First-Principles Study for Gas Sensing of Defective SnSe$_2$ Monolayers

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Abstract: We report the interaction between gas molecules (NO$_2$ and NH$_3$) and the SnSe$_2$ monolayers with vacancy and dopants (O and N) for potential applications as gas sensors. Compared with the gas molecular adsorbed on pristine SnSe$_2$ monolayer, the Se-vacancy SnSe$_2$ monolayer obviously enhances sensitivity to NO$_2$ adsorption. The O-doped SnSe$_2$ monolayer shows similar sensitivity to the pristine SnSe$_2$ monolayer when adsorbing NO$_2$ molecule. However, only the N-doped SnSe$_2$ monolayer represents a visible enhancement for NO$_2$ and NH$_3$ adsorption. This work reveals that the selectivity and sensitivity of SnSe$_2$-based gas sensors could be improved by introducing the vacancy or dopants.

Keywords: SnSe$_2$; defect; O-doped; N-doped; gas sensors; first-principle study

1. Introduction

Recently, two-dimensional transition metal dichalcogenide (2D-TMD) materials have gained great attention due to their unique structural and electrical properties. Since graphene was introduced into the research, other families of 2D materials with layered structures are also fast emerging for some better applications. 2D-TMD materials with a narrow tunable band gap and replaceable cation and anion [1–3] are more advantageous than the pristine graphene which lacks band gap. SnSe$_2$, a IV–VI semiconductor, has been widely studied for optoelectronic and thermoelectric applications [4,5]. For example, SnSe$_2$ is used as a high-performance photodetector that shows relatively fast photoresponse at room temperature with a high photo-to-dark ratio [4].

2D-TMDs materials have been applied as gas sensors due to their large surface-area-to-bulk ratio. The layered SnX$_2$ (X = S, Se) nanosheets show a significant sensitivity to individual molecules, such as NO$_2$ and NH$_3$ [3, 6–8]. The SnX$_2$ (X = S, Se)-based gas sensors show a good response to NO$_2$ at room temperature [6–8]. Furthermore, the SnSe$_2$: monolayer shows a higher sensitivity for NO$_2$ molecule adsorption than SnS$_2$ in our related work [7,8]. Also, the charge transfers and the flat band contributed by gas adsorption induces the conductivity difference of the SnSe$_2$: monolayer reported in our previous study [8].

More recently, the doped SnSe$_2$: nanosheets have been widely studied because of its interesting electronic and optoelectronic properties, [9–13]. Huang et al. [9] systematically studied n-type/p-type and isoelectronic doping cases on SnSe$_2$: nanosheets based on density functional theory (DFT). Huang et al. [9] suggest that P and As are not promising candidates for p-type doping because those atoms contribute trap states near the Fermi level (Ef). Although the N atom is a promising candidate for p-type doping which induces states near the valence band maximum (VBM), it is difficult to achieve
the N-doped SnSe\textsubscript{2} in reality. For O-, S-, Te-doped SnSe\textsubscript{2}, the density of states (DOS) of all doped SnSe\textsubscript{2} are similar to that of pristine SnSe\textsubscript{2} monolayer \cite{9}. On the other hand, n-type doping of F, Cl and Br are highly recommended, especially Br, since the states near both the VBM and the conduction band minimum (CBM) result in a high carrier density and conductivity \cite{10–12}. For the gas sensor, the SnSe\textsubscript{2} monolayer demonstrates a high sensitivity and charge transfer to NO\textsubscript{2} \cite{8}.

The defective graphene would enhance sensitivity for gas sensing which has been theoretically and experimentally reported \cite{14,15}. Zhang et al. \cite{14} theoretically reveal that the defective graphene has stronger interaction with CO, NO and NO\textsubscript{2} than the pristine graphene. Also, the B-doped graphene gives the tightest binding with NH\textsubscript{3}. Lee et al. \cite{15} demonstrate the defect-engineered graphene oxide chemical sensors, which exhibit ultrahigh sensitivity for NO\textsubscript{2} and NH\textsubscript{3} from the experimental data. However, there is no related study regarding the gas-sensing properties of the doped SnSe\textsubscript{2} nanosheets.

In this work, on the basis of DFT, we investigate the gas detection properties for NO\textsubscript{2} and NH\textsubscript{3} adsorbed on the defective SnSe\textsubscript{2} monolayer by substitution of the Se site with a single vacancy, O or N atoms. To the best of our knowledge, the gas sensors of the defective SnSe\textsubscript{2} monolayers are investigated for the first time. In order to understand the sensing mechanism, we report adsorption energy, charge transfer, DOS and structural parameters of gas molecules adsorption on defective SnSe\textsubscript{2} monolayers. We also discuss and compare the gas-sensing parameters of defective SnSe\textsubscript{2} monolayers with the pristine SnSe\textsubscript{2} monolayer. We find that the vacancy and doped SnSe\textsubscript{2} monolayer can enhance the selectivity and sensitivity of gas sensing.

