Gas Sensing Mechanism and Adsorption Properties of C$_2$H$_4$ and CO Molecules on the Ag$_3$–HfSe$_2$ Monolayer: A First-Principle Study

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The detection of dissolved gases in oil is an important method for the analysis of transformer fault diagnosis. In this article, the potential-doped structure of the Ag$_3$ cluster on the HfSe$_2$ monolayer and adsorption behavior of CO and C$_2$H$_4$ upon Ag$_3$–HfSe$_2$ were studied theoretically. Herein, the binding energy, adsorption energy, band structure, density of state (DOS), partial density of state (PDOS), Mulliken charge analysis, and frontier molecular orbital were investigated. The results showed that the adsorption effect on C$_2$H$_4$ is stronger than that on CO. The electrical sensitivity and anti-interference were studied based on the bandgap and adsorption energy of gases. In particular, there is an increase of 55.49% in the electrical sensitivity of C$_2$H$_4$ after the adsorption. Compared to the adsorption energy of different gases, it was found that only the adsorption of the C$_2$H$_4$ system is chemisorption, while that of the others is physisorption. It illustrates the great anti-interference in the detection of C$_2$H$_4$. Therefore, the study explored the potential of HfSe$_2$-modified materials for sensing and detecting CO and C$_2$H$_4$ to estimate the working state of power transformers.

Keywords: the first-principle study, HfSe$_2$ monolayer, Ag$_3$ doping, gas adsorption, transformer oil

INTRODUCTION

Two-dimensional transition metal dichalcogenides (TMDs) have recently emerged as a focus of the scientific community in virtue of their versatile and tunable physical properties (Xu et al., 2013; Duerloo et al., 2014; Si et al., 2020; Ju et al., 2021). Layered transition metal disulfides (LTMDs) own the properties of large specific surface value, high electronic activity, and sensitivity (Choi and Kim, 2018). The properties mentioned previously contribute to the great potential of the chemical sensors. Hafnium dichalcogenides (HfX$_2$, X = S, Se, or Te) belong to middle-gap semiconductors and have a high chemical reactivity and various energy dispersions (Yue et al., 2015; Mirabelli et al., 2016; Mleczko et al., 2017; Cruzado et al., 2021). As a consequence, all the excellent properties mentioned previously embody their future applications in optoelectronics and electronics. As the most important and valuable piece of equipment, the operation status of the oil-immersed power transformers affects the safety and stability of the electric power system operation directly (Gui et al., 2020). The malfunction that occurred in oil or the insulating paper is inevitable during the long-running process of the transformer. The malfunction mainly includes overheating of oil or the insulating paper, arc discharge, partial discharge, and spark discharge (Tang et al., 2020). Under the
effect of electricity and heat, the transformer oil will undergo a chemical reaction and generate gases. The gases generated are mostly hydrocarbons and some other related gases, such as CH₄, C₂H₄, CO₂, and CO. Their composition and contents are closely linked to the type and severity of the transformer faults (Singh and Bandyopadhyay, 2010). Dissolved gas analysis (DGA) could discover the hidden faults sensitively. DGA mainly includes infrared spectroscopy, gas chromatography, Raman spectroscopy, and the gas sensor method (Tran et al., 2018). Due to its simple structure, high reaction sensitivity, low cost, and low power consumption, the gas sensor method is proposed to be applied for detecting gases by more and more scientists (Wei et al., 2020).

