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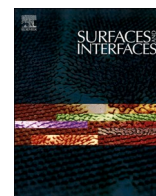
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Strain-engineered S-HfSe₂ monolayer as a promising gas sensor for detecting NH₃: A first-principles study

Huiru Yang^{a,b}, Junfeng Li^b, Ziyuan Shao^b, Chunjian Tan^c, Chenshan Gao^b, Hongyuan Cui^d, Xiaosheng Tang^e, Yufei Liu^d, Huaiyu Ye^{b,d,*}, Guoqi Zhang^f

^a Harbin Institute of Technology, Harbin 150001, China

^b School of Microelectronics, Southern University of Science and Technology, Shenzhen 518055, China

^c Electronic Components, Technology and Materials, Delft University of Technology, Delft 2628 CD, the Netherlands

^d College of Optoelectronic Engineering, Chongqing University, Chongqing 400044, China

^e College of Optoelectronic Engineering, Chongqing University of Posts and Telecommunications, Chongqing 400065, China

^f Department of Microelectronics, Faculty of Electrical Engineering, Mathematics and Computer Science, Delft University of Technology, Delft 2628 CD, the Netherlands

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ABSTRACT

The development of high-performance gas sensing materials is one of the development trends of new gas sensor technology. In this work, in order to predict the gas-sensitive characteristics of HfSe₂ and its potential as a gas-sensitive material, the interactions of nonmetallic element (O, S, Te) doped HfSe₂ monolayer and small molecules (NH₃ and O₃) have been studied by first-principles based on density functional theory. The results show that the adsorption of NH₃ and O₃ on pristine HfSe₂ monolayer is weak, and the adsorption strength can be significantly improved by doping O. And O-HfSe₂ is chemical adsorption to O₃ with large adsorption energy and transfer charge, and the band gap of O-HfSe₂ disappears after adsorbing O₃, indicating that the adsorption of O₃ has a significant effect on the electrical properties of the substrate. These mean that O₃ is difficult to recover from the substrate surface, thus preventing O-HfSe₂ from developing into a sensitive material for O₃ detection. After doping S, the charge transfers and adsorption strength to NH₃ are the largest, but it is still small. So, the strain effect on the S-HfSe₂/NH₃ adsorption system is also studied. The results indicate that the adsorption strength of S-HfSe₂ to NH₃ can be enhanced by stretching S-HfSe₂ along x-axis. After absorbing NH₃, the conductivity of x-axis strained S-HfSe₂ changes, which suggest its sensitivity. And the predicted recovery times of S-HfSe₂ surfaces with $\epsilon_x=4\%$, 6% and 8% are 0.027 s, 1.153 s and 102.467 s, respectively, which suggests that the S-HfSe₂ monolayer has the potential to be developed as a sensitive material for NH₃ detection. These adsorption mechanism studies can also serve as a theoretical foundation for the experimental design of gas-sensing materials.

1. Introduction

Gas sensors can detect gas concentration and composition, which is critical in environmental protection and safety monitoring. Gas sensors are now widely used to detect toxic, hazardous, explosive, and volatile substances, as well as to monitor the greenhouse effect and air pollution [1–3]. In the face of more and more special signals and special environments, the development of high-performance gas sensing materials is one of the development trends of new gas sensor technology. Due to their excellent mechanical, electrical, and optical properties, such as ultra-high carrier mobility, tunable band structure and gas sensing

properties, two-dimensional (2D) materials have attracted the attentions of researchers in the field of gas-sensitive materials [4–6]. In particular, two-dimensional transition metals disulfides (TMDs; MX₂; M = Mo, W; X = S, Se) are promising gas sensing materials that attracts attention due to their large specific surface area, excellent electrical properties, and active surface [7,8]. Perhaps the most attractive feature of TMDs-based gas sensors is their ability to detect gas molecules at room temperature (RT), which stems from the unique electronic properties presented by the two-dimensional atomic structure. Based on this unique feature, the TMDs can be used as low-power gas sensors.

To date, TMDs materials such as MoS₂ [9,10], MoSe₂ [11,12], WS₂

* Corresponding author at: School of Microelectronics, Southern University of Science and Technology, Shenzhen 518055, China.

E-mail address: h.ye@tudelft.nl (H. Ye).

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[13,14], WSe_2 [15] have been extensively studied for gas sensing. Guo et al. [12] fabricated a high-performance epidermal gas detector based on MoSe_2 nanosheets that can monitor NO_2 and NH_3 at room temperature and respond quickly. Kumar et al. [10] review and discuss the results of MoS_2 -based gas sensors, indicating that 2D MoS_2 could be a promising material for developing high-performance room-temperature gas sensors. Modifying the surface of TMDs is also desirable in order to improve and optimize device performance. Surface modification techniques include the use of dopants to replace or bond to specific atoms in the substrate material. Baek et al. [16] functionalized the MoS_2 surface with Pd, fabricating a sensor with high sensitivity to hydrogen. Through the sulfurization of WSe_2 , Kim's team [17] created a large-area uniform $\text{WS}_{2-x}\text{Se}_{2-2x}$ alloy, and the results indicated that the large-area $\text{WS}_{2-x}\text{Se}_{2-2x}$ alloy's gas sensing capability was significantly improved.

While other kinds of TMDs are less studied, such as HfX_2 and ZrX_2 ($\text{X} = \text{S}, \text{Se}$ and Te). HfSe_2 monolayer with high carrier mobility and small band gap has been predicted theoretically [18,19], and the monolayer has been successfully prepared through experiments [20,21], which indicates that it has the potential to be used as a gas sensing material. Cui Hao et al. [22,23] have studied the adsorption behavior of intrinsic, Pd-doped and Pt-doped HfSe_2 monolayer to some toxic gases (SOF_2 , SO_2 , NO_2) by first-principles. However, there is a lack of research on other small molecules. Ammonia (NH_3) is a very important raw material in many fields such as industry, agriculture, food processing, medicine [24, 25]. But NH_3 is also a harmful gas that can cause serious harm to the body even in low concentrations by injuring the skin, eyes, throat, or lungs [26,27]. Ozone (O_3) also belongs to this type of gas, which has a very important impact on people's lives. Besides being used for water purification and disinfection, O_3 is also widely used for disinfection in the food and pharmaceutical industries [28,29]. However, excess ozone can have many adverse effects on human health, ecosystems and agricultural production [30,31]. Therefore, in the field of production and life, the monitoring of O_3 and NH_3 content is particularly important.

Herein, for the first time, we construct adsorption models of NH_3 and O_3 adsorption on pristine and X-doped ($\text{X}=\text{O}, \text{S}$, and Te) HfSe_2 monolayer surface, and calculate the adsorption behaviors to explore their potential as NH_3 and O_3 gas sensors. The adsorption strength of the X- HfSe_2 /gases system is higher than that of pristine HfSe_2 , with O- HfSe_2 having the highest adsorption strength. The results show that O_3 is chemisorbed on the surface of O- HfSe_2 with larger adsorption energy and charge transfer. The electrical property of O- HfSe_2 also change with the disappearance of the band gap after adsorbing O_3 . Besides, the interaction of S- HfSe_2 with gas molecules is physical adsorption, and the adsorption energy is small. The adsorption of NH_3 by S- HfSe_2 can be enhanced by applying tensile strain, and the fast recovery is maintained. Therefore, S- HfSe_2 has potential applications as a sensitive material for NH_3 detection. This research offers theoretical guidance for the manufacturing of HfSe_2 -based gas sensors as well as new insights into the design of atomic-scale high-sensitivity gas sensors.

