Ab Initio Study of SOF$_2$ and SO$_2$F$_2$ Adsorption on Co-MoS$_2$

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ABSTRACT: The detection of partial discharge by analyzing the decomposition components of SF$_6$ gas in gas-insulated switchgears plays an important role in the diagnosis and assessment of the operational state of power equipment. Recently, the application of transition metal-modified MoS$_2$ monolayer dioxide in gas detection has received wide attention. In this paper, first-principle density functional theory calculations were adopted to study the gas-sensitive response of Co-MoS$_2$ monolayer to SOF$_2$ and SO$_2$F$_2$. It is found that the conductivity of the Co-MoS$_2$ monolayer has been effectively enhanced after Co atom doping on the MoS$_2$ monolayer. After gas adsorption, electrons transfer from the Co-MoS$_2$ monolayer to the gas molecules, resulting in significant reduction of conductivity of the adsorption system. The calculation results reveal that the Co-MoS$_2$ monolayer is sensitive and selective to SOF$_2$ and SO$_2$F$_2$ gases. This study provides the theoretical possibility of using Co-MoS$_2$ as a gas sensor for SOF$_2$ and SO$_2$F$_2$ gas detection.

1. INTRODUCTION

It is well known that SF$_6$ has excellent insulation and arc extinguishing capability, which makes it a widely used insulating medium in gas-insulated switchgear (GIS).1–2 Because of the critical role of SF$_6$-insulated GIS in power systems, its running stability is crucial for the entire power system. However, partial discharge inevitably occurs when potential insulation faults exist in GIS during the design, production, and long-term operation process.3–5 Research showed that SF$_6$ will decompose into fluoride (SF$_x$, x = 1–5) under strong energy of partial discharge. Then, the unstable SF$_6$ will quickly react with trace of H$_2$O and O$_2$ present in GIS to various decomposition products, including the main components: SOF$_2$ and SO$_2$F$_2$.6–8 These decomposition products can significantly accelerate the corrosion of the insulation medium and further reduce the electrical insulation strength of GIS.7–9 In addition, continuous partial discharge may turn into flashover or destructive discharge and even lead to sudden breakdown of GIS without timely handling.10–11 Therefore, detecting and analyzing the type and concentration of SF$_6$ decomposition products is of great significance for diagnosing the type and damage degree of partial discharge. Thanks to high sensitivity and fast response of gas sensors, it can be an effective method to detect the SF$_6$ decomposition products.12–14

In recent years, two dimensional-layered MoS$_2$ nanomaterials have attracted much attention because of its large specific surface area, high surface activity, good thermal conductivity, and strong chemical stability.15–17 The semiconductor properties and high specific surface area of the MoS$_2$ monolayer, makes it a promising material for gas detection.18–20 Recently, studies showed that MoS$_2$ monolayer sensors can effectively detect NH$_3$, NO$_2$, H$_2$, and other gases.21,22 However, because of the limited gas sensing properties of intrinsic MoS$_2$, surface modification is usually adopted,23 such as metallic and nonmetallic nanoparticles doping: Au, Pt, Ni, and Si.24–26 Previous study results showed that surface modification significantly improves the sensitivity and selectivity of MoS$_2$-based materials to gas molecules.27–29 Liu et al. found that Si-doped MoS$_2$ has obvious sensing properties for H$_2$ at room temperature even at a low gas concentration of 0.5%.30 According to previous studies, Co is one of the most used doping atoms among transition metals, which shows outstanding performance in enhancing the adsorption, gas sensitivity, and catalytic ability of MoS$_2$.31,32 In addition, Co doping on MoS$_2$ is easy to be prepared, which makes it to be widely used as an adsorbent and gas sensor.33,34 However, as far as we know, the Co-MoS$_2$ monolayer has not been reported for its application in SF$_6$ decomposition product detection.