HfSe₂ has the atomic stacking structure with a layer of Hf atoms stuck in the middle of two layers of Se atoms. Cui et al. explored the adsorption behavior of Pd-doped and Pt-doped HfSe₂ monolayers upon several kinds of gases, such as NO₂, SO₂, and SO₂F₂ (Cui et al., 2020a; Cui et al., 2020c). It is found that the Pd-doped monolayer behaves better for NO₂, while the Pt-doped HfSe₂ monolayer behaves better for SO₂. Wang et al. studied the adsorption nature and behavior of Rh-doped HfSe₂, and it shows a stronger interaction between the SO₂ molecule and the monolayer than SO₂F₂ (Wang and Liao, 2019). Wu et al. studied the doping behavior of Pd atoms and the sensing character of the Pd-doped HfSe₂ (Pd–HfSe₂) monolayer upon CO and C₂H₄ (Wu et al., 2022). They found that the Pd-doped HfSe₂ monolayer possesses a better adsorption behavior on CO. Yang et al. investigated the adsorption of CO, C₂H₂, and C₂H₄ based on the Cu-doped Se-vacant MoSe₂ (Cu–MoSe₂) monolayer (Yang et al., 2020). But Cu–MoSe₂ is not selective for the detection of C₂H₄. Xu et al. explored four characteristic dissolved gases in transformer oil: H₂, CH₄, C₂H₂, and C₂H₄ (Xu et al., 2020). It was found that the adsorption effects on C₂H₂ and C₂H₄ are stronger than those of the others. Speaking of the methods of modifying the material monolayer, Asif et al. integrated positively charged semiconductive sheets of Zn-NiAl LDH and negatively charged layers of rGO to modify the glassy carbon electrode (Asif et al., 2019a). The modified electrode exhibited excellent electrocatalytic activity. The doping formation of the Ag₃ cluster and the adsorption behavior of C₂H₂ and CO were not explored yet. In this article, the adsorption of C₂H₂ and CO of Ag₃-doped HfSe₂ monolayers was investigated. The doping formation adopted is the Ag₃ cluster, and three atoms contribute to the formation of a stable triangle structure. The results showed that the Ag₃-doped HfSe₂ monolayer behaves better for C₂H₂ adsorption but is inactive for CO.

### RESULTS AND DISCUSSION

#### Analysis of Pristine and the Ag₃-Doped HfSe₂ Monolayer

First, the geometric structure of the free-standing HfSe₂ monolayer was optimized to obtain the most stable configuration, as shown in Figures 1A,B. It holds the atomic stacking structure with a layer of Hf atoms stuck in the middle of two layers of Se atoms (Wang and Liao, 2019). The Hf–Se bond in the intrinsic HfSe₂ monolayer is measured as 2.70 Å, which is

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**COMPUTATIONAL DETAILS**

The first-principle calculations based on the DFT (density functional theory) framework emerged as an important and dominant method in quantum mechanics simulation (Delley, 2000). All the calculations in this article adopted the Dmol³ package in Materials Studio software to establish the adsorption model of pristine and Ag₃-doped HfSe₂ upon C₂H₄ and CO. Moreover, Perdew–Burke–Ernzerhof (PBE) functional with a generalized gradient approximation (GGA) was used for the electron exchange and correlation function (Chen et al., 2019b). To better deal with the van der Waals interactions and the relativistic effect of doped atoms, Tkatchenko and Scheffler’s (TS) method and the DFT semi-core pseudopotential (DSSP) method were employed, respectively. The atomic orbital basis set was described by the double numerical plus polarization (DNP) method (Cui et al., 2020b). The supercell geometry optimizations were calculated under the Monkhorst-Pack k-point mesh of 5 × 5 × 1, while 7 × 7 × 1 was sampled for the more accurate electronic structure calculations. To ensure the precision of total energy, smearing was set as 0.005Ha, and the energy tolerance accuracy, maximum force, and displacement were set as 10⁻⁶ Ha, 2 × 10⁻³ Ha/Å, and 5 × 10⁻³ Å, respectively (Topsakal et al., 2009; Sharma et al., 2018). To mimic a free-standing graphene sheet of HfSe₂, a periodic 4 × 4 × 1 HfSe₂ supercell was established with a 20-Å vacuum region imposed in the direction where the sheet is not periodic, and the vacuum region is large enough to ensure the doping and gas adsorption processes, as well as eliminate the interaction between adjacent units (Yang et al., 2020).