2. Method

The SnSe\textsubscript{2} monolayer structure is based on the experimental lattice parameters of bulk SnSe\textsubscript{2} \cite{16}. The initial lattice constants of SnSe\textsubscript{2} monolayer are $a = b = 3.81$ Å and thickness of vacuum is set about 16 Å. All calculated structures contain the fully lattice constants and atom positions optimization. After structure optimization, the lattice constants of the SnSe\textsubscript{2} monolayer are $a = b = 3.87$ Å and the energy gap is 0.78 eV. The Visualization for Electronic and Structural Analysis (VESTA) software is a 3D visualization program for structural models \cite{17}. We use VESTA to show the crystal structure and the defective single layer in this work. The calculation was implemented in the Vienna Ab initio Simulation Package (VASP) and performed by the projector augmented wave (PAW) method with the Perdew–Burke–Ernzerhofer (PBE) generalized gradient approximation (GGA) \cite{18,19}. The SnSe\textsubscript{2} monolayer is constructed with a $3 \times 3 \times 1$ supercell in order to perform gas molecules adsorption calculation. The energy cutoff for a plane-wave basis was set up to 400 eV within the $12 \times 12 \times 1$ Monkhorst–Pack $k$-point grid for all study cases. The energy convergence threshold and force convergence criteria were set to $10^{-5}$ eV per unit cell and 0.01 eV Å$^{-1}$.

We also discussed the vacancy and doped SnSe\textsubscript{2} monolayers that adsorb NO\textsubscript{2} and NH\textsubscript{3} gas molecules. First of all, we put the NO\textsubscript{2} and NH\textsubscript{3} molecules on 3 Å above the Se site or the dopants. We calculated two orientations of N atom, the N atom of gas molecules toward and backward the defective SnSe\textsubscript{2} monolayers, named N-bottom and N-top, respectively. In order to understand the defect effect of SnSe\textsubscript{2} monolayers adsorbing gas molecule, a Se atom was substituted by a vacancy or a dopant atom (N and O). In this paper, the structures of the SnSe\textsubscript{2} monolayers with gas adsorption were relaxed. The initial configurations for gases adsorption on the defective SnSe\textsubscript{2} monolayers are illustrated in Figures S1 and S2 of the supplementary material.

3. Results

3.1. SnSe\textsubscript{2} Monolayers

The pristine 1T phase SnSe\textsubscript{2} monolayer is a hexagonal crystal structure as shown in Figure 1a. A Sn atom is sandwiched between two Se atoms which form a Se–Sn–Se arrangement with ABC stacking as shown in Figure 1e. The defective SnSe\textsubscript{2} monolayer with Se vacancy in the center of supercell is represented in Figure 1b and 1f. Figure 1c and 1g are the defective SnSe\textsubscript{2} monolayer in
which a Se atom is substituted by O atom. Furthermore, Figure 1d and 1h are the defective SnSe2 monolayer in which a Se atom is substituted by a N atom. The O and N dopants are sucked into the vacancy site as shown in Figure 1g and 1h.

Figure 2 is the DOS with or without defects on the SnSe2 monolayer. The pristine SnSe2 monolayer has an indirect band gap of 0.78 eV as shown in Figure 2a, which is consistent with the previous reported value [8, 20]. In the Se-vacancy SnSe2 monolayer, there are occupied states very near E_F as shown in Figure 2b. However, the DOS are very different between the O-doped and the N-doped SnSe2 monolayer. The DOS of the O-doped SnSe2 monolayer is similar to the pristine SnSe2 monolayer with the energy gap 0.84 eV because the states contributed from impurities are far from E_F, as shown in Figure 2c. The resultant impurity state from the doped O atom is near the band edge, above 0.8 eV and below ~0.1 eV denoted by the orange line in Figure 2c. For the N-doped SnSe2 monolayer, the partial density of state (PDOS) induced by the N dopant is near VBM denoted by the blue line in Figure 2d. The DOS of the SnSe2 monolayer with N and O dopant also is consistent with the result of Huang et al. [9].

Figure 1. The structures of different SnSe2 monolayer systems which including the top view of (a) pristine, (b) Se vacancy, (c) O-doped and (d) N-doped SnSe2 monolayer and the side view of (e) pristine, (f) Se vacancy, (g) O-doped and (h) N-doped SnSe2 monolayer, respectively. The Sn, Se, O, and N atom are purple, green, red and grey, respectively.
3.2. Gases Adsorbed on Different SnSe2 Monolayers

In this section, we discuss the most stable configurations of NO2 and NH3 molecules adsorbed on different SnSe2 monolayer systems, which are listed in Table 1.