2. Method

The code DMOL³ is used to calculate all structural relaxation and electrical characteristics in this work [32]. To approximate the exchange correlation energy, generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) function type is used in this work [33, 34]. This may make the calculation more precise due to the uneven distribution of electrons being taken into account [34]. The Tkatchenko and Scheffler's (TS) method was applied to depict the long-range effects and the weak intermolecular forces in the dispersion corrections (DFT-D) parameters [35]. The substrate (X- HfSe_2) contains transition metals, so it is processed with DFT Semi-core pseudopotential (DSPP) [36,37]. In the basis set, the Double- ζ basis plus polarization (DNP) numerical atomic orbital is used [38]. The orbit cutoff radius is set to 5.3 Å, the test results are shown in Table. S1 of Supplementary Material. The convergence conditions for the structural relaxation are as follows, total

energy and maximum displacement convergence requirements are 10^{-5} Ha (1 Ha = 27.21 eV) and 0.005 Å, respectively [22,23]. Also, until the maximum residual force is less than 0.002 Ha/Å, the geometry is relaxed. In the Z direction, a space layer of 25 Å is utilized to reduce interactions between adjacent layers. For the k-point mesh generation, we calculate the total energy and average atomic energy of HfSe_2 cell with different k-point values, as shown in Fig. S1 of Supplementary Material. The result indicates $3 \times 3 \times 1$ for HfSe_2 supercell can meet the convergence condition. So, the $5 \times 5 \times 1$ and $9 \times 9 \times 1$ Monkhorst-Pack grid are used for structural relaxation and electrical properties, respectively.

The formula (1) is used to calculate the adsorption energy (E_a) of the gas with the X- HfSe_2 monolayer:

$$E_a = E_{(\text{Sub}+\text{gas})} - E_{(\text{Sub})} - E_{(\text{gas})} \quad (1)$$

where $E_{(\text{Sub}+\text{gas})}$, $E_{(\text{Sub})}$ and $E_{(\text{gas})}$ are the total energy of substrate/gases adsorption system, isolated substrate and the separated gases molecules, respectively. Positive value means the adsorption cannot proceed spontaneously, while negative value means the adsorption can occur spontaneously. And the smaller the E_a , the stronger the adsorption of gas molecules on the HfSe_2 monolayer.

In order to completely analyze the charge transfer between the gas and X- HfSe_2 monolayer, Mulliken charge [39] analysis was conducted in this work. The charge difference for the gas i after and before adsorption, was calculated using the following equation:

$$\Delta Q_i = Q_{i(\text{in system})} - Q_{i(\text{vacuum})} \quad (2)$$

where Q_i is the value of Mulliken charge of the i . Subscript "i" denotes the gas molecule. The charge difference, ΔQ , is a measure of the extent of charge shifted to, or, from the gas molecule. The positive ΔQ means that the gas is electron donors, while negative ΔQ means gas is electron acceptors.

The following formula (3) is used to compute the charge density difference (CDD):

$$\Delta \rho = \rho_{(\text{Sub}+\text{gas})} - \rho_{(\text{Sub})} - \rho_{(\text{gas})} \quad (3)$$

where $\rho_{(\text{Sub}+\text{gas})}$, $\rho_{(\text{Sub})}$ and $\rho_{(\text{gas})}$ are the charge densities of the whole adsorption system, separated substrate and gas molecule, respectively.

The unit cell of HfSe_2 monolayer is relaxed firstly, with the optimized lattice constant of 3.77 Å, which is consistent with the values (3.76 Å) in the literature [40]. And then using the optimized unit cell, the 3×3 supercell of HfSe_2 monolayer is generated. The X-doped HfSe_2 (X- HfSe_2 , $\text{X} = \text{O}, \text{S}, \text{Te}$) monolayer is constructed by replacing one Se atom on the

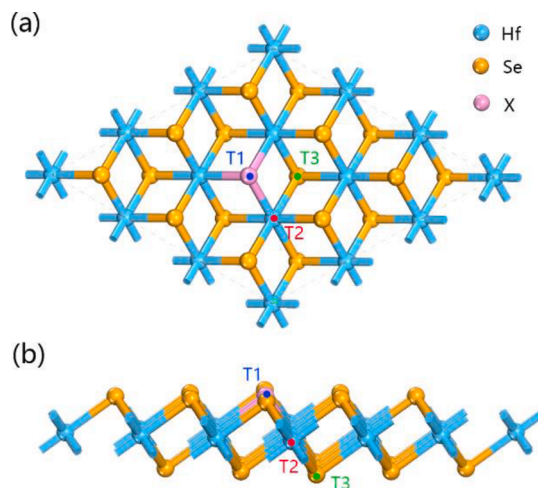


Fig. 1. The structure of pristine and doped HfSe_2 (X- HfSe_2 , $\text{X} = \text{O}, \text{S}, \text{Te}$) monolayer and its adsorption sites. (a) top view, (b) side view.

upper surface with an X atom, as shown in Fig. 1. And the optimized structure of X-HfSe₂ monolayer is shown in Fig. S2. In addition, the AIMD simulations were set by 5000 fs with the temperature of 300 K to check the stability for all X-HfSe₂ structures, as displayed in Fig. S3.

To study the adsorption properties between the X-HfSe₂ monolayer and the gases (NH₃ and O₃), the initial model needs to be established considering the adsorption sites of the substrate and the placement of the gases. We considered three possible adsorption sites for X-HfSe₂, including on the top of Se/X (T1 site), Hf (T2 site), and Se-down (T3 site), as shown in Fig. 1. And the gas can be placed parallel or vertical to the different adsorption sites of X-HfSe₂, so six configurations are considered for each gas molecule. The initial adsorption distance is set as 3 Å. All of these initial adsorption models are relaxed using the same method. First, the optimal adsorption configuration and adsorption property of pristine HfSe₂ interacting with gas are calculated as a comparison to study the adsorption properties of doped HfSe₂. Then, the adsorption properties of doped HfSe₂ are investigated.

3. Result and discussion

3.1. The adsorption of pristine and X-HfSe₂

To investigate the adsorption properties of pristine and X-doped HfSe₂ (X-HfSe₂, X=O, S, Te) for NH₃ and O₃, an adsorption model is built using the method described above, and the best adsorption configuration, adsorption energy, and charge transfer are estimated. Fig. 2 shows the best adsorption configurations of pristine and X-HfSe₂ for NH₃ and O₃ with the minimum energy.

The optimized pristine HfSe₂ adsorption systems are shown in Fig. 2 (a)-(b). When adsorption of NH₃, H atom tends to be close to Se atoms

with the large adsorption distance (3.258 Å). When O₃ is adsorbed, O1 atom (O atoms on the edge of O₃) get close to Se atom on the surface of HfSe₂ and the adsorption distance (3.114 Å) is also large. And the structure of both the substrate and the gas molecules hardly changed. In the adsorption of Te-HfSe₂, a similar result can be seen, as shown in Fig. 2(g)-(h). Fig. 2(c)-(d) shows the optimized O-HfSe₂/gas adsorption system. Remarkably, NH₃ and O₃ are closer to the surface of O-HfSe₂ monolayer than pristine HfSe₂. Both the N atom of NH₃ and the O1 (O atom at the edge of O₃) atom of O₃ are close to the Hf atom of the O-HfSe₂ monolayer, resulting in shorter adsorption distances of 2.402 Å and 1.992 Å, respectively. The O-Hf bond length measured in the experiment is larger than 2 Å [41], while the adsorption distance is less than this value, which suggests that a chemical bond could form between the O and Hf atom, and there should be chemisorption between O₃ and O-HfSe₂. And after adsorption of O₃, the structures of O-HfSe₂ and O₃ changed significantly, as shown in Fig. 2(d). Both O1-O2 bond and O-Hf bond are elongated from 1.279 Å and 2.134 Å to 1.736 Å and 2.173 Å, and the angle of O-Hf-Se increases from 103.851° to 120.862° (Fig. S4(d)), which can be explained by the significant contact between the O and Hf atom. In the adsorption of NH₃, a similar condition can be observed, where the angle of O-Hf-Se is also increased from 103.851° to 120.387°, as shown in Fig. S4(c), causing the N atom to more easily approach the Hf atom, thereby increasing their interaction. In S-HfSe₂/NH₃ adsorption system, as shown in Fig. 2(e), N atom of NH₃ is also close to Hf atom with shorter adsorption distance (2.515 Å), which is similar to O-HfSe₂ but no obvious deformation. While adsorption of O₃, as shown in Fig. 2(f), the adsorption configuration is similar to the pristine HfSe₂ and adsorption distance is also large (3.172 Å).

