Adsorption and Gas Sensing Properties of the Pt₃-MoSe₂ Monolayer to SOF₂ and SO₂F₂

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ABSTRACT: SF₆ acts as an insulation gas in gas-insulated switchgear (GIS), which inevitably decomposes under partial discharge caused by insulation defects. This work is devoted to finding a new gas-sensing material for detecting two characteristic SF₆ decomposition products: SOF₂ and SO₂F₂. The platinum-cluster-modified molybdenum diselenide (Pt₃-MoSe₂) monolayer has been proposed as a gas sensing material. Based on first-principles calculations, the adsorption properties and the mechanism were studied by analyzing the adsorption structures, adsorption energy, charge transfer, density of states, and molecular orbitals. The adsorption ability of Pt₃-MoSe₂ to SO₂F₂ is stronger than that to SOF₂ due to its chemisorption property. The obvious change of conductivity of the adsorption system during the gas adsorption process shows that Pt₃-MoSe₂ is sensitive to both of the gas molecules. In addition, the modest adsorption energy signifies that the gas adsorption process can be reversible, which confirms the feasibility of Pt₃-MoSe₂-based gas sensors. Our calculation suggests that Pt₃-MoSe₂-based gas sensors can be employed in GIS for partial discharge detection.

1. INTRODUCTION

Gas-insulated switchgear (GIS) plays a key role in modern electric systems, which is mostly filled with SF₆ gas, a kind of colorless and nontoxic inert gas with high chemical stability and excellent arc extinguishing performance.1−3 However, electric discharge inevitably occurs in GIS during the long-term running process. Among them, partial discharge is one of the most serious electric discharges because of its strong concealment property.4,5 Under the high energy density of partial discharge, SF₆ breaks to various unstable fluorides.6,7 Then, these fluorides quickly react with micro-water and micro-oxygen that existed in GIS to some characteristic decomposition products, such as SOF₂ and SO₂F₂. On the one side, the insulation strength of these decomposition products is obviously weaker than that of SF₆. On the other side, these decomposition products can corrode the GIS under the micro-water condition, which decreases the stability of GIS. Partial discharge may ultimately lead to the breakdown of GIS. Currently, online detection of the partial discharge in GIS has attracted great concerns.8,9 It is of great significance to explore a new type of gas sensing material for the detection of SF₆ decomposition products.

As a transition metal semiconductor material, molybdenum diselenide (MoSe₂) has been widely used in various application fields.12−14 It is a layered structure with inactive chemical property, which shows high-temperature resistance and strong acid and alkali resistance.15,16 Accompanying its large specific surface area, it has been applied to gas adsorption and sensing studies. Thus, MoSe₂ was proposed as a gas sensing material for the detection of SF₆ decomposition products. However, intrinsic MoSe₂ shows limitations on SOF₂ and SO₂F₂ adsorption.17 Studies showed that transition metal cluster modification could effectively improve the adsorption effect of MoSe₂ by enhancing its surface activity. Platinum is one of the most commonly used transition metal for surface modification, which shows excellent surficial activity for gas adsorption.18,19 Thus, platinum-cluster-modified MoSe₂ may be a candidate gas sensing material employed in SOF₂ and SO₂F₂ detection.
Sensor performance could change dramatically according to different numbers of modification platinum atoms. Studies demonstrated that Pt$_3$ modification could significantly improve the adsorption activity of the MoSe$_2$ surface.$^{2,20,21}$ In addition, Pt$_3$-MoSe$_2$ shows weak adsorption to SF$_6$ according to our calculation, which makes it compatible with the SF$_6$ environment. Therefore, Pt$_3$-MoSe$_2$ was adopted as a gas sensing material for SOF$_2$ and SO$_2$F$_2$ detection. Based on density functional theory (DFT), a detailed study of the entire adsorption process, adsorption energy, charge transfer, and molecular orbital analysis was conducted and analyzed. A comparative analysis of the adsorption mechanism to SOF$_2$ and SO$_2$F$_2$ gases confirms that Pt$_3$-MoSe$_2$ is an ideal material for these two gases. This study not only analyzes the adsorption mechanism of Pt$_3$-MoSe$_2$ to SOF$_2$ and SO$_2$F$_2$ but

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**Figure 1.** Structures of (a) SOF$_2$, (b) SO$_2$F$_2$, (c) MoSe$_2$, and (d, e) Pt$_3$-MoSe$_2$. The distance is in angstroms.