The adsorption energy ($E_{ad}$) of gas molecules on SnSe2 monolayers is defined as

$$E_{ad} = E_{Gas} + SnSe2 - ESnSe2 - E_{Gas}$$  \hspace{1cm} (1)

where $E_{Gas} + SnSe2$ is the total energy of the gas molecules adsorbed on SnSe2 monolayers, $ESnSe2$ is the total energy of the SnSe2 monolayer and $E_{Gas}$ is the energy of isolated gas molecule. A negative $E_{ad}$ value means that gas molecules on the SnSe2 monolayer is energetically favorable. In our previous work [8], the adsorption energy of NO2 adsorbed on the pristine SnSe2 monolayer is higher than that of NH3 adsorption in theoretical prediction. In experimental demonstrations, the pristine SnSe2 monolayer can detect NO2 in lower concentrations than NH3. Although the value of adsorption energy is not direct and not the only relation to the sensitivity, both of them could coincide in terms of theoretical calculation and experimental measurements. Generally, the $E_{ad}$ values of NO2 on SnSe2 monolayer systems ($-0.29$ to $-2.98$ eV) are larger than NH3 ($-0.13$ to $-0.82$ eV). This indicates that the sensitivity of NO2 is higher than NH3 on SnSe2 monolayers. Moreover, the distance between NO2 and SnSe2 monolayers is smaller than the distance between NH3 and SnSe2 monolayer.

The Bader charge population analysis [21] is summarized in Table 1 where negative $\Delta Q_b$ indicates electron charge transfer from SnSe2 to a gas molecule and a positive $\Delta Q_b$ shows charge transfer from a gas molecule to SnSe2 monolayers. Our calculation shows that the NO2 is an electron charge acceptor, whereas NH3 is an electron charge donor in all of the study cases. Moreover, the absolute values of $\Delta Q_b$ for NO2 adsorbed on SnSe2 monolayers are greater than that for NH3 adsorbed on SnSe2 monolayers.

In Table 1, we use the two parameters, $d_{atom-atom}$ and $h$, to describe the position of gas molecules adsorbed on the SnSe2 monolayers. The $d_{atom-atom}$ means the shortest distance between the lowest atom of a gas molecule and the highest atom of SnSe2 monolayer. The $h$ indicates the vertical distance between them. We mark $d_{atom-atom}$ and $h$ in the structure of gas adsorbed on the SnSe2 monolayers to compare the positions of gas adsorption in different SnSe2 monolayers. This would be shown in following figures. Furthermore, we also discuss the $h$, $E_{ad}$ and $\Delta Q_b$ to analyze the gas-sensing mechanism for defective SnSe2 monolayers as shown in Table 1.

In the following sections, the detail will be discussed about adsorption energy, charge transfer, DOS and structural parameters of gas molecules adsorption on defective SnSe2 monolayers.
Table 1. The most stable structural configurations of different gas molecules adsorbed on SnSe2 monolayer systems. E_ad, d_atom-atom, h and ΔQ_b of molecules adsorbed on the pristine and defective SnSe2 monolayers.

| Gas   | SnSe2 System | Gas Orientation | E_ad (eV) | d_atom-atom (Å) | h (Å)  | ΔQ_b (e) | Source               |
|-------|--------------|----------------|-----------|-----------------|--------|----------|----------------------|
| NO2   | Pristine     | N-top          | -0.29     | 2.97            | 2.45   | -0.164e  | Reference [8]        |
|       | Se vacancy   | N-bottom       | -1.84     | 2.28            | -0.08  | -0.926e  | This work            |
|       | O-doped      | N-top          | -0.32     | 3.05            | 1.75   | -0.145e  | This work            |
|       | N-doped      | N-bottom       | -2.98     | 1.38            | 0.72   | -0.368e  | This work            |
| NH3   | Pristine     | N-bottom       | -0.18     | 3.35            | 2.47   | 0.028e   | Reference [8]        |
|       | Se vacancy   | N-bottom       | -0.82     | 2.90            | 0.45   | 0.016e   | This work            |
|       | O-doped      | N-top          | -0.13     | 3.06            | 1.93   | 0.000e   | This work            |
|       | N-doped      | N-bottom       | -0.36     | 2.46            | 1.45   | 0.215e   | This work            |