When compared to the other doped monolayers considered in this study, the adsorption between O-HfSe₂ and gases is the greatest. The

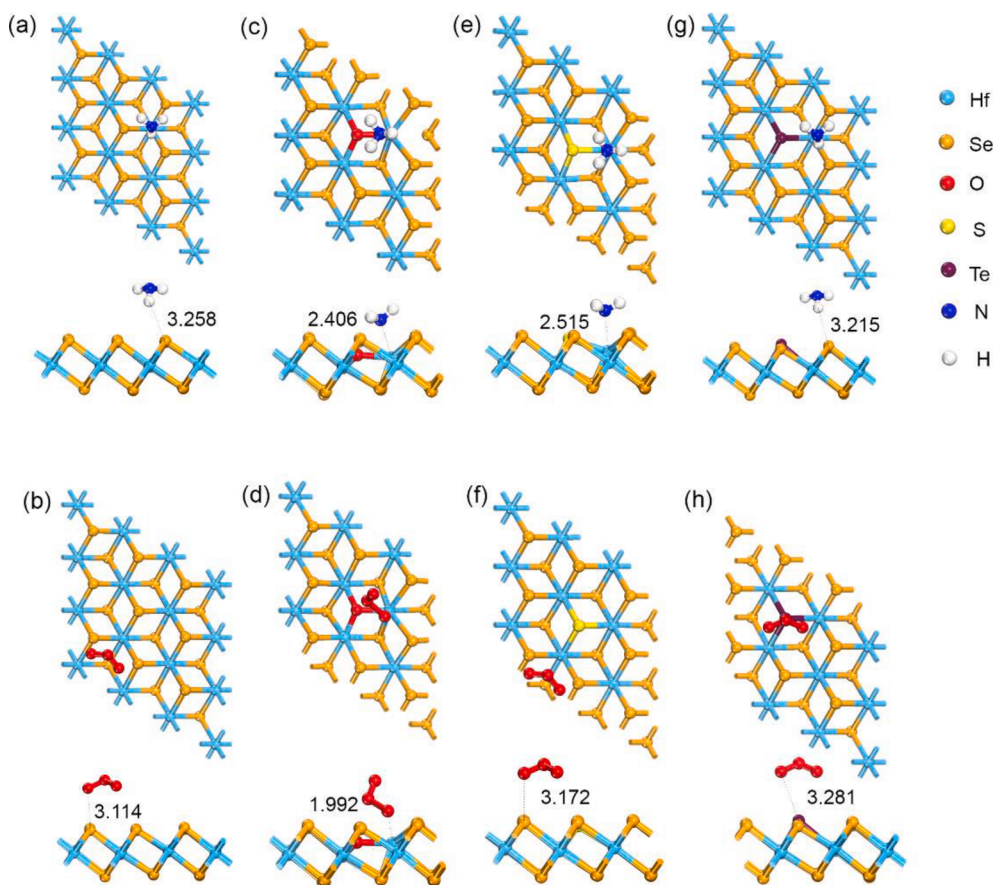


Fig. 2. The optimal adsorption configuration of (a) pristine HfSe₂/NH₃, (b) pristine HfSe₂/O₃, (c) O-HfSe₂/NH₃, (d) O-HfSe₂/O₃, (e) S-HfSe₂/NH₃, (f) S-HfSe₂/O₃, (g) Te-HfSe₂/NH₃ and (h) Te-HfSe₂/O₃. The adsorption distance is marked in the figure (unit: Å).

electronegativity, bond length and bond angle of the substrate and gases are utilized to explain why O-HfSe₂ is more active. The substrate atoms (X-HfSe₂) include Hf, Se, O, S, and Te, with electronegativities of 1.31, 2.55, 3.44, 2.58, and 2.10, respectively, with the Hf atom being the least electronegative. And the electronegativities of N and H in NH₃ are 3.04 and 2.20, respectively. Therefore, it is easier for N and Hf to approach and interact theoretically. However, in pristine HfSe₂, due to its sandwich structure, Hf atom is in the middle layer, and the bond angle of Se-Hf-Se is small (89.058°), which prevents them from approaching each other, so only H atom interact with the surface Se. After doping with O, the bond angle of O-Hf-Se increases to 103.851°, which reduces the obstacle of N approaching Hf. Therefore, the N of NH₃ interacts strongly with Hf, which finally reduces the adsorption distance and enhance their interaction so that the adsorption configuration deforms significantly. Similarly, the electronegativity of O in O₃ are 3.44, which makes it easier to approach and interact with Hf in theory. Thus, the adsorption of O₃ is also enhanced by doping O.

The adsorption energy (E_a) is calculated to study the adsorption strength between the X-HfSe₂ monolayer and gas, as shown in Table 1. The smaller the value, the stronger the adsorption of the gas to the substrate. For the adsorption of NH₃ and O₃ by pristine HfSe₂, the adsorption energies are −0.340 eV and −0.416 eV, respectively, indicating that the interactions between gases and the substrate are weak. After doping with O, the absolute value of the adsorption energy increases significantly, which are −1.138 eV and −1.183 eV, respectively, indicating that the adsorption strength of the gas on the substrate surface is improved. For the S-HfSe₂/gases and Te-HfSe₂/gases adsorption systems, the adsorption energy only changed slightly. After doping with S and Te, the adsorption energy for NH₃ (O₃) decreases from −0.340 eV (−0.416 eV) to −0.466 eV (−0.425 eV) and −0.444 eV (−0.446 eV), which means that the increase in adsorption strength is not obvious.

As a result, the interaction strengths of different substrates with NH₃ are as follows: O-HfSe₂ > S-HfSe₂ > Te-HfSe₂ > HfSe₂. The order of adsorption strength for O₃ by X-HfSe₂ monolayer is O-HfSe₂ > Te-HfSe₂ > S-HfSe₂ > HfSe₂. When compared to pristine HfSe₂, the adsorption strength of O-HfSe₂ for NH₃ and O₃ is clearly enhanced, while the other two doping systems have little effect.

As one of the important parameters for studying the adsorption strength between the X-HfSe₂ monolayer and gas, charge transfer has been studied further by calculating Mulliken charge [42]. The results also show in Table 1. In the pristine HfSe₂/gases system, charge transfer of NH₃ and O₃ are 0.056 e and −0.157 e, respectively, which indicates that they are electron donors and acceptors, respectively. For the adsorption of NH₃, the charge transfer increases to 0.268 e and 0.270 e after doping with O and S, while it decreases to 0.033 e after doping Te. When adsorbing O₃, the charge transfer also increases to −0.417 e after doping with O, while after doping S and Te, the change is small. Detailed charge analysis is specifically analyzed in the Fig. S5 of Supplementary Material. The charge transfer of the O-HfSe₂/gas and S-HfSe₂/NH₃ system is significant, indicating the strong interaction between them, which is consistent with the previous calculations of adsorption energies and optimal adsorption configurations.

In the following section, the electrical properties of the X-HfSe₂/gas adsorption systems are calculated in order to fully study and understand the mechanism.

Table 1

The adsorption energy (E_a) and charge transfer (ΔQ) of pristine HfSe₂ and X-HfSe₂ for NH₃ and O₃.

	E_a (eV)		ΔQ (e)	
	NH ₃	O ₃	NH ₃	O ₃
Pristine HfSe ₂	−0.340	−0.416	0.056	−0.157
O-HfSe ₂	−1.138	−1.183	0.268	−0.417
S-HfSe ₂	−0.466	−0.425	0.270	−0.154
Te-HfSe ₂	−0.444	−0.446	0.033	−0.179

3.2. Electrical properties of X-HfSe₂ adsorption system

The gas interaction with X-HfSe₂ can be understood by the charge density difference (CDD), which helps to predict the charge redistribution behavior between the substrate and gas, and can get a deeper insight into the interaction mechanism between gas molecule and substrate.