The binding energy \( E_b \), which plays an important role in estimating the most stable configuration, is calculated as follows.

\[
E_b = E_{Ag_3-HfSe_2} - E_{Ag_3} - E_{HfSe_2}. \tag{2-1}
\]

The aforementioned equation represents the total energy of the Ag₃-HfSe₂ monolayer subtracting the total energies of the free-standing sheet of the HfSe₂ and Ag₃ cluster. Comparing the binding energy of different doping sites, the configuration with the lowest binding energy is defined as the most stable one (Asif et al., 2022).

The adsorption energy \( E_{ad} \) generated during the adsorption process is calculated as follows.

\[
E_{ad} = E_{gas/Ag_3-HfSe_2} - E_{gas} - E_{Ag_3-HfSe_2}. \tag{2-2}
\]

Here, in the aforementioned equation, \( E_{gas/Ag_3-HfSe_2} \) represents the total energy of the system of the Ag₃-doped HfSe₂ monolayer with the adsorbed gas molecule. \( E_{gas/Ag_3-HfSe_2} \) and \( E_{Ag_3-HfSe_2} \) mean the energy of the adsorbed gas molecule and the energy of the Ag₃-doped HfSe₂ monolayer, respectively. By comparing the value of the adsorption energy \( E_{ad} \) with 0.8, the type of the adsorption can be judged. If greater than 0.8, it is defined as chemisorption, otherwise, it is physisorption (Liu et al., 2021).
consistent with the articles published previously. Speaking of the performance of Ag₃ doping on the HfSe₂ monolayer, three doped sites were taken into account. They are named T₁se₁ (a tripod site right upside the lower-layer Se atoms), T₁se₂ (right upside the upper-layer Se atoms), and T₁Hf (a tripod site right upside the mid-layer Hf atoms) (Ambrusi et al., 2017; Ju et al., 2017; Mi et al., 2021). As far as the most stable doped configuration, the lower the binding energy (Eₜₐₕ), the more stable is the structure. Eₜₐₕ is calculated as shown in Eq. 2-1, and the lowest one was chosen as the most stable doping system in this article. The Ag₃ cluster favored to be doped through the T₁se₁ site with the numerical value of −2.512 eV, of which the Eₜₐₕ is lower than −1.347 and −1.155 eV for T₁se₂ and T₁Hf, respectively.

As is depicted in Figures 1D,E, there is a slight deformation after the doping of the Ag₃ cluster in the HfSe₂ monolayer, of which the Ag–Se bonds are 2.646, 2.628, and 2.648 Å, respectively. From the result of the Mulliken method (Chen et al., 2019a), it can be seen that the Ag₃ cluster is positively charged by 0.267 e after doping. As is shown in Figure 1F, Ag atoms are surrounded by blue areas, in which the red and blue...
regions indicate electron accumulation and deletion independently (Cui et al., 2019). As a consequence, the analysis of the Mulliken method is in good accordance with the DCD, showing that the Ag₃ cluster is an electron donor. Compared with the bandgap obtained as 0.539 eV of the pristine HfSe₂ monolayer in Figure 2A, Ag₃-HfSe₂ is 0.553 eV with a decrease of 0.14 eV in Figure 2B. In comparison of the pristine and Ag₃-doped HfSe₂’s TDOS, it can be seen that there is a right shift, which is keeping with the result of the bandgap analysis.

As illustrated in Figure 2D, it can be seen from the PDOS that there are several overlapping regions among the Ag-4d, Se-4p, and Hf-5d orbitals at 0~1.5 eV. The PDOS verifies the conclusion that there are strong interactions existing among Ag, Se, and Hf atoms (Hu et al., 2019; Gao et al., 2020). As a consequence, due to the doping performance of the Ag₃ cluster, it is among the Ag-4d, atoms (Hu et al., 2019; Gao et al., 2020). As a consequence, due to the doping performance of the Ag₃ cluster, it is among the Ag-4d, atoms (Hu et al., 2019; Gao et al., 2020).

The most stable adsorption configuration after doping, manifesting the charge transfer from the Ag₃ cluster to the Se and Hf atoms (Yang et al., 2019). In terms of the adsorption site of different gases upon the pristine HfSe₂ monolayer and Ag₃-HfSe₂ monolayer, all the possible adsorption sites were taken into account, but only the site with the lowest adsorption energy was adopted for further study (Zhang et al., 2009).