In this study, the first-principles density functional theory (DFT) was used to study the gas sensing properties of Co-MoS$_2$ to SOF$_2$ and SO$_2$F$_2$ by analyzing the adsorption structure, adsorption energy, charge transfer, density of states (DOS), charge density difference (CDD), and molecular orbital. The theoretical analysis explains the effect of Co doping on the response performance of the MoS$_2$ monolayer to SOF$_2$ and SO$_2$F$_2$. This study not only puts forward an application of Co-MoS$_2$ material in the SF$_6$ decomposition...
components detection but also provides a theoretical foundation for the gas sensor design.

2. RESULTS AND DISCUSSION

2.1. Simulation Structure of the Co-MoS2 Monolayer. The structure of Co-MoS2 is built based on the perfect MoS2 monolayer. The most stable configuration for the Co-MoS2 monolayer has been thoroughly studied. Figure 1 and Table 1 show the optimized geometry and corresponding structural parameters of the most stable configuration of the Co-MoS2 monolayer. The Co atom locates at the top of the MoS2 monolayer protruding out of the MoS2 surface, which forms stable chemical bonds with three adjacent S atoms labeled as S1, S2, and S3 with bond lengths of 2.114, 2.089, and 2.114 Å, respectively. The structure of MoS2 away from the Co doping site is almost unchanged after Co atom doping. $E_{ads}$ of Co-MoS2 is $-0.325$ eV, and 0.144 e of electrons transfers from the Co atom to MoS2.

Figure 1. Structure of the Co-MoS2 monolayer from different views: (a) top view; (b) side view.

Table 1. Structural Parameters of the Co-MoS2 Monolayer

| system   | $d_{Co-S1}$/Å | $d_{Co-S2}$/Å | $d_{Co-S3}$/Å | $Q_{Co}$/e | $E_{ads}$/eV |
|----------|---------------|---------------|---------------|------------|--------------|
| Co-MoS2  | 2.114         | 2.089         | 2.114         | 0.144      | $-0.325$     |

The electron transfer behavior was analyzed based on the molecular orbital theory as shown in Figure 3. For the distribution of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), the HOMO and LUMO are mainly located around the Co doping site, indicating that Co doping benefits the electron transfer. $E_g$ of the intrinsic MoS2 monolayer is 2.058 eV, and it dramatically reduces to 0.387 eV for the Co-MoS2 monolayer. Therefore, the electrons in the valence band are more likely to jump and effectively improve the electrical conductivity of the intrinsic MoS2 monolayer.

2.2. Adsorption of SOF2 on the Co-MoS2 Monolayer. To analyze the adsorption performance of the Co-MoS2 monolayer to the target SOF2 molecule, a large number of potential structures have been built and optimized to obtain the most stable adsorption structure. Two typical adsorption structures, labeled as P1 and P2, are obtained as shown in Figure 4. Its corresponding adsorption parameters are presented in Table 2.

For the P1 structure given in Figure 4a, though the SOF2 molecule has not directly bonded to the surface of the Co-MoS2 monolayer, $E_{ads}$ still reaches $-1.468$ eV during the adsorption process, which means that the adsorption structure is relatively stable. The distance from the S atom of SOF2 to the Co atom is 2.043 Å, and $-0.026$ e transfers from Co-MoS2 to SOF2. Because of the strong adsorption energy between the SOF2 molecule and Co-MoS2, its interaction belongs to chemical adsorption. By comparing $E_g$ before and after gas

Figure 2. TDOS and PDOS of intrinsic MoS2 and Co-MoS2 monolayers: (a) TDOS; (b) PDOS.

Figure 3. HOMO and LUMO orbitals on Co-MoS2 from different views: (a) HOMO of Co-MoS2; (b) LUMO of Co-MoS2.

Figure 4. Adsorption structure of SOF2 on the Co-MoS2 monolayer: (a) P1 structure; (b) P2 structure.
molecule adsorption, $E_g$ has only decreased 0.057 eV, indicating that the conductivity of the Co-MoS$_2$ system is almost unchanged before and after adsorption.