CDD: The calculated CDD results are shown in Fig. 3, with the two isosurfaces in light green (0.02 e/Å³) and pink (−0.02 e/Å³), respectively. Electron density accumulates and dissipates in light green and pink areas, respectively. In all the adsorption systems depicted in Fig. 3, significant charge accumulation and dissipation occurred between the O₃ and O-HfSe₂ monolayer, as shown in Fig. 3(b), which further illustrates the strong interaction between them. The charge accumulation in the shared region represents the formation of important chemical bonds, which indicates the formation of chemisorption between the O₃ and O-HfSe₂ monolayer. It is consistent with the results of adsorption performance. While there is little charge redistribution between Te-HfSe₂, S-HfSe₂ and O₃, as shown in Fig. 3(d) and (f), which is much smaller than that of O-HfSe₂/O₃ system. As for NH₃, as shown in Fig. 3(a) and (c), there is a relatively large charge accumulation and dissipation. The charge is dissipated near H atom of NH₃ and Hf atom of substrate, and accumulated near N atom of NH₃. The results are in agreement with the above conclusions that NH₃ prefers to be close to Hf atom. However, there is almost no charge redistribution between Te-HfSe₂ and NH₃, as shown in Fig. 3(e), which is consistent with the results of the above adsorption parameters ($\Delta Q=0.033$ e).

The electrical properties of O-HfSe₂: The electrical properties of O-HfSe₂ after gas adsorption are calculated, including band structure, density of states (DOS), and partial density of states (PDOS), which can help to better understand the adsorption mechanism and study the electrical properties of O-HfSe₂. The band structure can describe band distribution curve and band gap. DOS and PDOS can be used to describe how gas molecules contribute to the total electronic state of an adsorption system. Fig. 4 depicts the band structures of the O-HfSe₂ monolayer before and after gas adsorption. After adsorption of NH₃, the band structure of the O-HfSe₂/NH₃ system hardly changed, and only the conduction band (CB) shifted up slightly. Therefore, after adsorption of NH₃, the band gap of O-HfSe₂ increases from 0.776 eV to 0.792 eV. While some impurity states are generated near the Fermi level of the O-HfSe₂ monolayer after O₃ adsorption, due to the partial contribution of the p-orbital of the O atom in O₃. And the valence band (VB) region moves up. So the band gap of O-HfSe₂ disappears after adsorbing O₃, which means that the O-HfSe₂ went from a semiconductor to a metallic material. These results show that the adsorption of O₃ has a significant impact on the electrical properties of O-HfSe₂, further indicating that the interaction between them is strong.

And, as shown in Fig. 4(d), after absorbing NH₃, the DOS is nearly identical to that of pristine O-HfSe₂. The O-HfSe₂ monolayer contributes the majority of the DOS of the entire adsorption system, indicating that the electrical properties of O-HfSe₂ are not significantly changed by NH₃ adsorption. Furthermore, according to the PDOS, there is no orbital hybridization between O-HfSe₂ and NH₃ near the Fermi level. These findings show that NH₃ is physically adsorbed onto the surface of the O-HfSe₂ monolayer. However, when O₃ is adsorbed to the surface of O-HfSe₂, the DOS significantly changes, as shown in Fig. 4(e). The peak of DOS is shifted to the right, especially in the valence band region (energy < 0 eV). And at 1.5 eV and −1.5 eV, obvious orbital hybridization occurs between the p orbital of O (O-p) and the d orbital of Hf (Hf-d), which indicates that chemical bond is likely to be formed between them. These findings help to explain the strong reaction between O₃ and Hf atoms in the O-HfSe₂ monolayer, which is consistent with the above adsorption property results.

A large number of literatures [42,43] show that physical adsorption is more favorable for sensitive materials due to its fast response and good repeatability, while chemisorption is not suitable due to its difficulty in

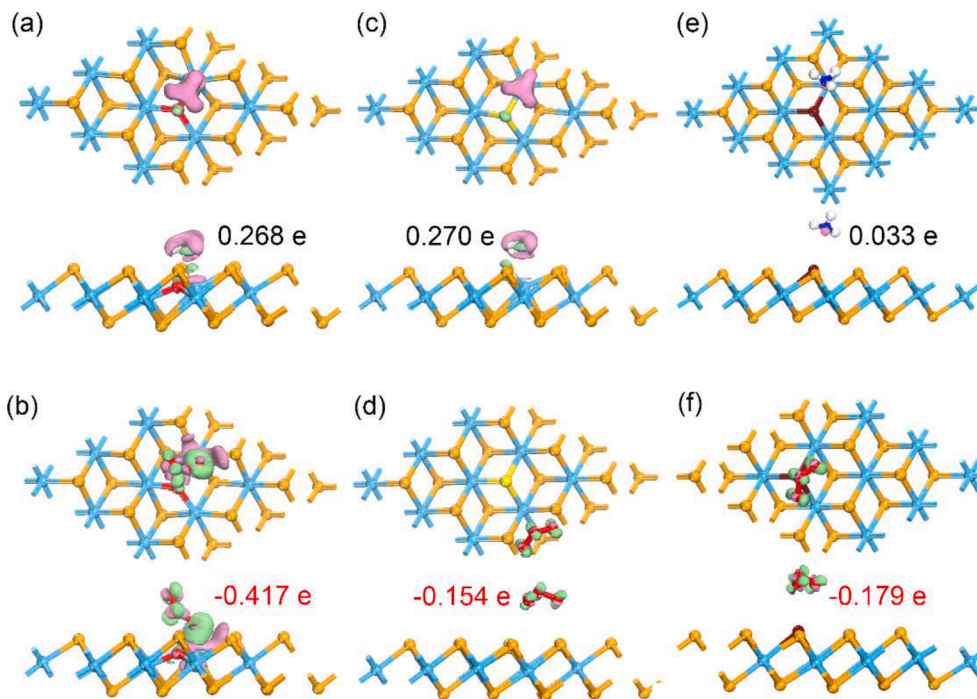


Fig. 3. CDDs of (a)O-HfSe₂/NH₃, (b)O-HfSe₂/O₃, (c)S-HfSe₂/NH₃, (d)S-HfSe₂/O₃, (e)Te-HfSe₂/NH₃ and (f)Te-HfSe₂/O₃ systems. The light green (pink) represents charge accumulation (dissipation). The isosurface value is set as 0.02 e/Å³.

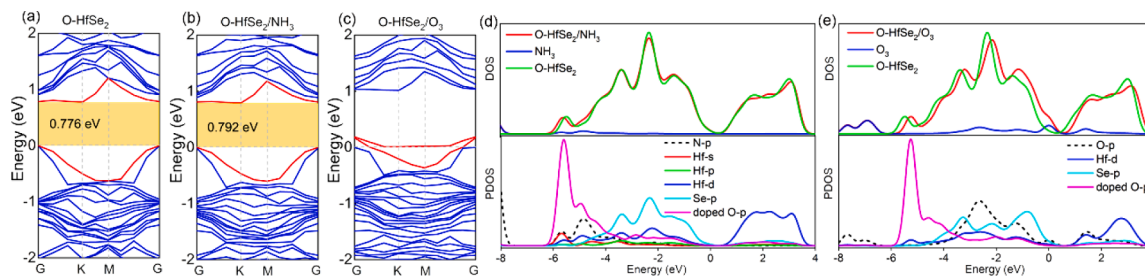


Fig. 4. The band structure of (a) O-HfSe₂, (b) O-HfSe₂/NH₃ and (c) O-HfSe₂/O₃. The DOS (up) and PDOS (down) of (d) O-HfSe₂/NH₃ and (e) O-HfSe₂/O₃ adsorption system. The Fermi level is at 0 eV.

recovery, which prevents the application of O-HfSe₂ as a O₃ sensor. The possibility of O-HfSe₂ as an NH₃ sensor is discussed later.

The electrical properties of S-HfSe₂: The electrical properties of the S-HfSe₂ monolayer before and after gas adsorption are shown in Fig. 5. After adsorption of NH₃, the band structure of S-HfSe₂ hardly changed, only CB and VB moved up and down slightly. Therefore, the band gap changes from 0.618 eV to 0.706 eV. Furthermore, Fig. 5(d) shows that the DOS of S-HfSe₂ after NH₃ adsorption is nearly the same as before adsorption, indicating that NH₃ is very little effect on the electrical

properties of the entire system. And based on PDOS, no orbital hybridization occurs between the S-HfSe₂ and NH₃ near the Fermi level. These findings show that NH₃ is physically adsorbed onto the surface of the S-HfSe₂ monolayer.