As for the adsorption of CO molecules on the pristine HfSe₂ monolayer, three different adsorption directions were simulated. The molecule accessed the Se atoms via C and O atoms vertically and parallelly to the monolayer, respectively (Ma et al., 2016). As shown in Table 1, C atoms tend to be adsorbed by Se atoms in the upper layer of the pristine HfSe₂ monolayer, with a distance of 4.055 Å between C and Se atoms. The length is significantly longer than the sum of the C and Se atoms’ covalent radii, verifying the existence of the C-Se bond (Zhou et al., 2018b). For the adsorption of CO on the pristine HfSe₂ monolayer, the adsorption energy is 0.159 eV, which is less than 0.8 eV and to be defined as physisorption. The amount of charge transfer Qₜ between the monolayer and CO molecule is very weak, with a value of 0.004 e. It includes 0.019 e of the C atom and −0.0105 e of the O atom (Late et al., 2014). Similarly, the DCD shown in Figure 3C reveals that the C atom and O atom are surrounded by blue and red areas, which is consistent with the Mulliken analysis. Furthermore, the bandgap, calculated as 0.691 eV, has an increase of 0.067 eV. As a consequence, based on the analysis mentioned previously, the adsorption effect of CO on the pristine monolayer is poor.

For the adsorption sites on the pristine monolayer of C₂H₄, two possible sites were investigated to simulate, with C₂H₄ being vertical and parallel to the upper layer (Qian et al., 2020). According to the calculated adsorption energy, it is the site that in a parallel direction holds the lowest energy. The C₂H₄ molecule is arrested by the Se atom, with a distance of 3.39 Å between C and Se atoms, which is longer than the sum of their covalent radii (Gao et al., 2019). The charge transfer Qₜ generated by the CO molecule is −0.015 e, including −0.378 e of C atoms and 0.363 e of H atoms, which is consistent with the DCD shown in Figure 3F. Compared with the monolayer before the adsorption, there is an increase of 0.067 eV for the bandgap. In terms of the adsorption energy, it is 0.3437 eV that reveals the property of physisorption, which is below the standard of 0.8 eV (Zhou et al., 2018a). By reason of the foregoing analysis, the adsorption capacity of the pristine monolayer for C₂H₄ is not very well either.

### Analysis of Gas Adsorption on the Pristine HfSe₂ Monolayer

After investigating the doping performance of the Ag₃ cluster, the adsorption behaviors of the pristine HfSe₂ monolayer upon CO and C₂H₄ were investigated as follows. In terms of the adsorption site on the pristine monolayer of C₂H₄, there is a right shift is observed for the TDOS state of the CO adsorbed system after adsorption. By

| Adsorbed gas | Bond length (Å) | Mulliken charge (e) | Q(e) | E_ads (eV) | d(Å) |
|--------------|----------------|---------------------|------|-----------|------|
| CO           | C-O 1.141      | C 0.108             | 0.004 | −0.159    | 4.055|
| C₂H₄         | C₁-C₂ 1.337    | C₁ −0.194           | 0.028 | −0.344    | 3.389|
|              | C₂-H₄ 1.092    | C₂ −0.196           |       |           |      |
|              | H₁ 0.102       | H₁ 0.101            |       |           |      |
|              | H₂ 0.101       | H₂ 0.101            |       |           |      |
|              | H₄ 0.101       | H₄ 0.101            |       |           |      |

### Adsorption Properties of Ag₃-HfSe₂

With regard to the adsorption of the doped monolayer, the adsorption of CO upon the Ag₃-doped monolayer was investigated first. The most stable adsorption configuration is as same as the pristine one. As is depicted in Figure 4A, there is a slight deformation in the configuration after doping, manifesting the reduction of the distance between the C atom and dopant, elongated from that of 4.055 Å in the pristine system to 3.65 Å. But the distance measured as 3.65 Å is still similarly longer than the sum of the covalent radii (Cortés-Arriagada et al., 2018). Although E_ads is raised to 0.388 eV, its property is still defined as physisorption.