**Figure 2.** (a) Band structure of MoSe$_2$, (b) band structure of Pt$_3$-MoSe$_2$, (c) DOS and PDOS of MoSe$_2$ and Pt$_3$-MoSe$_2$. 

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also provides a theoretical basis to develop Pt3-MoSe2 sensors in experiment.

2. RESULTS AND DISCUSSION

2.1. Structures and Electronic Properties of SOF2, SO2F2, and Pt3-MoSe2. The structures of SOF2, SO2F2, and Pt3-MoSe2 monolayer were optimized, respectively. As shown in Figure 1a–e, both SOF2 and SO2F2 belong to the three-dimensional spatial structure. The bond lengths of the S–F and the S–O in the SOF2 molecule are 1.67 and 1.46 Å, respectively. The tetrahedral structure and high electronegativity make the SOF2 molecule extremely stable. SO2F2 shows similar physicochemical properties to SOF2. However, more oxygen atoms in SO2F2 make it slightly more active, and the effect of orbital hybridization reduces the bond length of the S–F bond. Intrinsic and Pt3-modified MoSe2 are presented in Figure 1d,e. The two-dimensional layered structure makes a great contribution to the large specific surface area. After Pt3 modification, it possesses a more brilliant feature, three Pt atoms form a triangular ring that stands parallel to the MoSe2 surface, which increases the metal activity and adsorption performance of MoSe2.

Figure 2 shows the band structure and total density of states (TDOS) of MoSe2 and Pt3-MoSe2, which facilitate the analysis of the change of the physical properties. For intrinsic MoSe2, its band gap is 1.75 eV, which is consistent with its semiconductor characteristics. After Pt3 cluster doping, the band structure changes dramatically, as the band gap reduces to only 0.16 eV as shown in Figure 2b. As a result, the conductivity of the system rises significantly, which is of great significance for gas sensing. As for the TDOS of MoSe2 and Pt3-MoSe2, TDOS distribution tends to move left. There is more electron filling at the Fermi level, indicating that the conductivity of the system enhances. From the analysis of the projected density of states (PDOS), the 5d orbital of the Pt atom contributes the most to the entire electron distribution.

2.2. Adsorption of the SOF2 Molecule on the Pt3-MoSe2 Monolayer. Figure 3 shows the different approaching methods of the SOF2 molecule to the Pt3-MoSe2 surface after geometry optimization. There are significant differences in these adsorption structures, and the maximum adsorption energy is up to ~1.73 eV by S atom approaching, which simultaneously has the shortest adsorption distance due to the stronger oxidizing ability of S compared with O and F elements. Throughout the various adsorption process, the adsorption distances are 2.12, 2.17, and 3.71 Å, respectively. Almost no charge transfer occurs, and the interaction between SOF2 and Pt3-MoSe2 bends the Pt3 plane. The structure of the SOF2 molecule nearly does not change during the interaction. It can be concluded that the M1 system belongs to chemisorption, and M2 and N3 systems belong to physisorption. According to the huge difference in the adsorption energy among different approaching methods (from −0.46 to −1.73 eV), M1 is the most stable adsorption structure, which has been chosen for further analyzing its adsorption and sensing effects (Table 1).

Table 1. \( E_{ad}, Q_{ad}, \) and Adsortion Distance (d) of SOF2 on Pt3-MoSe2

| Parameter | \( E_{ad} \) (eV) | \( Q_{ad} \) (e) | d (Å) |
|-----------|-----------------|-----------------|-------|
| M1 system | −1.73           | −0.05           | 2.12  |
| M2 system | −0.51           | −0.02           | 2.17  |
| M3 system | −0.46           | −0.04           | 3.71  |

As shown in Figure 4a, the most stable structure (M1) is adopted for the analysis of physical properties, including TDOS, PDOS, and differential charge density. Once the target gas molecule adsorbs on the surface of Pt3-MoSe2, the electronic properties of the entire system could obviously change, thus the corresponding gas sensor can be prepared based on the different change rule of conductivity.