3.2.1. NO2 Adsorption

Figure 3 shows the optimized structures of NO2 adsorbed on SnSe2 monolayers, including top views as shown in Figure 3a–d and side views, as shown in Figure 3e–h. When NO2 is adsorbed on the pristine SnSe2 monolayer, the site of NO2 adsorption is near the Se atom, the d_O-Se is 2.97 Å and the orientation is N-top, as shown in Figure 3a and 3e. When NO2 is adsorbed on the Se-vacancy SnSe2 monolayer, the site is near the Sn atom, the d_O-Sn is 2.28 Å and the orientation is N-bottom, as shown in Figure 3b and 3f. The optimized structure of NO2 on the O-doped SnSe2 monolayer is upon the site of the O atom, the d_O-O is 3.05 Å and the orientation is N-top, as shown in Figure 3c and Figure 3g. The optimized structure of NO2 on the N-doped SnSe2 monolayer is located on the N site and the d_N-N is 1.38 Å with the orientation N-bottom, as shown in Figure 3d and 3h. The vertical distances h between NO2 and the defective SnSe2 monolayers are 2.45 Å, 1.75 Å, 0.72 Å, respectively. The negative value of h means the gas molecule is sucked into the SnSe2 monolayer. In conclusion, the values of h between NO2 and the defective SnSe2 monolayer are shorter than NO2 adsorbed on the pristine SnSe2 monolayer. When comparing with orientation and the h, the structures of NO2 adsorbed on the SnSe2 monolayers could divide into two groups. First, the NO2 adsorption on the pristine and O-doped SnSe2 monolayer are both N-top orientation. Second, the NO2 adsorption on the Se-vacancy and N-doped SnSe2 monolayer are both with N-bottom orientation. The values of h are smaller for NO2 adsorption on the Se-vacancy and N-doped SnSe2 monolayer than those on the pristine and O-doped SnSe2 monolayer.

The value of E_ad and ΔQ_b of NO2 adsorbed on the pristine SnSe2 monolayer are −0.29 eV and −0.164e, respectively [8]. Furthermore, the E_ad of NO2 adsorbed on the Se-vacancy and doped SnSe2 monolayer are greater than NO2 adsorbed on the pristine SnSe2 monolayer, as shown in Table 1.

The value of h between NO2 and the Se-vacancy SnSe2 monolayer is −0.08Å. This induces a large adsorption energy and Bader charge because the NO2 molecule is sucked into the vacancy site. The E_ad and ΔQ_b are up to −1.84 eV and −0.926e, respectively, as listed in Table 1. The value of E_ad is greater than the pristine and the O-doped SnSe2 monolayer but smaller than the N-doped SnSe2 system. The value of ΔQ_b = −0.926e of NO2 adsorbed on the Se-vacancy SnSe2 monolayer is the maximum of that on the SnSe2 monolayers. This result indicates that NO2 molecule would strongly interact with the Se-vacancy SnSe2 monolayer.

As mentioned, the structure of NO2 adsorbed on the O-doped SnSe2 monolayer is similar with on the pristine SnSe2 monolayer despite of the O atom replacing the Se atom. In the detail, the value of h between NO2 and the O-doped SnSe2 monolayer is 1.75 Å, which is also a little smaller than that on the pristine SnSe2 monolayer. Furthermore, the O-doped SnSe2 monolayer adsorsbs the NO2 molecule and would induce a little increase in the adsorption energy but decrease the Bader charge by about −0.32 eV and −0.145e, respectively, as shown in Table 1.

When NO2 is adsorbed on the N-doped SnSe2 monolayer, the value of h between NO2 and the N-doped SnSe2 monolayer is 0.72 Å. This indicates that the strong interaction comes from the N-N
atoms interaction between NO2 and the N dopant. The $E_{ad} = -2.98$ eV of NO2 adsorbed on the N-doped SnSe2 monolayer is greater than on the Se-vacancy SnSe2 monolayer. $\Delta Q_b = -0.368$ eV of NO2 adsorbed on the N-doped SnSe2 monolayer is smaller than on the Se-vacancy SnSe2, but greater than the pristine and O-doped SnSe2. The relatively high $E_{ad}$ and $\Delta Q_b$ demonstrate strong interaction between NO2 and the N-doped SnSe2 monolayer.

![Figure 3](image)

**Figure 3.** The most stable configurations of different SnSe2 monolayers adsorbing NO2 molecule. The top view of (a) pristine, (b) Se vacancy, (c) O-doped and (d) N-doped SnSe2 monolayer; the side view of (e) pristine, (f) Se vacancy, (g) O-doped and (h) N-doped SnSe2 monolayer, respectively. The Sn, Se, O, and N atom are purple, green, red and grey, respectively.