After adsorbing O₃, new band is generated around 0.5 eV, resulting the band gap decreases from 0.618 eV to 0.432 eV. And the peak of DOS around -1.4 eV is increased, as shown in Fig. 5(e). These are all because of the contribution of O₃. The orbital hybridization weakly occurs at -1.4 eV between O-p of O₃ and Se-p, S-p of S-HfSe₂. And there is a new

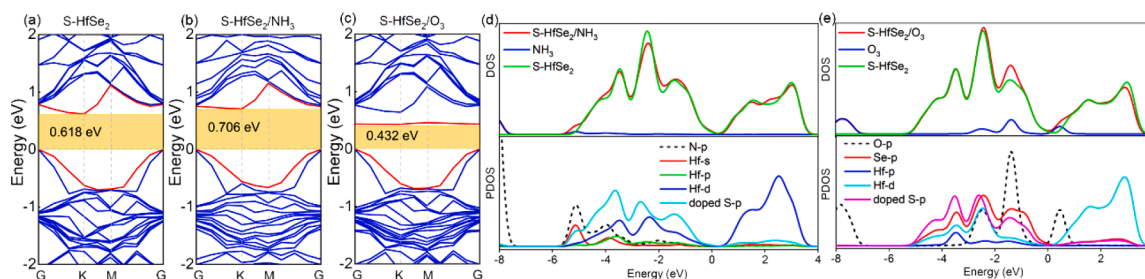


Fig. 5. The band structure of (a) S-HfSe₂, (b) S-HfSe₂/NH₃ and (c) S-HfSe₂/O₃. The DOS (up) and PDOS (down) of (d) S-HfSe₂/NH₃ and (e) S-HfSe₂/O₃ adsorption system. The Fermi level is at 0 eV.

peak generated near 0.5 eV. Therefore, the band gap and DOS of S-HfSe₂ change after adsorption of O₃. But the adsorption energy is not large, which prevents S-HfSe₂ from detecting O₃.

The electrical properties of Te-HfSe₂: Fig. 6 shows the electrical properties of Te-HfSe₂ monolayer after gas adsorption, which is similar to S-HfSe₂. After adsorption of NH₃, the band structure of Te-HfSe₂ hardly changed, and only the CB shifted slightly downward. Therefore, the band gap decreases from 0.500 eV to 0.442 eV. Furthermore, Fig. 6 (d) shows that the DOS of Te-HfSe₂/NH₃ is almost the same as before adsorption, indicating that NH₃ has little effect on the electrical properties of the whole system. And near the Fermi level, there is no orbital hybridization between Te-HfSe₂ and NH₃. These results suggest that NH₃ is physically adsorbed on the surface of the Te-HfSe₂ monolayer.

After adsorption of O₃, the band structure of Te-HfSe₂ shows that a new energy band is generated around 0.4 eV, which reduces the band gap from 0.500 eV to 0.392 eV. And the DOS peak around −1.4 eV increases, and a new weak peak is generated around 0.5 eV, as shown in Fig. 6(e). As can be seen from PDOS, these are all because of the O-p contribution of O₃. Weak orbital hybridization occurs at −1.4 eV and −2.5 eV between O-p of O₃ and Te-p, Hf-d of Te-HfSe₂. Therefore, the band gap and DOS of Te-HfSe₂ changes after adsorbing O₃.

The above calculation results show that O-HfSe₂ has a strong adsorption effect on NH₃ and O₃, with O₃ adsorption being chemical and NH₃ adsorption being physical. Both O₃ and NH₃ are physically adsorbed by S-HfSe₂ and Te-HfSe₂, but the adsorption strength is weak. And the above analysis shows that the reason for the adsorption of NH₃ onto S-HfSe₂ monolayer is the large charge transfer between N atom of NH₃ and Hf of S-HfSe₂. These imply that the adsorption strength of NH₃ can be improved by enhancing the interaction between N atom and Hf atom. When stretching S-HfSe₂ along the x axis, N atom and Hf atom are closer to each other and their interaction could be enhanced. Therefore, the next section calculates the effect of the x-axis strain on the S-HfSe₂/NH₃ adsorption system. In addition, the coverage of NH₃ on S-HfSe₂ surfaces have been calculated and discussed. The results have been added in Supplementary Material.

3.3. Improvement of NH₃ sensing performance by x-axis strained S-HfSe₂

The adsorption energy and charge transfer of S-HfSe₂ to NH₃ under different strains (from −4% to 8%) along the x-axis, y-axis and biaxial strain are calculated to validate that the adsorption strength of S-HfSe₂ for NH₃ may be improved by stretching S-HfSe₂.

Fig. 7 shows the trend of E_a , ΔQ and d with x-axis, y-axis and biaxial strain from −4% to 8%. Both the E_a and d of S-HfSe₂/NH₃ adsorption system briefly decrease at tensile strain of $\epsilon_x=0\sim 8\%$, and increase at compression of $\epsilon_x=0\sim -4\%$. And the charge transfer (ΔQ , Fig. 7b) increases systematically with increasing x-axis tensile strain. The same goes for the variation trends of E_a , ΔQ and d when y-axis (red) or biaxial strain (blue) is applied. The above results indicate that the tensile strains in different directions significantly increase the adsorption strength of S-HfSe₂ for NH₃, thereby improving the performance of the strained S-HfSe₂-based NH₃ sensor. The difference is that the amount of change

induced by biaxial strain is larger. However, it is more difficult to realize biaxial strain than uniaxial strain experimentally. In addition, since the structure of the substrates along the x-axis or y-axis is the same, there is no significant difference in the effect of the strain on the adsorption parameters (E_a , ΔQ and d), which is almost the same. Therefore, the following studies mainly focus on the x-axis strain effect.

And the adsorption of x-axis strained S-HfSe₂ to O₃ is also calculated as a comparison. For O₃, the variation trend of E_a with x-axis strain is completely different from that for NH₃, as shown in Table S1. When O₃ is adsorbed on the unstrained S-HfSe₂ monolayer, the E_a is −0.126 eV. As the x-axis tensile strain increases from 0% to 6%, it increases from −0.126 eV to −0.118 eV, suggesting the adsorption strength weakens with increasing strain. The ΔQ also decreases with increasing x-axis tensile strain, in the opposite direction of NH₃. As a result, x-axis strain can help to improve the selectivity of an NH₃ sensor based on S-HfSe₂ monolayer to some extent.

In addition, at strain of $\epsilon_x=4\%$, the band structure, DOS and PDOS of S-HfSe₂/NH₃ are calculated and described in Fig. 8. When NH₃ is adsorbed onto S-HfSe₂ with $\epsilon_x=4\%$, the band gap increased from 0.700 eV to 0.819 eV, indicating that the conductivity of the substrate changed significantly after adsorption of NH₃ compared to before adsorption. In addition, after adsorption of NH₃, the S-HfSe₂ monolayer with $\epsilon_x=4\%$ is transformed from an indirect band-gap to a direct band-gap, which makes it easier for electrons to be excited from the valence band to the conduction band, so the optical properties of the substrate after adsorption of NH₃ will also change accordingly.

And according to Fig. 8(c), after adsorption of NH₃, the DOS of S-HfSe₂ with $\epsilon_x=4\%$ is almost the same as before adsorption, further indicating that the DOS of the entire S-HfSe₂/NH₃ system is mainly contributed by the substrate. The PDOS also shows that no orbital hybridization occurs between S-HfSe₂ with $\epsilon_x=4\%$ and NH₃ near the Fermi level. At approximately −5.5 eV, far from the Fermi level, apparent orbital hybridization occurs between N-p and Hf-s, p, d. These results demonstrate that NH₃ is still physically adsorbed on the S-HfSe₂ monolayer with $\epsilon_x=4\%$, just like when no strain is applied. This also further indicates that the adsorption strength of S-HfSe₂ for NH₃ can be enhanced by stretching S-HfSe₂ along the x-axis, which can provide theoretical guidance for sensitive materials design.