Figure 5B exhibits the total TDOS distribution of the adsorption system of CO, where a right shift is observed for the TDOS state of the CO adsorbed system after adsorption. By
FIGURE 3 | Geometric and electronic structures of the adsorption system of CO and C$_2$H$_4$ on the intrinsic monolayer. (A–C) Adsorption system of CO and related DCD. (D–F) Adsorption system of C$_2$H$_4$ and related DCD.

FIGURE 4 | Geometric and electronic structures of the adsorption system of CO and C$_2$H$_4$ on the doped Ag$_3$–HfSe$_2$ monolayer. (A,B) Adsorption system of CO and related DCD. (C,D) Adsorption system of C$_2$H$_4$ and related DCD.
analyzing the band structure of the system after the adsorption of CO, it was found that the bandgap is 0.554 eV, which is shown in Figure 5A. Furthermore, as is shown in Table 2, there is 0.014 e transferred from the doped system to the CO molecule based on the analysis of Mulliken atomic charges (Allian et al., 2011). Combined with the Mulliken analysis, the demonstration of the DCD shown in Figure 5B is logical, in which the Ag atoms are surrounded by blue areas. In other words, the dopant Ag$_3$ cluster plays an important role as an electron donator in the system. According to the PDOS in Figure 5C, it can be found that the Ag-4d orbital is highly hybrid with the C-2s and C-2p orbitals at $-5.4$ eV, whereas the Ag-5s orbital is hybrid with the C-2p orbital at $-1.0$ eV (Khan Musa et al., 2020). Also, after the adsorption of the CO molecule, the bandgap of the adsorbed system is raised to 0.554 eV, which has an increase of 0.015 eV.

As a consequence, compared with the pristine system, there is a rise in the absolute value of the change in the bandgap. The change of the electronic parameters of the monolayer after the adsorption of CO molecules could be observed. Compared to the adsorption energy, adsorption distance, and charge transfer with those of pristine mentioned before, it can be seen that the adsorption performance of CO has been improved to a certain extent but is not ideal (Zhang et al., 2017). To draw a conclusion, it is not suitable for Ag$_3$-doped HfSe$_2$ either as a sensor material or as an adsorbent.

**Adsorption of the C$_2$H$_4$ Molecule on the Ag$_3$-Doped HfSe$_2$ Monolayer**

To better investigate the property of the adsorption of the C$_2$H$_4$ molecule upon the doped monolayer, three possible adsorption sites and directions were considered. They are as follows, approaching the Ag$_3$ cluster in a parallel way and in a vertical way but in two different directions, respectively. Compared with the results of the adsorption energy for different sites, it is the parallel way that holds the lowest value, which is calculated as $-0.911$ eV. After adsorption, it can be seen that the gas molecule is arrested by the dopant Ag$_3$ cluster. The detailed adsorption performance may be depicted, as in Figure 4C, in which the distance between the C atom and Ag atom is measured as 2.400 Å. It confirms that the interaction exists between the C and Ag atoms, and the structure has an obvious change. From the DCD

