



Article Adsorption and Sensing of CO₂, CH₄ and N₂O Molecules by Ti-Doped HfSe₂ Monolayer Based on the First-Principle

Yingxiang Wang¹, Benli Liu², Rengcun Fang¹, Lin Jing¹, Peng Wu³ and Shuangshuang Tian^{2,*}

¹ State Grid HBEPC. Ltd. Economic & Technology Research Institute, Wuhan 430077, China

- ² Hubei Engineering Research Center for Safety Monitoring of New Energy and Power Grid Equipment,
- Hubei University of Technology, Wuhan 430068, China
- ³ School of Electrical Engineering, Wuhan University, Wuhan 430072, China
- * Correspondence: tianss@hbut.edu.cn; Tel.: +86-158-2757-4383

Abstract: With the continuous emission of greenhouse gases, the greenhouse effect is becoming more and more serious. CO_2 , CH_4 , and N_2O are three typical greenhouse gases, and in order to limit their emissions, it is imperative that they are accurately monitored. In this paper, the doping behavior of Ti on the surface of HfSe₂ is investigated, based on the first-nature principle. Additionally, the parameters of adsorption energy and the transfer charges of Ti–HfSe₂ for CO_2 , CH_4 , and N_2O are calculated and compared, while the sensing characteristics of Ti–HfSe₂ are analyzed. The results show that the structure is most stable when Ti is located above the lower-layer Se atom. The CO_2 and N_2O adsorption systems with large adsorption energies and transfer charges are a chemical adsorption, while the CH_4 system is a physical adsorption with small adsorption energies and transfer charges. In addition, Ti–HfSe₂ has a good sensitivity and recovery time for CO_2 at 298 K, which is feasible for industrial application. All the contents of this paper provide theoretical guidance for the implementation of Ti–HfSe₂ as a gas-sensitive material for the detection of greenhouse gas components.

Keywords: greenhouse gas; first-principle; Ti-HfSe2; adsorption

1. Introduction

With the development of the industry, the environmental impact of greenhouse gases is increasing and the global extreme climate problems caused by greenhouse gases have attracted the attention of countries around the world [1–3]. Due to the economy and population growth, anthropogenic greenhouse gas emission has been rising since the beginning of the industrial era. Meanwhile, the concentrations of carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O) have reached their current highest levels [4]. In order to limit carbon emissions, it is necessary to monitor each emission source.

Currently, greenhouse gases are mainly monitored by means of gas sensors, which include electrochemical gas sensors [5], semiconductor gas sensors [6], infrared gas sensors [7], and new nano-gas sensors. Compared with other gas sensors, the new nano-gas sensors have a specific surface area close to the theoretical extremes, excellent semiconductor properties, and abundant active sites, which lead to the advantages of smaller size and higher accuracy and broaden the application fields of sensors greatly [8,9]. Gassensitive material is at the core of nano gas sensors, which mainly includes metal oxide semiconductors [10–12], carbon nanotubes [13–16], graphene [17–19], and transition metal dichalcogenides (TMDs) [20–23]. Among them, TMDs are a new two-dimensional layered nanomaterial with the chemical formula MX₂, where M stands for transition metal elements (Mo, W, Ti, Hf, etc.) and X stands for sulfur group elements (S, Se, and Te). Its structure includes three layers, in which two layers of X atoms are sandwiching a single layer of M atoms in between [24]. Compared with graphene, TMDs have greater potential for gas adsorption and sensing because of their certain band gap [25]. However, since TMD sheets



Citation: Wang, Y.; Liu, B.; Fang, R.; Jing, L.; Wu, P.; Tian, S. Adsorption and Sensing of CO₂, CH₄ and N₂O Molecules by Ti-Doped HfSe₂ Monolayer Based on the First-Principle. *Chemosensors* **2022**, *10*, 414. https://doi.org/10.3390/ chemosensors10100414

Academic Editor: Eleonora Alfinito

Received: 19 September 2022 Accepted: 6 October 2022 Published: 12 October 2022

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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). tend to form a dense stacking structure during the formation of the conductive network, their sensitivity and recovery time at room temperature still need to be improved. Some studies have shown that doping the surface of adsorbent materials with metals such as Ti, Mn, Ag, and Pt can improve the adsorption performance of adsorbent materials [26,27]. As a representative material in TMDs, MoS_2 has received much attention for its application in gas sensors [28]. Li et al. studied the adsorption properties of Mn-doped MoS_2 for dissolved gases in transformer oil [29], and Zhang et al. investigated the adsorption properties of Ti-doped MoS_2 on CF_4 , C_2F_6 , and COF_2 [30].