The DOS of NO2 adsorbed on different SnSe2 monolayers is shown in Figure 4. The shadowed area is the total DOS. The blue and orange lines are the PDOS of N and O, respectively. The $E_F$ is denoted by a dashed line. DOS of NO2 adsorption on different SnSe2 monolayers, as shown in Figure 4a–d, are quite different to Figure 2a–d without NO2 adsorption cases. This indicates that all the SnSe2 monolayers could induce obvious difference of electronic structure before/after NO2 adsorption.

When NO2 is adsorbed on the pristine SnSe2, the total DOS presents a trap state across $E_F$ in the energy range about $-0.04$ eV to $-0.02$ eV, as shown in Figure 4a. A large amount of PDOS induced by N and O atoms of gas molecule is located in the aforementioned trap state, which induces the flat band and trap electron on it as mentioned in previous work [8]. The pattern of DOS in Figure 4a is different from DOS of the pristine SnSe2 monolayer without adsorption as shown in Figure 2a.

For NO2 adsorption on the Se-vacancy SnSe2 monolayer, the total DOS presents a bandwidth near the $E_F$ with an energy range of $-0.19$ eV to $-0.12$ eV, as shown in Figure 4b. A considerable amount of PDOS contributed by N and O atoms of the gas molecule is located the aforementioned bandwidth. Therefore, the pattern of DOS in Figure 4b is quite different from DOS of the Se-vacancy SnSe2 without adsorption as shown in Figure 2b.

When NO2 is adsorbed on the O-doped SnSe2 monolayer, the total DOS presents a trap state across $E_F$ in the energy range about $-0.06$ eV to $-0.03$ eV, as shown in Figure 4c. A large amount of PDOS induced by N and O atoms of the gas molecule is located in the aforementioned trap state, which corresponds to a flat band. The trap state would trap electrons on it and decrease the carrier mobility. The DOS of NO2 adsorption the O-doped SnSe2 monolayer is very similar with the pristine SnSe2 monolayer, but different from the O-doped SnSe2 monolayer without adsorption as shown in Figure 2c.

For NO2 adsorption on the N-doped SnSe2 monolayer, the total DOS shown in Figure 4d demonstrates a pattern for a semiconductor with an energy gap of about 0.86 eV. The PDOS introduced by N and O atoms of gas molecule below $E_F$ and above 0.86 eV marked in blue and orange lines as shown in Figure 4d, which is quite different from Figure 4a–c. It is worth noting that the peak of PDOS of the N atom near the $E_F$ shifts to $-0.20$ eV when NO2 is adsorbed as shown in Figure 4d. It indicates that PDOS of the N atoms near $E_F$ in Figure 2d are moved to below $E_F$ because the strong interaction occurred after NO2 adsorption.
Figure 4. DOS of NO\textsubscript{2} adsorption on the (a) pristine, (b) Se-vacancy, (c) O-doped and (d) N-doped SnSe\textsubscript{2} monolayer. The shadowed area is the total DOS. The blue and orange lines are the PDOS of N and O, respectively. The EF is denoted by a dashed line and shift to zero.

3.2.2. NH\textsubscript{3}

Figure 5 shows the optimized structures of NH\textsubscript{3} adsorbed on SnSe\textsubscript{2} monolayers, including top views as shown in Figure 5a–d and side views as shown in Figure 5e–h. When NH\textsubscript{3} is adsorbed on the pristine SnSe\textsubscript{2} monolayer, the site is positioned above the Sn atom, the d\textsubscript{N-Se} is 3.35 Å and the orientation is N-bottom as shown in Figure 5a and 5e. When NH\textsubscript{3} is adsorbed on the Se-vacancy SnSe\textsubscript{2} monolayer, the site is positioned above the site of the single vacancy, the d\textsubscript{H-Se} is 2.90 Å and the orientation is N-bottom, as shown in the Figure 5b and 5f. The most stable configuration of NH\textsubscript{3} adsorbed on the O-doped SnSe\textsubscript{2} monolayer is positioned at the O site, the d\textsubscript{H-O} is 3.06 Å and the orientation is N-top as shown in Figure 5c and 5g. The optimized structure of NH\textsubscript{3} adsorbed on the N-doped SnSe\textsubscript{2} monolayer is positioned on the N site, the d\textsubscript{N-N} is 2.46 Å and the orientation is N-bottom as shown in Figure 5d and 5h. It is worth noting that the orientation of NH\textsubscript{3} adsorbed on O-doped SnSe\textsubscript{2} monolayer is different from the other SnSe\textsubscript{2} monolayers, which is N-top orientation but others are N-bottom. The vertical distances h between NH\textsubscript{3} and the different SnSe\textsubscript{2} monolayers are 2.47 Å, 0.45 Å, 1.93 Å, 1.45 Å as shown in Figure 5e–5h, respectively. The values of h of NH\textsubscript{3} adsorbed on the Se-vacancy and doped SnSe\textsubscript{2} monolayer are smaller than NH\textsubscript{3} adsorbed on the pristine SnSe\textsubscript{2} monolayer.

