor based on rather aligned ZnO nanorods with flower-like structures. Sens. Actuators, B 2015, 207, 865–871.

(15) Xu, Y. N.; Ching, W. Y. Electronic, optical, and structural properties of some wurtzite crystals. Phys. Rev. B 1993, 48, No. 4335.

(16) Diebold, U.; Kopitz, L. V.; Dulob, O. Atomic-scale properties of low-index ZnO surfaces. Appl. Surf. Sci. 2004, 237, 336–342.

(17) Fink, K. Ab initio cluster calculations on the electronic structure of oxygen vacancies at the polar ZnO (0001) surface and on the adsorption of H2, CO, and CO2 at these sites. Phys. Chem. Chem. Phys. 2006, 8, 1482–1489.

(18) Prades, J. D.; Cirera, A.; Morante, J. R. Ab initio calculations of NO2 and SO2 chemisorption onto non-polar ZnO surfaces. Sens. Actuators, B 2009, 142, 179–184.

(19) Ling, L.; Wu, J.; Song, J.; Han, P.; Wang, B. The adsorption and dissociation of H2S on the oxygen-deficient ZnO (1010) surface: A density functional theory study. Comput. Theor. Chem. 2012, 1000, 26–32.

(20) Tang, Q. L.; Luo, Q. H. Adsorption of CO2 at ZnO: a surface structure effect from DFT+U calculations. J. Phys. Chem. C 2013, 117, 22954–22966.

(21) Gao, Y.; Zhao, N.; Wei, W.; Sun, Y. Ab initio DFT study of urea adsorption and decomposition on the ZnO (1010) surface. Comput. Theor. Chem. 2012, 992, 1–8.

(22) Shannumag, R.; Thamaravelchelvan, A.; Viswanathan, B. Methanol formation by catalytic hydrogenation of CO2 on a nitrogen doped zinc oxide surface: an evaluative study on the mechanistic pathway by density functional theory. RSC Adv. 2015, 5, 60524–60533.

(23) Vo, C. T.; Huynh, L. K.; Hung, J. Y.; Jiang, C. C. Methanol adsorption and decomposition on ZnO (1010) surface: A density functional theory study. Appl. Surf. Sci. 2013, 280, 219–224.

(24) Medford, A. J.; Sehested, J.; Rossmeisl, J.; Chorkendorff, I.; Studt, F.; Nørskov, J. K.; Moses, P. G. Thermochemistry and microkinetic analysis of methanol synthesis on ZnO (0001). J. Catal. 2014, 309, 397–407.