| Adsorbed gas | Bond length (Å) | Mulliken charge (e) | Q(e) | $E_{ads}$ (eV) | d(Å) |
|-------------|----------------|----------------------|-----|----------------|------|
| CO          | C-O            | 1.143                | C   | 0.0491         | 3.652|
|             |                |                      | O   | $-0.031$       |      |
|             |                |                      |     | $-0.388$       |      |
| C$_2$H$_4$  | C$_1$-C$_2$    | 1.367                | C$_1$| $-0.191$       | 2.200|
|             | C$_1$-H$_1$    | 1.092                | C$_2$| $-0.188$       | 0.221|
|             | C$_1$-H$_3$    | 1.092                | H$_1$| 0.152          |      |
|             | C$_2$-H$_3$    | 1.092                | H$_2$| 0.162          |      |
|             | C$_3$-H$_4$    | 1.091                | H$_3$| 0.143          |      |
|             | H$_4$          |                      |     | 0.143          |      |
in Figure 4D, it can be observed that the C atoms are surrounded by red areas, and the H atoms are surrounded by blue areas. It means that the H and Ag atoms act as electron donators (Wang et al., 2020). As is shown in Figure 6A, the band structure reveals that the bandgap of the adsorption system is 0.674 eV, which has an increase of 0.156 eV. Compared with the band structure before the adsorption, it can be found that it becomes denser and adds more impurity tracks. It widens the impurity band of the adsorption system, makes the transfer of electrons more conducive, and presents a better adsorption effect (Wu et al., 2017). The result obtained from the TDOS in Figure 6B demonstrates that there is a slight right shift, which is coincident with the analysis of the bandgap mentioned earlier. As demonstrated in Figure 6C, the PDOS reveals that there is a hybridization between the C-2p orbital and Ag-5s and Ag-4d orbitals at $-6 \sim -2$ eV. On the basis of the analysis of Mulliken atomic charges, there is 0.221 e transferred from the C$_2$H$_4$ molecule to the doped system.
Moreover, according to the adsorption of the two gases, it can be concluded that the doped Ag$_3$–HfSe$_2$ monolayer is more selective for C$_2$H$_4$ gas molecules. Compared to the electronic properties of the monolayer after the adsorption of CO and C$_2$H$_4$, it can be seen that the latter holds lower adsorption energy, a wider bandgap, and a higher charge transfer capacity. All the properties mentioned previously contribute to its better performance of adsorption. As a consequence, from the aspect of electron property, it is the C$_2$H$_4$ system that holds the stronger interaction compared with the CO system. This also indicates its strong potential for applying gas sensing for detecting C$_2$H$_4$ gas molecules (Chen et al., 2020).

### Analysis of the Frontier Molecular Orbital Theory

On the basis of the electronic mechanism, the dopant changes the electrostatic potential on the HfSe$_2$ monolayer because of its different electron affinities. It contributes to a change in the height of the surface potential barrier or a corresponding change in the resistance value of the semiconductor. Gas molecules are trapped on the monolayer by the Ag$_3$ cluster, and the dopant could be defined as a catalyst during the adsorption process (Asif et al., 2019b). It means the dopant can enhance the adsorption nature of gas molecules and accelerate the sensing electron exchange. Based on the frontier molecular orbital theory, the reasons that affect the conductivity change can be reacted directly (Liao et al., 2021). As is known, the resistive gas sensor demonstrates the effect of adsorption on different gas molecules by detecting the resistance change of the material (Asif et al., 2018). As is depicted in **Figure 7**, it shows the highest occupied orbital (HOMO) and the lowest free orbital (LOMO) before and after the adsorption of C$_2$H$_4$ and CO molecules on pristine and doped HfSe$_2$. Compared with the pristine substrate material, the difference value between the LOMO and HOMO has a slight increase, which is 0.11 and 0.10 eV, respectively. **Figure 7** shows the frontier molecular orbital of the doped system, in which the corresponding bandgap between the LOMO and HOMO is 0.52 eV. Moreover, the LOMO and HOMO orbitals are mainly distributed on the side of the doped sites of the Ag$_3$ cluster. However, the distribution of the LOMO and HOMO is stretched to the C$_2$H$_4$ and CO molecules obviously after the interaction between Ag$_3$–HfSe$_2$ and adsorbed gas molecules. During the adsorption process of the doped system, there have been incremental changes to various extents, which are 0.15 and 0.03 eV for C$_2$H$_4$ and CO systems, respectively. In accordance with the molecular orbital theory, the decrease in the bandgap means that the charge transfer of the system is harder. In other words, at a constant temperature, the wider the forbidden band, the harder it is for the electrons to be transferred from the valence band to the conduction band. As a result, from a macro point of view, it is demonstrated as an increase in the resistance but a decrease in the conductivity (Wu et al., 2022). The relation between resistivity and bandgap can be described as follows.