When NH\textsubscript{3} is adsorbed on the pristine SnSe\textsubscript{2} monolayer, the value of h, E\textsubscript{ad} and ΔQ\textsubscript{b} are 2.47 Å, −0.18 eV and 0.028e \cite{8}, respectively. Compared to the value of E\textsubscript{ad} and h in the Table 1, the E\textsubscript{ad} of NH\textsubscript{3} adsorption almost follows a positive correlation to h, except for NH\textsubscript{3} adsorption on the O-doped SnSe\textsubscript{2} monolayer.
When NH$_3$ is adsorbed on the Se-vacancy SnSe$_2$ monolayer, the value of $h = 0.45$ Å is the minimum among NH$_3$ adsorption on SnSe$_2$ monolayers. Furthermore, the value of $E_{ad} = -0.82$ eV of NH$_3$ on the Se-vacancy SnSe$_2$ monolayer reaches the maximum compared with other cases. However, the charge transfer amount $\Delta Q_b = 0.016e$ of NH$_3$ adsorbed on the Se-vacancy SnSe$_2$ monolayer is smaller than gas molecule on the pristine SnSe$_2$ (0.028e).

For NH$_3$ adsorption on the O-doped SnSe$_2$ monolayer, the value of $h = 1.93$ Å between NH$_3$ and the O-doped SnSe$_2$ monolayer is smaller than that on the pristine SnSe$_2$ monolayer. The values of $E_{ad}$ and $\Delta Q_b$ of NH$_3$ on the O-doped SnSe$_2$ monolayer are $-0.13$ eV and 0.000e, which are both the minimum among the NH$_3$ adsorption. This indicates that the ability of NH$_3$ adsorption of the O-doped SnSe$_2$ monolayer is weaker than the pristine SnSe$_2$ monolayer.

For NH$_3$ adsorption on the N-doped SnSe$_2$ monolayer, the value of $h = 1.45$ Å between NH$_3$ and the O-doped SnSe$_2$ monolayer is smaller than that on the pristine SnSe$_2$ monolayer. $E_{ad}$ also has a greater value $-0.36$ eV than that on the pristine SnSe$_2$ monolayer, and $\Delta Q_b$ of NH$_3$ on the N-doped SnSe$_2$ monolayer has a maximum value 0.215e. This shows an enhancement of NH$_3$ adsorption on the N-doped SnSe$_2$ monolayer.

Figure 5. The most stable configurations of different SnSe$_2$ monolayers adsorbing NH$_3$ molecule. The top view of (a) pristine, (b) Se vacancy, (c) O-doped and (d) N-doped SnSe$_2$ monolayer; the side view of (e) pristine, (f) Se vacancy, (g) O-doped and (h) N-doped SnSe$_2$ monolayer, respectively. The Sn, Se, O, N and H atoms are purple, green, red, grey and cyan, respectively.

Figure 6 shows DOS of NH$_3$ adsorption on different SnSe$_2$ monolayers. The blue, orange, cyan lines are the PDOS of N, O, H, respectively. The DOS of NH$_3$ adsorption on the pristine SnSe$_2$ monolayers demonstrates a pattern of a semiconductor with energy gap as shown in Figure 6a. However, the DOS of NH$_3$ adsorption on the defective SnSe$_2$ monolayers presents a flat band as shown in Figure 6b–d.

When NH$_3$ adsorbed on the pristine SnSe$_2$ monolayer, the total DOS shown in Figure 6a demonstrates a pattern for a semiconductor with an energy gap about 0.81 eV. The PDOS introduced by N and H atoms of gas molecules below $E_f$ and above 0.81 eV is marked in blue and cyan lines as shown in Figure 6a. There is no obviously change of the electronic structure of the pristine SnSe$_2$ as shown in Figure 2a, which is consistent with our previous work [8].

When NH$_3$ adsorbed on the Se-vacancy SnSe$_2$ monolayer, the total DOS presents a bandwidth in energy range of $-0.17$ eV to $E_f$ as shown in Figure 6b. The DOS pattern of Figure 6b is a semiconductor with energy gap about 0.27 eV. Only a small amount of PDOS contributed by N and H atoms of gas molecule is located the aforementioned bandwidth. This is so that NH$_3$ adsorption does not induce obvious difference on the DOS of the Se-vacancy SnSe$_2$ without adsorption as shown in Figure 2b.