3.4. Sensing behavior prediction of S-HfSe₂ for NH₃

Aforementioned studies show that S-HfSe₂ is a potentially sensitive material for the detection of NH₃, and it is worth mentioning that the conductivity (σ) and recovery time (τ) are important factors for gas sensors. Therefore, this section predicts the potential of x-axis strain-engineered S-HfSe₂ as an NH₃ sensor by calculating conductivity and recovery time.

After NH₃ adsorption, the conductivity of the substrate changes. And its change rate determines the sensitivity of the device. The band gap value is an important factor in determining S-HfSe₂ conductivity. The following formula (4) expresses the relationship between the band gap and conductivity [44]:

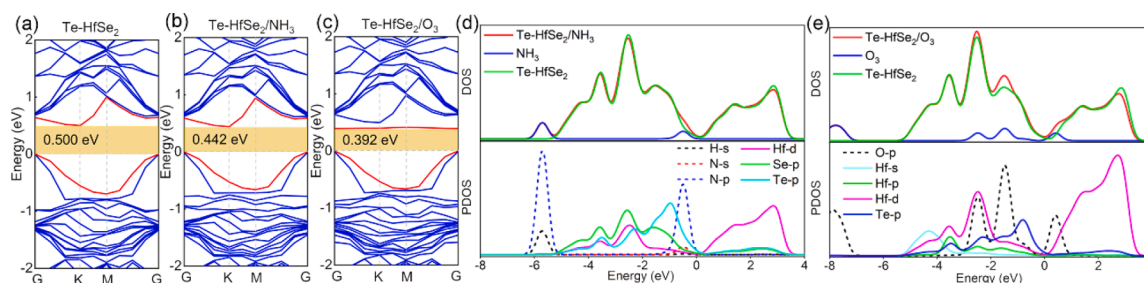


Fig. 6. The band structure of (a) Te-HfSe₂, (b) Te-HfSe₂/NH₃ and (c) Te-HfSe₂/O₃. The DOS (up) and PDOS (down) of (d) Te-HfSe₂/NH₃ and (e) Te-HfSe₂/O₃ adsorption system. The Fermi level is at 0 eV.

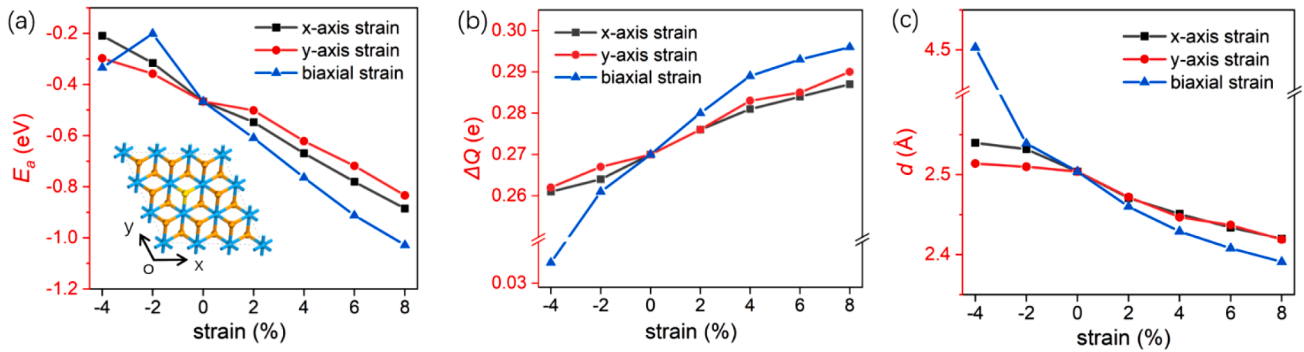


Fig. 7. The variation curves of (a) E_g , (b) ΔQ and (c) d with x-axis, y-axis and biaxial strain from -4% to 8% in S-HfSe₂/NH₃ adsorption system.

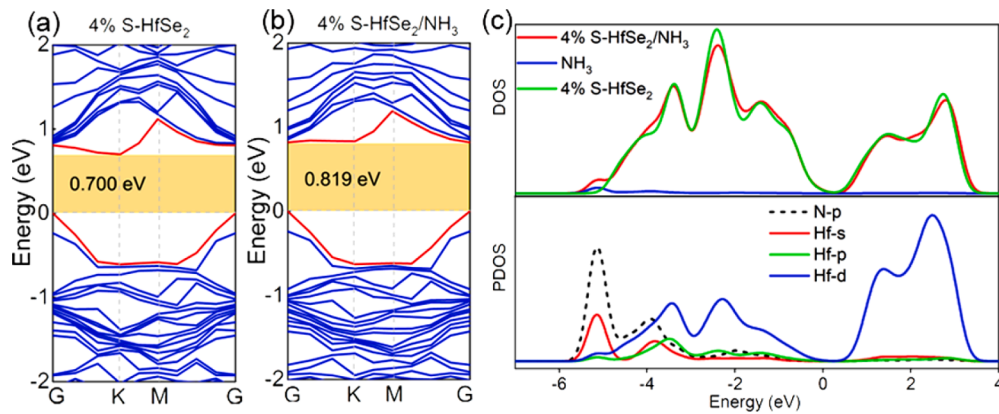


Fig. 8. The band structure for S-HfSe₂ with $\epsilon_x=4\%$ (a) before and (b) after adsorbing NH₃, (c) the DOS (up) and PDOS (down) of S-HfSe₂/NH₃ with $\epsilon_x=4\%$. Fermi level is at 0 eV.

$$\sigma \propto e^{-E_g/2kT} \quad (4)$$

where k and T represent the Boltzmann constant and temperature, respectively, and E_g represents the band gap.

This formula states that the larger the band gap of the substrate material, the lower the conductivity at a given temperature T . In addition, it is also demonstrated that the greater the rate of change in the band gap, the greater the rate of change in conductivity. And sensitivity can be characterized by the change rate of conductivity, which suggests that the greater the change rate of band gap, the higher the sensitivity. After adsorption NH₃, the band gap change rates of S-HfSe₂ under $\epsilon_x=2\%$, 4% , 6% , and 8% strain are 16.3%, 17.0%, 14.2% and 11.2%, respectively, which imply that conductivity of substrate decreases after adsorbing NH₃ and the change rate of S-HfSe₂ with $\epsilon_x=4\%$ is the largest. Combined with the adsorption properties and electrical properties studied above, it is suggested that x-axis strained S-HfSe₂ can be used as a potential sensing material for the detection of NH₃.

To further validate the reusability of the x-axis strained S-HfSe₂ monolayer as a gas sensor for NH₃ detection, the recovery time is calculated, which is a known parameter that determines the quality of a gas sensor. Theoretical methods for estimating recovery time are based on transition state theory, which can be calculated using formula (5) [45]:

$$\tau = w^{-1} e^{-E^*/kT} \quad (5)$$

where w , k , T , E^* are the attempt frequency, the Boltzmann constant, the temperature, and the desorption energy barrier, with the value equaling the adsorption energy (E_a), respectively.

We use an attempt frequency of 10^{12} s^{-1} [45,46] and kT of 25.852 meV when T is 300 K. According to this formula, the larger the absolute

value of the adsorption energy, the longer the recovery time. In this work, the recovery time of desorption of NH₃ from the substrate surface at 300 K is calculated, and the results are shown in Table 2. The predicted recovery times of NH₃ on the S-HfSe₂ surfaces with $\epsilon_x=4\%$, 6% and 8% strained are 0.027 s, 1.153 s and 102.467 s, respectively, suggesting that NH₃ can be rapidly desorbed from the substrate surface. In addition, the results show that the recovery time of NH₃ from the O-HfSe₂ surface is longer, with the recovery time of 1.311×10^7 s at 300 K, as shown in Table 2. And after adsorption of NH₃, the band gap change rate of O-HfSe₂ is small (2.06%), indicating that its sensitivity to NH₃ is low, so O-HfSe₂ is not very suitable for detecting NH₃.