For the P2 structure given in Figure 4b, it is found that one S$^-$F bond in SOF$_2$ breaks and interacts with the Co atom of Co-MoS$_2$ by forming Co$-$S and Co$-$F bonds upon SOF$_2$ adsorption. The bond lengths of Co$-$S and Co$-$F are 2.187 and 1.842 Å, respectively. The charge transfer from Co-MoS$_2$ to the SOF$_2$ molecule is $-0.491$ e based on the Milliken population results. In addition, Co-MoS$_2$ shows strong interaction with SOF$_2$ with an $E_{ads}$ of $-1.765$ eV, which is significantly larger than that in the P1 structure. Comparing with $E_g$ (0.387 eV) of Co-MoS$_2$, it increases to 0.800 eV after SOF$_2$ molecule adsorption, indicating that SOF$_2$ adsorption leads to the conductivity of the Co-MoS$_2$ system.

To understand the electronic behavior and analyze the gas sensitivity of Co-MoS$_2$ to SOF$_2$, the TDOS, PDOS, and CDD were further analyzed. Because of the main contribution of the outmost orbitals of the interacted atom in the adsorption process, only the F 2p, S 3p, and Co 3d orbitals were discussed in the PDOS, as seen in Figure 5.

As shown in Figure 5a, the TDOS slightly moves to the right side, and the TDOS near the Fermi level drops between 0 and 1 eV after SOF$_2$ adsorption, indicating a reduction in the conductivity of Co-MoS$_2$-based material. According to the distribution of PDOS in Figure 5b, this change of TDOS is mainly because of the obvious hybridization of the S 3p orbital of SOF$_2$ and the Co 3d orbital in the range of $-6$ to $-4$ eV and the hybridization of the F 2p orbital with Co 3d from $-2$ to $-1$ eV. The analysis of TDOS and PDOS confirms that it is a strong interaction between SOF$_2$ and Co-MoS$_2$ monolayers.

To further analyze the change of the electron distribution, the CDD of the P2 structure was studied as shown in Figure 6, where the acquisition and loss of electrons are represented by red and blue, respectively. It can be seen that two F atoms of SOF$_2$ get a large number of electrons. According to the results of Mulliken population analysis, the obtained quantity of electrons by two F atoms reaches $-0.780$ e. On the contrary, Co and Mo atoms lose during gas adsorption. Therefore, it further verifies that the conductivity of the Co-MoS$_2$ monolayer decreases after SOF$_2$ adsorption.

2.3. Adsorption of SO$_2$F$_2$ on the Co-MoS$_2$ Monolayer.

In order to obtain the most stable adsorption structure of SO$_2$F$_2$-adsorbed Co-MoS$_2$, single SO$_2$F$_2$ was set to approach the surface of the Co-MoS$_2$ monolayer from different initial approaches sites. After geometry optimization, two typical adsorption structures were obtained as shown in Figure 7, labeled as P1 and P2. Table 3 shows $E_{ads}$, $Q$, and $E_g$ of SO$_2$F$_2$-adsorbed Co-MoS$_2$ by P1 and P2.

For the P1 structure shown in Figure 7a, it can be seen that one S$^-$F bond of SO$_2$F$_2$ breaks during the adsorption process. The dissociated F atom builds a bond with the Co atom with a bond length of 1.841 Å, and the dissociated SO$_2$F gas keeps away from the surface of Co-MoS$_2$. SO$_2$F$_2$ gas gets $-0.636$ e from Co-MoS$_2$ and the adsorption process releases 0.881 eV. Because of the obvious charge transfer and strong adsorption energy, Co-MoS$_2$ adsorbs on the surface of Co-MoS$_2$ by a stable structure. $E_g$ of SO$_2$F$_2$-adsorbed Co-MoS$_2$ is 0.540 eV, which is distinctly larger than that of Co-MoS$_2$ (0.387 eV). As a result, SO$_2$F$_2$ adsorption leads to the decrease of conductivity.