For the O-doped SnSe$_2$ monolayer with NH$_3$ adsorption, the total DOS presents a flat band below $E_f$ as shown in Figure 6c. A large amount of PDOS contributed by N and H atoms of gas molecules is located in the aforementioned flat band denoted by blue and cyan lines in Figure 6c. Because the
flat band is located below $E_F$, the DOS pattern of Figure 6c is a semiconductor with energy gap about 0.70 eV. Therefore, the NH$_3$ adsorption does not change the pattern of DOS of the O-doped SnSe$_2$ monolayer as shown in Figure 2c.

For the N-doped SnSe$_2$ monolayer with NH$_3$ adsorption, the total DOS presents a trap state across $E_F$ in the energy range about $-0.10$ eV to $-0.03$ eV as shown in Figure 6d. A large amount of PDOS induced by N and H atoms of gas molecules is located in the aforementioned trap state. The trap state responds to a flat band which would decrease the mobility of the SnSe$_2$ systems after gas adsorption. The pattern of DOS in Figure 6d is different from that of the N-doped SnSe$_2$ monolayer without adsorption as shown in Figure 2d.

Comparing the DOS of NH$_3$ adsorption on different SnSe$_2$ monolayers as shown in Figure 6a–d with the SnSe$_2$ monolayers without adsorption as shown in Figure 2a–d, only the N-doped SnSe$_2$ monolayer could induce obvious differences of electronic structure before/after NH$_3$ adsorption.

![Figure 6](image)

**Figure 6.** DOS of NH$_3$ adsorption on the (a)pristine, (b)Se vacancy, (c)O-doped and (d)N-doped SnSe$_2$ monolayer. The shadowed area is the total DOS. The blue, orange, cyan lines are the PDOS of N, O, H, respectively. The $E_F$ is denoted by a dashed line and shift to zero.

## 4. Discussion

We discuss the gas-sensing parameters, including $E_{ad}$ and $\Delta Q_b$, compared to gas molecules adsorbed on the pristine SnSe$_2$ monolayer and have demonstrated the high selectivity and sensitivity of the defective and doped SnSe$_2$ monolayer for gas-sensor candidates. The alteration of electronic structure is reflected by the change in electrical conductance of the SnSe$_2$ monolayers. We also discuss the DOS of gas adsorptions in the SnSe$_2$ monolayers to illustrate the change in the electrical conductance due to alteration of the electronic structure.

### 4.1. Gas Molecules on the Se-Vacancy SnSe$_2$ Monolayer
When NO₂ adsorbed on the Se-vacancy SnSe₂ monolayer, the values of \( E_{\text{ad}} = -1.84 \) eV and \( \Delta Q_b = -0.926e \) were the maximum among that of the SnSe₂ monolayers. This reveals strong interaction between NO₂ molecule and the Se-vacancy SnSe₂ monolayer. For the Se-vacancy SnSe₂ monolayer, NO₂ adsorption induces wide-ranging trap states crossover \( E_F \) to decrease the carrier mobility as represented by the pattern of DOS in Figure 4b.

However, the NH₃ molecule is adsorbed on the Se-vacancy SnSe₂ monolayer with higher \( E_{\text{ad}} = -0.82 \) eV and lower \( \Delta Q_b = 0.016e \) compared to the pristine SnSe₂ monolayer \( (E_{\text{ad}} = -0.18 \) eV, \( \Delta Q_b = 0.028e \) [8]). NH₃ adsorption on the Se-vacancy SnSe₂ monolayer contributes DOS below \( E_F \), as shown in Figure 6b. However, the charge transfer amount of NH₃ on the Se-vacancy SnSe₂ monolayer is smaller than that of NH₃ on the pristine SnSe₂ monolayer. Therefore, we cannot be sure of the conductivity difference of the Se-vacancy SnSe₂ monolayer with/without NH₃ adsorption.

The Se-vacancy SnSe₂ monolayer shows excellent sensitivity for NO₂ molecules, whereas the Se-vacancy SnSe₂ monolayer cannot show obvious conductivity difference for NH₃ adsorption. In brief, the Se-vacancy SnSe₂ monolayer shows enhancement only for NO₂.

4.2. Gas Molecules on the O-Doped SnSe₂ Monolayer

When NO₂ adsorbed on the O-doped SnSe₂ monolayer, the values of \( E_{\text{ad}} = -0.32 \) eV and \( \Delta Q_b = -0.145e \) are close to the molecule on the pristine SnSe₂ monolayer \( (E_{\text{ad}} = -0.29 \) eV, \( \Delta Q_b = -0.164e \) [8]). The DOS of the O-doped SnSe₂ monolayer is similar to that of the pristine SnSe₂ monolayer, so that the similar appearance of DOS occurs in NO₂ adsorption on the pristine and O-doped SnSe₂ monolayer as shown in Figure 4a and Figure 4c. The DOS of NO₂ on the O-doped SnSe₂ monolayer induces trap state crossover \( E_F \) and decreases the carrier mobility. The electronic structure altered by NO₂ adsorbed on the O-doped SnSe₂ monolayer would contribute a change of electrical conductance, just like NO₂ adsorption on the pristine SnSe₂ monolayer [8].