Figure 4b shows the TDOS changes before and after gas adsorption. TDOS has a minor change after the SOF2 molecule adsorbs on the Pt3-MoSe2 surface, mainly reflecting in less electron filling at the Fermi level. The redistribution of charge decreases the conductivity of the entire system. According to PDOS, the decrease in TDOS at the Fermi level is mainly caused by the 5d orbital of Pt. In the energy range from −6 to 0 eV, the 3p and 3s orbits of S, the 5d orbital of Pt have a certain degree of orbital hybridization, which causes a slight increase of electron filling in the valence band. Two small peaks aroused by the 3p orbital of S occur at −9 and −7.5 eV energy levels. The change of TDOS shows that
the gas molecule adsorption has a great influence on the electronic redistribution in the valence band, and the decline in the conductivity of the entire system depends on the gas itself and the interaction with Pt$_3$-MoSe$_2$.

To intuitively display the change of charge redistribution after gas adsorption, differential charge density was studied as shown in Figure 4c, where blue and red areas represent the loss and reception of electrons, respectively. It can be seen that there is no obvious charge transfer in the adsorption process, because there is only a little charge redistribution according to the red- and blue-color-marked areas. This conclusion is also consistent with the amount of $Q_T$ analysis above. In conclusion, Pt$_3$-MoSe$_2$ shows chemisorption to SO$_2$F$_2$ molecules with suitable adsorption energy.

### 2.3. Adsorption of the SO$_2$F$_2$ Molecule on the Pt$_3$-MoSe$_2$ Monolayer

As shown in Figure 5, three potential adsorption structures of SO$_2$F$_2$ on the Pt$_3$-MoSe$_2$ surface were obtained, labeled N1, N2, and N3. Table 2 shows the corresponding parameters of adsorption structures. It is evident that the interaction between SO$_2$F$_2$ and the Pt$_3$-MoSe$_2$ monolayer is much stronger than SO$_2$F$_2$ adsorption, especially when approaching the surface by the F atom in the N3 system. Dissociation occurs during the adsorption process, and the free F atom and the SO$_2$ group bond to the Pt atom with bond lengths of 2.07 and 2.30 Å by S–Pt and F–Pt, respectively. The adsorption energy for SO$_2$F$_2$ adsorption is up to −3.51 eV with a charge transfer of 0.91 e, and the reflection belongs to strong chemisorption. When SO$_2$F$_2$ approaches Pt$_3$-MoSe$_2$ by S and O atoms in N1 and N2 systems, the adsorption energy is −1.61 and −0.44 eV, and the amount of charge transfer is significantly lower than that in the N3 system. Especially in the N2 system, all atoms of SO$_2$F$_2$ are far away from the doped Pt cluster and the MoSe$_2$ surface, which leads to the lowest adsorption energy. According to the adsorption energy and adsorption distance, it can be concluded that strong chemisorption occurs between SO$_2$F$_2$ and Pt$_3$-MoSe$_2$.

### Table 2. $E_{\text{ads}}$, $Q_T$, and Adsorption Distance ($d$) of SO$_2$F$_2$ on Pt$_3$-MoSe$_2$

| parameter | $E_{\text{ads}}$ (eV) | $Q_T$ (e) | $d$ (Å) |
|-----------|-----------------|----------|---------|
| N1 system | −1.61           | −0.42    | S–Pt: 2.07 |
|           |                 |          | O–Pt: 2.30 |
| N2 system | −0.44           | −0.01    | O–Pt: 2.76 |
| N3 system | −3.51           | −0.91    | F–Pt: 1.95 |
|           |                 |          | S–Pt: 2.17 |
To analyze the adsorption mechanism of SO$_2$F$_2$ on Pt$_3$-MoSe$_2$, the adsorption properties of were further studied as shown in Figure 6. The approaching method of SO$_2$F$_2$ to Pt$_3$-MoSe$_2$ in N1 and N3 systems are considered in this work as shown in Figure 6a. From the distribution of TDOS in Figure 6b, only a small change of TDOS occurs during SO$_2$F$_2$ adsorption when approaching the N1 system. The electron filling reduces at the Fermi level, which increases the number of electron fills in the valence band. In addition, some peaks of PDOS appear near the $-9$ eV level, which is caused by the 3p orbital of S, the 2p orbital of O, and the 5d orbital of Pt. The PDOS distribution shows obvious orbital hybridization.