We have also added the comparison of adsorption energy (E_a), charge transfer (ΔQ), band gap change (ΔE_g) and band gap change rate ($\Delta E_g/E_g$) and recovery time (τ) for NH₃ gas adsorption by different materials, as shown in Table 2. It can be seen from the table that applying x-axis tensile strain to the S-HfSe₂ can increase the adsorption energy and charge transfer, and the charge transfer and change rate of band gap is larger than that of literature. The band gap change rate reaches the maximum at $\epsilon_x=4\%$, its corresponding recovery time is 0.027 s, indicating that the detection of NH₃ by S-HfSe₂ with $\epsilon_x=4\%$ is sensitive and fast recovery.

4. Conclusion

In conclusion, pristine and X-doped HfSe₂ (X-HfSe₂, X=O, S, Te) monolayers have been used to study their interactions with NH₃ and O₃ according to first principles based on density function theory. The results show that the adsorption of NH₃ and O₃ by pristine HfSe₂ is weak. Their adsorption strength can be significantly improved by doping O. Chemisorption occurs between O-HfSe₂ and O₃ with largest charge transfer, and the band gap of O-HfSe₂ monolayer disappears after the

Table 2Summary of adsorption energy (E_a), charge transfer (ΔQ), band gap change (ΔE_g) and band gap change rate ($\Delta E_g/E_g$) for NH_3 gas adsorption by different materials.

Substrate	E_a (eV)	ΔQ (e)	ΔE_g (eV)	$\Delta E_g/E_g$	τ ($T = 300$ K)	Reference
pure O—HfSe ₂	−1.138	0.257	0.016	2.06%	1.311×10^7 s	This work
pure S-HfSe ₂	−0.466	0.268	0.088	14.24%	67.368 μ s	
2% S-HfSe ₂	−0.501	0.274	0.107	16.31%	0.261 ms	
4% S-HfSe ₂	−0.621	0.278	0.119	17.00%	0.027 s	
6% S-HfSe ₂	−0.718	0.283	0.104	14.17%	1.153 s	
8% S-HfSe ₂	−0.834	0.285	0.085	11.17%	102.467 s	
PtAs ₂	−0.510	0.036	−0.010	−2.70%	0.370 ms	[47]
PtP ₂	−0.500	0.033	−0.010	−3.57%	0.251 ms	
graphene	−0.316	−0.039	0.007	—	0.204 μ s	[48]
MnPS ₃	−0.150	−0.010	0.008	0.36%	33.105 ns	[49]
WO ₃ (001)	−0.110	0.010	0.033	11.54%	704.561 ns	[50]

adsorption of O_3 , indicating that O_3 has a great influence on its electrical properties, and further implies that O-HfSe₂ is not suitable as a O_3 gas sensor. Besides, the S-HfSe₂/ NH_3 system has larger adsorption energy and charge transfer than O_3 . However, it is still small. To enhance sensing performance of NH_3 by S-HfSe₂, the strain effect on the S-HfSe₂/ NH_3 adsorption system is also studied. The results indicate that the adsorption strength of NH_3 on S-HfSe₂ can be enhanced by stretching S-HfSe₂ along x-axis. After absorbing NH_3 , the conductivity of x-axis strained S-HfSe₂ changes obviously, which suggest its sensitivity. And the predicted recovery times of S-HfSe₂ surfaces with $\epsilon_x=4\%$, 6% and 8% are 0.027 s, 1.153 s and 102.467 s, respectively, which indicates that x-axis strained S-HfSe₂ monolayer has potential applications prospect in NH_3 detecting. Furthermore, this study sheds light on gas-surface interactions, which may help in the future experimental development of two-dimensional materials for strain-based NH_3 sensing and performance optimization.

CRediT authorship contribution statement

Huiru Yang: Formal analysis, Investigation, Writing – original draft. **Junfeng Li:** Software, Investigation, Writing – review & editing. **Ziyuan Shao:** Methodology, Visualization. **Chunjian Tan:** Methodology, Investigation. **Chenshan Gao:** Data curation, Visualization. **Hongyuan Cui:** Investigation. **Xiaosheng Tang:** Visualization. **Yufei Liu:** Investigation. **Huaiyu Ye:** Supervision, Funding acquisition, Writing – review & editing, Validation. **Guoqi Zhang:** Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] J. Zhang, X. Liu, G. Neri, N. Pinna, Nanostructured materials for room-temperature gas sensors, *Adv. Mater.* 28 (2016) 795–831.
- [2] X. Tang, A. Du, L. Kou, Gas sensing and capturing based on two-dimensional layered materials: overview from theoretical perspective, *WIREs Comput. Mol. Sci.* 8 (2018).
- [3] H.T. Jung, The present and future of gas sensors, *ACS Sens.* 7 (2022) 912–913.
- [4] S. Yang, C. Jiang, S.-h. Wei, Gas sensing in 2D materials, *Appl. Phys. Rev.* 4 (2017).
- [5] D. Tyagi, H. Wang, W. Huang, L. Hu, Y. Tang, Z. Guo, Z. Ouyang, H. Zhang, Recent advances in two-dimensional-material-based sensing technology toward health and environmental monitoring applications, *Nanoscale* 12 (2020) 3535–3559.
- [6] H.S. Tsai, Y. Wang, C. Liu, T. Wang, M. Huo, The elemental 2D materials beyond graphene potentially used as hazardous gas sensors for environmental protection, *J. Hazard. Mater.* 423 (2022), 127148.
- [7] Q. Li, J. Meng, Z. Li, Recent progress on Schottky sensors based on two-dimensional transition metal dichalcogenides, *J. Mater. Chem. A* 10 (2022) 8107–8128.
- [8] R. Kumar, N. Goel, M. Hojamberdiev, M. Kumar, Transition metal dichalcogenides-based flexible gas sensors, *Sens. Actuators A* 303 (2020).
- [9] H. Li, Z. Yin, Q. He, H. Li, X. Huang, G. Lu, D.W. Fam, A.I. Tok, Q. Zhang, H. Zhang, Fabrication of single- and multilayer MoS₂ film-based field-effect transistors for sensing NO at room temperature, *Small* 8 (2012) 63–67.
- [10] R. Kumar, W. Zheng, X. Liu, J. Zhang, M. Kumar, MoS₂-based nanomaterials for room-temperature gas sensors, *Adv. Mater. Technol.* 5 (2020).
- [11] D. Zhang, M. Wang, W. Zhang, Q. Li, Flexible humidity sensing and portable applications based on MoSe₂ nanoflowers/copper tungstate nanoparticles, *Sens. Actuators B* 304 (2020).
- [12] S. Guo, D. Yang, S. Zhang, Q. Dong, B. Li, N. Tran, Z. Li, Y. Xiong, M.E. Zaghoul, Development of a cloud-based epidermal MoSe₂ device for hazardous gas sensing, *Adv. Funct. Mater.* 29 (2019).
- [13] H. Guo, C. Lan, Z. Zhou, P. Sun, D. Wei, C. Li, Transparent, flexible, and stretchable WS₂ based humidity sensors for electronic skin, *Nanoscale* 9 (2017) 6246–6253.
- [14] K.Y. Ko, J.G. Song, Y. Kim, T. Choi, S. Shin, C.W. Lee, K. Lee, J. Koo, H. Lee, J. Kim, T. Lee, J. Park, H. Kim, Improvement of gas-sensing performance of large-area tungsten disulfide nanosheets by surface functionalization, *ACS Nano* 10 (2016) 9287–9296.
- [15] A. Eftekhari, Tungsten dichalcogenides (WS₂, WSe₂, and WTe₂): materials chemistry and applications, *J. Mater. Chem. A* 5 (2017) 18299–18325.
- [16] D.-H. Baek, J. Kim, MoS₂ gas sensor functionalized by Pd for the detection of hydrogen, *Sens. Actuators B* 250 (2017) 686–691.
- [17] K.Y. Ko, S. Lee, K. Park, Y. Kim, W.J. Woo, D. Kim, J.G. Song, J. Park, J.H. Kim, Z. Lee, H. Kim, High-performance gas sensor using a large-area WS₂ xSe₂-2 x alloy for low-power operation wearable applications, *ACS Appl. Mater. Interfaces* 10 (2018) 34163–34171.
- [18] S. Lebègue, T. Björkman, M. Klintonberg, R.M. Nieminen, O. Eriksson, Two-dimensional materials from data filtering and ab initio calculations, *Phys. Rev. X* 3 (2013).
- [19] C. Gong, H. Zhang, W. Wang, L. Colombo, R.M. Wallace, K. Cho, Band alignment of two-dimensional transition metal dichalcogenides: application in tunnel field effect transistors, *Appl. Phys. Lett.* 103 (2013).
- [20] R.Y. Yue, A.T. Barton, H. Zhu, A. Azcatl, L.F. Pena, J. Wang, X. Peng, N. Lu, L. X. Cheng, R. Addou, S. McDonnell, L. Colombo, J.W.P. Hsu, J. Kim, M.J. Kim, R. M. Wallace, C.L. Hinkle, HfSe₂ thin films: 2D transition metal dichalcogenides grown by molecular beam epitaxy, *ACS Nano* 9 (2015) 474–480.
- [21] Y.M. Jahn, A. Ya'akovovitz, Outstanding stretchability and thickness-dependent mechanical properties of 2D HfS₂, HfSe₂, and hafnium oxide, *Nanoscale* 13 (2021) 18458–18466.
- [22] H. Cui, P. Jia, X. Peng, Adsorption of SO₂ and NO₂ molecule on intrinsic and Pd-doped HfSe₂ monolayer: a first-principles study, *Appl. Surf. Sci.* 513 (2020).
- [23] H. Cui, H. Zhu, P. Jia, Adsorption and sensing of SO₂ and SOF₂ molecule by Pt-doped HfSe₂ monolayer: a first-principles study, *Appl. Surf. Sci.* 530 (2020).
- [24] Z. Yan, M. Ji, J. Xia, H. Zhu, Recent advanced materials for electrochemical and photoelectrochemical synthesis of ammonia from dinitrogen: one step closer to a sustainable energy future, *Adv. Energy Mater.* 10 (2019).
- [25] S. Giddey, S.P.S. Badwal, C. Munnings, M. Dolan, Ammonia as a renewable energy transportation media, *ACS Sustain Chem Eng* 5 (2017) 10231–10239.
- [26] B. Timmer, W. Olthuis, A.v.d. Berg, Ammonia sensors and their applications—a review, *Sens. Actuators B* 107 (2005) 666–677.
- [27] H.Y. Li, C.S. Lee, D.H. Kim, J.H. Lee, Flexible room-temperature NH₃ sensor for ultrasensitive, selective, and humidity-independent gas detection, *ACS Appl. Mater. Interfaces* 10 (2018) 27858–27867.
- [28] Z. Zhu, J.-L. Chang, R.-J. Wu, Fast ozone detection by using a core-shell Au@TiO₂ sensor at room temperature, *Sens. Actuators B* 214 (2015) 56–62.
- [29] Z. Zhu, J.-L. Chang, C.-H. Wu, T.-L. Chou, R.-J. Wu, Promotion effect of silver on Indium(III) oxide for detecting trace amounts of ozone, *Sens. Actuators B* 232 (2016) 442–447.
- [30] Y.J. Onofre, A.C. Catto, S. Bernardini, T. Florido, K. Aguir, E. Longo, V. R. Mastelaro, L.F. da Silva, M.P.F. de Godoy, Highly selective ozone gas sensor based on nanocrystalline Zn_{0.95}Co_{0.05}O thin film obtained via spray pyrolysis technique, *Appl. Surf. Sci.* 478 (2019) 347–354.
- [31] N. Sui, P. Zhang, T. Zhou, T. Zhang, Selective ppb-level ozone gas sensor based on hierarchical branch-like In₂O₃ nanostructure, *Sens. Actuators B* 336 (2021).