For the P2 structure shown in Figure 7b, it is found that both of the F atoms dissociate from SO$_2$F$_2$ and form two stable Co$-$F bonds by lengths of 1.798, 1.864 Å, respectively. The dissociated SO$_2$ was away from the surface of Co-MoS$_2$. In the

![Figure 4](image-url) Adsorption structures of SOF$_2$-adsorbed Co-MoS$_2$ monolayer: (a) P1 structure; (b) P2 structure.

![Figure 5](image-url) TDOS and PDOS of the SOF$_2$-adsorbed Co-MoS$_2$ monolayer: (a) TDOS; (b) PDOS.

![Figure 6](image-url) CDD of the SOF$_2$-adsorbed Co-MoS$_2$ monolayer by the P2 structure: (a) side view 1; (b) side view 2.

![Figure 7](image-url) Adsorption structures of SO$_2$F$_2$-adsorbed Co-MoS$_2$ monolayer: (a) P1 structure; (b) P2 structure.
process, a large amount of electrons transfer from the Co-MoS2 monolayer to SO2F2. Meanwhile, \(E_{\text{ads}}\) of the P2 structure is up to \(-2.390\) eV, exhibiting it as a strong interaction. Moreover, \(E_g\) increases sharply from 0.387 to 1.040 eV after adsorption. We conclude that P2 is the most stable adsorption structure by comparing the adsorption property of Co-MoS2 to SO2F2 in P1 and P2 structures.

To further analyze the adsorption behavior of SO2F2 gas on the Co-MoS2 monolayer, the TDOS, PDOS were also discussed as shown in Figure 8. After SO2F2 adsorption, the TDOS is apparently shifted to the right side, signifying that the energy level of the electron filling increases, which is favorable for the free movement of electrons. The TDOS increases between \(-1\) and 0 eV, but decreases to zero in the range of 0.3–1 eV. According to the distribution of PDOS, its can be found that the change of TDOS is mainly owing to the orbital hybridization of the F 2p orbital and the S 3p orbital of Co-MoS2 in the range of \(-4.8\) to \(-3.5\) and \(-2\) to \(-1.5\) eV. In addition, the Co 3d orbital hybrids with F 2p range from \(-1.5\) to 0.8 eV.

The CDD of the P2 structure is shown in Figure 9, where red and blue represent acquisition and loss of electrons, respectively. During the strong chemical interaction between SO2F2 and Co-MoS2, the O atoms and the F atoms of the SO2F2 molecule receive a large amount of electrons, and the electron density surrounding the S atom of SO2F2 decreases. Mulliken population analysis shows that the F atom and O atom receive 0.947 and 0.608 e of electrons, respectively, while the S atom loses 0.493 e of electrons. In general, SO2F2 acts as an electron acceptor during the adsorption process.

2.4. Comparison of SOF2 and SO2F2 Adsorbed on the Co-MoS2 Monolayer. The adsorption properties of the Co-MoS2 monolayer to SOF2 and SO2F2 gases are compared below. For adsorption structures, SOF2 was completely bonded onto the surface of Co-MoS2 by a stable chemical bond while two F atoms of SO2F2 break away from the gas molecule and builds a new bond with the Co atom, and the dissociated SO2 gas adsorbs on the surface of MoS2 by weak interaction. Because of the strong electronegativity of the F atom, SO2F2 receives more electrons from the Co-MoS2 during the adsorption process. In addition, the redistribution of electrons leads to change of the DOS. The DOS shows different change rules for different gas molecules adsorption, indicating that the adsorption of these two types of gases causes a difference change in the conductivity of Co-MoS2. It builds up the theoretical basis for gas sensors to sensitively detect different gases. Generally, Co-MoS2 shows a better gas sensing property to SO2F2 than SOF2.