$$\sigma \propto e^{-E_g/2k_BT}.$$  \hspace{1cm} (3 – 1)

### TABLE 3 | Desorption time (s) of the adsorbed gas under different test temperatures.

| Temperature(K) | CO–HfSe$_2$ | CO–Ag$_3$–HfSe$_2$ | C$_2$H$_4$–HfSe$_2$ | C$_2$H$_4$–Ag$_3$–HfSe$_2$ |
|---------------|-------------|-------------------|-------------------|-------------------|
| 298           | $4.79 \times 10^{-10}$ | $3.59 \times 10^{-6}$ | $6.47 \times 10^{-7}$ | 2.603.7408        |
| 358           | $1.70 \times 10^{-10}$ | $2.86 \times 10^{-7}$ | $6.87 \times 10^{-6}$ | 6.7917           |
| 418           | $8.15 \times 10^{-11}$ | $4.71 \times 10^{-8}$ | $1.39 \times 10^{-8}$ | 0.09774          |

**FIGURE 8** | Electrical sensitivity of (A) CO and (B) C$_2$H$_4$ on pristine and doped adsorption systems. (C) Comparison of the adsorption energy of different gases.
Here, \( \sigma \) and \( E_g \) are the conductivity and bandgap of the sensing material, and \( T \) and \( K_B \) mean the Boltzmann constant and the temperature, respectively.

### ANALYSIS OF RECOVERY CHARACTERISTICS AND ELECTRICAL SENSITIVITY

Last but not the least, it is the recovery properties that must be considered for the sensing materials, in which the recovery time is an important reference. Recovery time, also regarded as desorption time, refers to the desorption rate of the adsorbed gas molecules on a gas sensor. Generally speaking, the faster the recovery time, the better is the performance of the gas sensor. The desorption time is defined as formula (4-1).

\[
T = A^{-1} e^{\frac{E_{ad}}{K_B T}}.
\]  

Here, \( T \) and \( A \) represent the desorption time and apparent frequency factor \( 10^{12} \, \text{s}^{-1} \), and \( E_{ad} \) and \( T \) mean the absolute value of the adsorption energy and different test temperatures, respectively. In this article, the test temperatures were defined as 289 K, 358 K, and 418 K, respectively, and the Boltzmann constant is \( 8.62 \times 10^{-5} \, \text{eV/K} \) (Gui et al., 2020). According to the equation given previously, the desorption time of the adsorbed gas \( \text{C}_2\text{H}_4 \) and \( \text{CO} \) under different test temperatures is demonstrated in Table 3. It can be seen that the desorption time reduces gradually with the increase in the test temperature. In other words, to a certain degree, the higher the ambient temperature of the gas sensing elements, the faster the gas detaches from the gas sensing material. The results calculated are consistent with the previous analysis, including the physisorption of \( \text{CO} \) and the electrical sensitivity (ES) that must be considered, which is good performance of adsorption (Aziz et al., 2022).

In addition to the desorption time analyzed previously, it is the electrical sensitivity (\( E_s \)) that must be considered, which is defined in the following equation.

\[
E_s = \left( \sigma_{\text{gas}}^{-1} - \sigma_{\text{Ag3-HfSe2}}^{-1} \right) / \sigma_{\text{Ag3-HfSe2}}^{-1},
\]  

Here, \( \sigma_{\text{gas}}^{-1} \) and \( \sigma_{\text{Ag3-HfSe2}}^{-1} \) represent the electrical conductivity of the \( \text{Ag}_3\text{HfSe}_2 \) monolayer before and after adsorption, respectively. The electrical conductivity could be calculated as in Eq. 4-2. The results of the electrical sensitivity are drawn in Figure 8, from which can be seen that after the doping of the \( \text{Ag}_3 \) cluster, there are obvious promotions for the electrical sensitivity of two gases. In particular, for the adsorption of \( \text{C}_2\text{H}_4 \), the electrical sensitivity changes from 39.71 to 95.2%, revealing its good performance of adsorption (Aziz et al., 2022).