A huge change in TDOS and PDOS is obtained in the N3 system in Figure 6b. TDOS moves to the right side as a whole with some new peaks appearing at different energy levels. The 5d orbital of Pt and the 2p orbital of F show strong hybridization, which contributes a lot to TDOS distribution. The formation of a Pt–F chemical bond is a good explanation to this huge change. It is certain that there is clear chemisorption between the SO$_2$F$_2$ molecule and the Pt$_3$-MoSe$_2$ surface. At the Fermi level, there is minimal electron filling after SO$_2$F$_2$ adsorption, and the conductivity drops obviously, which shows a significant meaning for gas sensing. From the perspective of PDOS, The 3p orbital peak of S appears at $-6$ eV energy level, and it causes a little effect on the electrical conductivity of the whole system. The 2p orbital of F and the 5d orbital of Pt have a large overlap between $-4$ and $0$ eV, which greatly changes the electron distribution at the Fermi level.

Similar to the above analysis, to more intuitively display the charge distribution after gas adsorption, the differential charge density was analyzed as shown in Figure 6c. When approaching the N1 system, Pt atoms lose a lot of electrons to the SO$_2$F$_2$ molecule. Therefore, the charge distribution near the S atom becomes dense, corresponding to the previous charge transfer. In the case of the N3 system, the charge transfer is more
distinct, especially near the F–Pt bond; a chemical bond plays a key role in this case. In summary, the surface activity of MoSe₂ is significantly enhanced after Pt₃ modification, and it shows good sensitivity to the SO₂F₂ gas.

2.4. Molecular Orbital Analysis for Gas Molecule Adsorption on the Pt₃-MoSe₂ Monolayer. Molecular orbital analysis was done for SO₂ and SO₂F₂ gas adsorption in M1 and N3 systems. Based on molecular orbital theory, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) distributions of the adsorption system were calculated as shown in Figure 7. The Eₙ between the HOMO and the LUMO was calculated to evaluate conductivity changes, as presented in Table 3.

| structure  | E_HOMO (eV) | E_LUMO (eV) | Eₙ (eV) |
|------------|-------------|-------------|---------|
| Pt₃-MoSe₂  | −3.92       | −3.92       | 0       |
| M1 system  | −4.17       | −4.05       | 0.12    |
| N3 system  | −4.53       | −4.31       | 0.22    |

As the distribution of the HOMO and the LUMO of the Pt₃-MoSe₂ monolayer before and after gas adsorption presented in Figure 7, the distribution of the HOMO and the LUMO mainly locates around the Pt atom and Mo atoms, which is related to their unique metal activity. After Pt₃ modification, both of the HOMO and the LUMO are −3.92 eV, namely zero gap, reflecting that the Pt₃-MoSe₂ material shows good electrical conductivity. In the case of SO₂ gas adsorption in the M1 system, a part of LUMO transfers to the gas molecule, and the Eₙ increases to 0.12 eV. Therefore, the conductivity of the system declines to some extent. As for SO₂F₂ gas adsorption in the N3 system, almost all LUMO on the Se atom transfers to the Pt atom and the SO₂F₂ molecule. The Eₙ has reached 0.22 eV after SO₂F₂ adsorption. Compared with the adsorption of the SO₂F₂ molecule, the bigger Eₙ leads to a larger decrease of conductivity of the entire system. In summary, after adsorbing SO₂ and SO₂F₂ gas molecules, the surface conductivity of the Pt₃-MoSe₂ material decreases in different ranges. As a new type of two-dimensional material, the Pt₃-MoSe₂ monolayer provides excellent adsorption properties to SO₂ and SO₂F₂.