3. CONCLUSIONS

In this study, Co-MoS2 has been proposed as the gas-sensing material to adsorb the characteristic decomposition components of SF6 under partial electric discharge: SOF2 and SO2F2.
The adsorption energy, charge transfer, energy gap, and CDD of all potential adsorption structures were calculated to analyze the adsorption mechanism based on the density functional theory. Following are the conclusions:

1. The doped Co atom builds a stable adsorption structure with MoS$_2$ by interacting with three adjacent S atoms. Because of the strong chemical activity of the Co atom, the DOS near the Fermi level becomes continuous after Co doping, and the conductivity of the Co-MoS$_2$ monolayer is greatly improved compared with intrinsic MoS$_2$.

2. SOF$_2$ and SO$_2$F$_2$ adsorb on the Co doping site of Co-MoS$_2$ by chemical adsorption. The gas molecules act as electron acceptors, and the Co-MoS$_2$ monolayer plays electron donors role in the adsorption process. Co-MoS$_2$ possesses different degrees of change in the electrical conductivity to different gas molecules adsorption. As a result, Co-MoS$_2$-based material is sensitive to SOF$_2$ and SO$_2$F$_2$, which builds up the theoretical basis for gas sensors to sensitively detect different gases.

4. COMPUTATIONAL DETAILS AND METHODS

All calculations were calculated based on the DFT with Tkatchenko–Scheffler dispersion correction. An MoS$_2$ monolayer was built with a 4 × 4 × 1 supercell, including 32 S atoms and 16 Mo atoms, which is large enough to explore its adsorption to monomolecular gases. In addition, a vacuum thickness of 15 Å was set to avoid the interaction between different layers. The exchange and correlation energy were calculated by the general gradient approximation with the PerdewBurke-Ernzerhof, which has been widely used in DFT calculations. The self-consistent field (SCF) approximation was calculated by double numerical basis set plus polarization functions (DNP). The Brillouin zone $k$-point sampling was sampled by 5 × 5 × 1. All of the optimized structures have an energy accuracy of 2 × 10$^{-5}$ Ha, and a maximum force of 4 × 10$^{-3}$ Ha/Å. The SCF convergence accuracy was set to 1 × 10$^{-6}$ Ha. In addition, the DIIS size was set to 6 to speed up the convergence of SCF.

The adsorption energy of Co on the MoS$_2$ monolayer is defined by eq 1, where $E_{Co-MoS_2}$, $E_{MoS_2}$, and $E_{Co}$ are the total energy of Co-MoS$_2$, MoS$_2$, and Co, respectively. The adsorption energy of the Co-MoS$_2$ monolayer to gas molecules is defined by eq 2, where $E_{Co-MoS_2/gas}$, $E_{Co-MoS_2}$, and $E_{gas}$ represent the total energy of the Co-MoS$_2$ monolayer after gas molecules adsorption, the Co-MoS$_2$ monolayer, and the free gas molecules before adsorption, respectively.

$$E_{ads} = E_{Co-MoS_2/gas} - E_{Co-MoS_2} - E_{gas}$$

The charge transfer $Q$ during gas adsorption was calculated using the Mulliken population analysis obtained by eq 3, where $Q_{iso}$ and $Q_{ads}$ are the carried charge of gas molecules (or Co atom) before and after adsorption. $Q > 0$ means that electrons transfer from gas molecules to the surface of the Co-MoS$_2$ monolayer.

$$Q = Q_{ads} - Q_{iso}$$

The energy gap of the molecular orbital was calculated through the energy levels of the HOMO and the LUMO, as defined in eq 4. It determines the probability of charge movement in the adsorption system composed of the gas molecules and the Co-MoS$_2$ monolayer. The wider the gap is, the more energy is required for electrons transferring from the valence band to the conduction band.

$$E_g = |E_{LUMO} - E_{HOMO}|$$

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