To elucidate the anti-interference for the detection of the \( \text{C}_2\text{H}_4 \) molecule, the adsorption energy of different dissolved gases in oil was compared. The gases are \( \text{H}_2 \), \( \text{CH}_4 \), \( \text{C}_2\text{H}_6 \), \( \text{CO} \), and \( \text{CO}_2 \) respectively. As is shown in Figure 8C, it can be seen that \( \text{C}_2\text{H}_4 \) is below the boundary at \( -0.8 \, \text{eV} \), while other gases are above the boundary. In other words, only the adsorption of \( \text{C}_2\text{H}_4 \) is chemisorption while others are defined as physisorption. As a consequence, it can be concluded that the detection of \( \text{C}_2\text{H}_4 \) based on the \( \text{Ag}_3\text{HfSe}_2 \) monolayer is of great anti-interference (Aziz et al., 2019).

### CONCLUSION

In this article, the adsorption properties of the transformer oil decomposition gases (\( \text{CO} \) and \( \text{C}_2\text{H}_4 \)) upon \( \text{Ag}_3\text{HfSe}_2 \) are investigated theoretically on the basis of the first principle. The electronic behavior of \( \text{Ag}_3\text{HfSe}_2 \) before and after the adsorption is analyzed and discussed by the band structure, DOS, DCD, and the Mulliken analysis. However, the desorption time is calculated through the adsorption energy, and the electrical sensitivity is analyzed through the bandgap and the frontier molecular orbital theory (Das and Shoji, 2011). After analyzing the adsorption behaviors and the response mechanisms of \( \text{CO} \) and \( \text{C}_2\text{H}_4 \), the main conclusions obtained are as follows. For the doping of the \( \text{Ag}_3 \) cluster, the simulation results show that the \( \text{Ag}_3 \) cluster is more inclined to be doped at the site \( T_{se1} \). There are different adsorption interactions between the gases \( \text{CO}, \text{C}_2\text{H}_4, \) and the \( \text{Ag}_3\text{HfSe}_2 \) monolayer, including the strong chemical adsorption of \( \text{C}_2\text{H}_4 \) and the weak physisorption of \( \text{CO} \), respectively. In the adsorption process, \( \text{C}_2\text{H}_4 \) was attracted to transfer electrons to the monolayer of \( \text{Ag}_3\text{HfSe}_2 \), whereas \( \text{CO} \) was just the reverse. After adsorption, the increase in the bandgap contributes to the increase in resistivity of \( \text{Ag}_3\text{HfSe}_2 \), which corresponds to a decrease in conductivity. The resistivity relationship corresponding to the two adsorption systems is as follows: \( \text{C}_2\text{H}_4 > \text{CO} \). After the doping of the \( \text{Ag}_3 \) cluster, the electrical sensitivity has a great change for both the gases, including the change from 39.71 to 50.78% for \( \text{CO} \) and the change from 39.71 to 95.2% for \( \text{C}_2\text{H}_4 \), respectively. Speaking of the anti-interference of the detection for \( \text{C}_2\text{H}_4 \), the adsorption energy of different gases was compared. The results illustrate that the detection for \( \text{C}_2\text{H}_4 \) based on \( \text{Ag}_3\text{HfSe}_2 \) is of great anti-interference. Our investigation highlights the high selectivity and better adsorption performance of \( \text{C}_2\text{H}_4 \) on the \( \text{Ag}_3\text{HfSe}_2 \) monolayer. It provides guidance for expanding the application range of \( \text{HfSe}_2 \) to the sensing materials and analyzes its feasibility to detect transformer oil decomposition theoretically.

### DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/supplementary material; further inquiries can be directed to the corresponding authors.

### AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct, and intellectual contribution to the work and approved it for publication.

### FUNDING

This work has been supported in part by the National Natural Science Foundation of China (Nos. 52077177 and 51507144) and the Fundamental Research Funds for the Central Universities (No. XDJK 2019B021).
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