- [32] B. Delley, DMol, a standard tool for density functional calculations: review and advances, *Theor. Comput. Chem.* 2 (1995) 221–254.
- [33] J.H. Yuan, N.N. Yu, J.F. Wang, K.H. Xue, X.S. Miao, Design lateral heterostructure of monolayer ZrS₂ and HfS₂ from first principles calculations, *Appl. Surf. Sci.* 436 (2018) 919–926.
- [34] S. Grimme, Semiempirical GGA-type density functional constructed with a long-range dispersion correction, *J. Comput. Chem.* 27 (2006) 1787–1799.
- [35] J. Behler, Atom-centered symmetry functions for constructing high-dimensional neural network potentials, *J. Chem. Phys.* 134 (2011), 074106.
- [36] C.S. Gao, Y.Y. Zhang, H.R. Yang, Y. Liu, Y.F. Liu, J.H. Du, H.Y. Ye, G.Q. Zhang, A DFT study of In doped Ti₂O: a superior NO₂ gas sensor with selective adsorption and distinct optical response, *Appl. Surf. Sci.* 494 (2019) 162–169.
- [37] B. Delley, Hardness conserving semilocal pseudopotentials, *Phys. Rev. B* 66 (2002).
- [38] B. Delley, An all-electron numerical method for solving the local density functional for polyatomic molecules, *J. Chem. Phys.* 92 (1990) 508–517.
- [39] A. Abbasi, J.J. Sardroodi, Adsorption and dissociation of H₂S on nitrogen-doped TiO₂ anatase nanoparticles: insights from DFT computations, *Surf. Interfaces* 8 (2017) 15–27.
- [40] H.-Y. Song, J.-J. Sun, M. Li, Enhancement of monolayer HfSe₂ thermoelectric performance by strain engineering: a DFT calculation, *Chem. Phys. Lett.* (2021) 784.
- [41] D.-Y. Cho, C.H. Min, J. Kim, S.J. Oh, M.G. Kim, Bond nature of oxygen-deficient HfO₂/Si(100) film, *Appl. Phys. Lett.* 89 (2006).
- [42] H. Ye, L. Liu, Y. Xu, L. Wang, X. Chen, K. Zhang, Y. Liu, S.W. Koh, G. Zhang, SnSe monolayer: a promising candidate of SO₂ sensor with high adsorption quantity, *Appl. Surf. Sci.* 484 (2019) 33–38.
- [43] L. Liu, Q. Yang, Z. Wang, H. Ye, X. Chen, X. Fan, G. Zhang, High Selective Gas Detection for small molecules based on Germanium selenide monolayer, *Appl. Surf. Sci.* 433 (2018) 575–581.
- [44] F. Opoku, P.P. Govender, Adsorption behaviour of Si anchored on g-C₃N₄/graphene van der Waals heterostructure for selective sensing of toxic gases: insights from a first-principles study, *Appl. Surf. Sci.* (2020) 525.
- [45] H. Cui, X. Zhang, G. Zhang, J. Tang, Pd-doped MoS₂ monolayer: a promising candidate for DGA in transformer oil based on DFT method, *Appl. Surf. Sci.* 470 (2019) 1035–1042.
- [46] H. Yang, Y. Liu, C. Gao, L. Meng, Y. Liu, X. Tang, H. Ye, Adsorption behavior of nucleobases on doped MoS₂ monolayer: a DFT study, *J. Phys. Chem. C* 123 (2019) 30949–30957.
- [47] V.B. Zala, R.S. Shukla, P.D. Bhuyan, S.K. Gupta, P.N. Gajjar, Highly selective and reversible 2D PtX₂ (X = P, As) hazardous gas sensors: ab-initio study, *Appl. Surf. Sci.* 563 (2021).
- [48] X.-Y. Liang, N. Ding, S.-P. Ng, C.-M.L. Wu, Adsorption of gas molecules on Ga-doped graphene and effect of applied electric field: a DFT study, *Appl. Surf. Sci.* 411 (2017) 11–17.
- [49] M. Jiang, K. Xu, N. Liao, H. Zhou, DFT investigation on highly selective NO₂ sensing properties of MnPS₃, *Appl. Surf. Sci.* 543 (2021).
- [50] X. Cheng, X. Jiang, K. Tao, Q. Su, Y. Wang, E. Xie, Microscopic nature of gas adsorption on WO₃ surfaces: electron interaction and localization, *J. Phys. Chem. Lett.* 11 (2020) 9070–9078.