On the other hand, the value of \( E_{\text{ad}} = -0.13 \) eV and \( \Delta Q_b = 0.000e \) for NH₃ on the O-doped SnSe₂ monolayer are both the minimum among the NH₃ adsorption. The DOS of NH₃ on the O-doped SnSe₂ monolayer is below the \( E_F \), which results in similar electrical properties with the O-doped SnSe₂ monolayer without gas adsorption. This means that there is no obvious change of electrical conductance.

In conclusion, gas molecules on the O-doped SnSe₂ monolayer shows high sensitivity for NO₂ adsorption and even with a weaker detection for NH₃ compared to gases on the pristine SnSe₂. This result indicates that the O-doped SnSe₂ monolayer has better selectivity to these two gases in comparison with pristine SnSe₂.

4.3. Gas Molecules on the N-Doped SnSe₂ Monolayer

When NO₂ adsorbed on the N-doped SnSe₂ monolayer, \( E_{\text{ad}} = -2.98 \) eV is the maximum among the NO₂ adsorption and \( \Delta Q_b = -0.368e \) has relatively high value. It indicates that the strong interaction occurred between NO₂ molecule and the N-doped SnSe₂ monolayer. Moreover, the DOS of the N-doped SnSe₂ monolayer before/after NO₂ adsorption are totally different, as shown in Figure 2d and Figure 4d. Compared to the DOS of the N-doped SnSe₂ monolayer before/after NO₂ adsorption, the DOS crossover \( E_F \) of the N-doped SnSe₂ moves to below the \( E_F \).

When NH₃ is adsorbed on the N-doped SnSe₂ monolayer, \( E_{\text{ad}} = -0.36 \) eV also has a greater value than that on the pristine SnSe₂ monolayer and \( \Delta Q_b = 0.215e \) has a maximum value. In the DOS of NH₃ adsorbed on the N-doped SnSe₂ monolayer, the trap state is induced to decrease the carrier mobility. This implies that there would be an obvious change of electrical conductance. The N-doped atom is high sensitivity gas sensor for NO₂ and NH₃ shown as in our DFT calculation.

When setting gas molecules on the N-doped SnSe₂, it reveals obvious enhancement for both NO₂ and NH₃ adsorption.

5. Conclusions
In summary, the adsorption of NO\textsubscript{2} and NH\textsubscript{3} on the Se-vacancy, O-doped and N-doped SnSe\textsubscript{2} monolayer are investigated and compared to the pristine SnSe\textsubscript{2} monolayer. Due to the high adsorption energy and large charge transfer of gas adsorption on the Se-vacancy SnSe\textsubscript{2} monolayer, the Se-vacancy SnSe\textsubscript{2} monolayer shows a better sensitivity only to NO\textsubscript{2}. However, the sensitivity of NH\textsubscript{3} adsorbed on the Se-vacancy SnSe\textsubscript{2} monolayer has higher adsorption energy but lower charge transfer amount than the pristine SnSe\textsubscript{2} monolayer. Furthermore, the O-doped SnSe\textsubscript{2} monolayer has similar interaction with NO\textsubscript{2} with the pristine SnSe\textsubscript{2} monolayer, but weaker interaction with NH\textsubscript{3} than the pristine SnSe\textsubscript{2} monolayer. This indicates that the O-doped SnSe\textsubscript{2} monolayer has similar sensitivity to the pristine SnSe\textsubscript{2} monolayer and better selectivity than the pristine SnSe\textsubscript{2} monolayer. The N-doped SnSe\textsubscript{2} strongly interacts both with NO\textsubscript{2} and NH\textsubscript{3} and shows obvious sensing enhancement for those two gases. In brief, the vacancy and doped SnSe\textsubscript{2} monolayers can enhance the selectivity and sensitivity of gas sensing for NO\textsubscript{2} and NH\textsubscript{3} molecules. This work demonstrates the potential of the SnSe\textsubscript{2}-based gas sensors by introducing defects and dopants in the SnSe\textsubscript{2} monolayer.

**Supplementary Materials:** The following are available online at www.mdpi.com/2076-3417/10/5/1623/s1: Figure S1: The initial configurations of the defective SnSe\textsubscript{2} monolayers adsorbing NO\textsubscript{2} molecule with N-top and N-bottom orientations, Figure S2: The initial configurations of the defective SnSe\textsubscript{2} monolayers adsorbing NH\textsubscript{3} molecule with N-top and N-bottom orientations.

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