3. CONCLUSIONS
The platinum-cluster-modified MoSe₂ (Pt₃-MoSe₂) monolayer has been proposed as a gas sensing material to detect SO₂ and SO₂F₂ based on first-principles calculations. Both of SO₂ and SO₂F₂ adsorption on the Pt₃-MoSe₂ molecule belongs to chemisorption. The adsorption energies of their optimized adsorption structures are −1.73 and −3.51 eV, respectively. From the analysis of DOS and molecular orbital theory, Pt cluster modification improves the surface activity and conductivity of MoSe₂-based materials. After the adsorption of SF₆ decomposition products on Pt₃-MoSe₂, the conductivity of the system obviously declines to some extent, verifying that Pt₃-MoSe₂ is sensitive to both of the gases. The simulation results show that Pt₃-MoSe₂ could be a very suitable material for SO₂ and SO₂F₂ adsorption and gas sensing, which lays the foundation for designing Pt₃-MoSe₂ monolayer-based gas sensors. In summary, our calculations suggest that Pt₃-MoSe₂-based gas sensors can be employed in GIS for partial discharge detection.

4. COMPUTATIONAL METHODS
The entire computations in this work were conducted in DMol³ based on DFT. A periodic boundary model with a supercell of 4 × 4 × 1 and a vacuum slab of 20 Å was used to avoid the influence of the adjacent supercell. Generalized gradient approximation (GGA) of the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional was taken in this work. The Brillouin-zone was carried out by the Monkhorst–Pack scheme with a k-point set to 7 × 7 × 1, which presents a good approximation for Pt₃-MoSe₂. The double numerical plus polarization basis set (DNP) and the DFT semicore pseudopotential (DSSP) method have been applied. The displacement, maximum stress, and energy convergence were set to 5 × 10⁻³ Ha, 2 × 10⁻³ Ha/Å, and 1 × 10⁻⁵ Ha, respectively. For the stationary electronic structure, a convergence criterion of 1.0 × 10⁻⁶ Ha for self-consistent field tolerance was employed.

To analyze the adsorption properties of the Pt₃-MoSe₂ surface, the geometries of SO₂, SO₂F₂, and intrinsic MoSe₂ surfaces were first optimized. Then, Pt₃ cluster modification was considered to obtain improved adsorption performance. Adsorption energy, charge transfer, and molecular orbital analysis were analyzed.

The adsorption energy (E_ads) shows the change of total energy during the adsorption process, which can be calculated by eq 1

\[ E_{\text{ads}} = E_{\text{surf/gas}} - E_{\text{surf}} - E_{\text{gas}} \]  

(E_{\text{surf/gas}} shows the total energy of the system after gas molecule adsorption, E_{\text{surf}} indicates the total energy of the Pt₃-MoSe₂ monolayer before adsorption, and E_{\text{gas}} represents the total energy of the isolated gas molecules before adsorption. If E_{\text{ads}} < 0, the adsorption process is exothermic and occurs spontaneously. To analyze the charge transfer in the adsorption process, Mulliken population analysis was used to obtain the charge redistribution and calculate the charge transfer amount. As shown in eq 2, the charge transfer (Qₚ₃) was used to evaluate the amount of charge transfer between the Pt₃-MoSe₂ monolayer and gas molecules during gas adsorption, where Qₐ and Qₐ are the net charge of gas molecules after and before gas adsorption.

\[ Q_{\text{f}} = Q_{\text{a}} - Q_{\text{b}} \]  

As shown in eq 3, the energy gap (Eₙ) of the molecular orbital between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) was calculated to evaluate the change of conductivity, where E_{\text{HOMO}} and E_{\text{LUMO}} represent the energy of the HOMO and the LUMO, respectively.

\[ E_{\text{n}} = |E_{\text{LUMO}} - E_{\text{HOMO}}| \]

![Image](https://dx.doi.org/10.1021/acsomega.0c00922)

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