However, there are other TMDs with good adsorption properties that have rarely been investigated. HfSe₂ has a larger work function than MoS_2 , which makes HfSe₂ less prone to losing electrons. At the same time, HfSe₂ experiences a more violent reaction when exposed to air, indicating a strong interaction between HfSe₂ and air. Above all, HfSe₂ is very suitable for gas sensors [31]. Cui et al. studied the adsorption properties of Pt-doped HfSe₂ on SO₂ and SOF₂, as well as Pd-doped HfSe₂ on SO₂ and NO₂ [32,33]; the results indicate that HfSe₂ has great adsorption and sensing properties. As a commonly used doping metal, Ti is often used to dope the surface of nanomaterials to improve their properties [34–36]. At present, the research for Ti-doped HfSe₂ is not clear enough, so this paper establishes the Ti-doped HfSe₂ model based on the first-principle to obtain the most stable structure of Ti-HfSe₂ and investigates the adsorption performance of Ti-HfSe₂ by analyzing the adsorption energy, transfer of electrons, and other adsorption parameters of CO_2 , CH_4 , and N_2O adsorption systems. Meanwhile, this paper also calculates the sensitivity and recovery time of Ti-HfSe2 for the three gases to evaluate the feasibility of Ti-HfSe2 as a gas-sensitive material. This study can provide a theoretical basis for the application of Ti-doped HfSe₂ nanomaterials in gas sensors.

2. Computation Details

Density functional theory (DFT) is a method for studying multi-electron systems that uses the electron density as the fundamental physical quantity to describe the system [37]. In the field of gas sensing, DFT is also a very effective research tool [38]. The calculations in this paper were all performed in the DMol3 module of Materials Studio based on DFT [39]. In this paper, a 3×3 monolayer HfSe₂ supercell containing 16 Hf atoms and 18 Se atoms was constructed. A vacuum layer with a thickness of 15 Å was built to prevent the interaction of periodic HfSe₂ crystals in the upper layer. The Perdew–Burke–Ernzerhof (PBE) functional within generalized gradient approximation (GGA) was used to deal with the exchange correlation interaction between electrons, while the Tkatchenko and Scheffler (TS) method was used to describe the van der Waals interactions, using Double Numerical Polarization (DNP) as the atomic orbital basis group [40], and the global orbital cut-off radius was 5 A. To simplify the process, a DFT semi-core pseudopotential (DSPP) containing relativistic effects was used. The Monkhorst-Pack k-point mesh of $3 \times 3 \times 1$ was used to geometrically optimize the structure in the paper, and the convergence criteria were set as follows: the tolerance accuracy, the maximum force, and the maximum displacement were 10^{-5} Ha, $0.002 \text{ Ha}/\text{\AA}$, and 0.005\AA , respectively.

3. Results and Discussions

Firstly, in this paper, the geometry of the gas molecules is optimized. The optimized gas molecules are shown in Figure 1. In Figure 1, both CO₂ and N₂O have linear structures, where the C-O, N-N, and N-O bond lengths are 1.178 Å, 1.141 Å, and 1.197 Å, respectively, and the structure of CH₄ is a regular tetrahedron with a C-H bond length of 1.097 Å.



Figure 1. Gas molecular structure. (a) CO₂; (b) CH₄; (c) N₂O.

3.1. Analysis of Ti-HfSe₂ Monolayer

For the structure of Ti doped on the surface of HfSe₂, three possible doping sites are considered: the sites above the upper-layer Se atom, the Hf atom, and the lower-layer Se atom. The doping sites are shown in Figure 2.



Figure 2. HfSe₂ pristine and three types of Ti doping. (**a**) HfSe₂ pristine; (**b**) above the upper-layer Se; (**c**) above the Hf; (**d**) above the lower-layer Se.

The binding energy E_{bind} of the Ti atom doped on the surface of HfSe₂ is calculated by Equation (1) [41]:

$$E_{bind} = E_{Ti-HfSe2} - E_{Ti} - E_{HfSe2} \tag{1}$$

in which $E_{Ti-HfSe2}$, E_{Ti} , and E_{HfSe2} denote the total energy of Ti–HfSe₂, the energy of Ti atoms, and the total energy of monolayer HfSe₂, respectively. Obviously, the lowest binding energy corresponds to the most stable configuration (MSC). Table 1 indicates the parameters of Ti atoms at different doping sites. Combined with the results of geometry optimization of the adsorption system, it can be found that the geometrical optimization results for the doping site above the upper-layer Se layer is consistent with the doping site above Hf, and both doping sites are not the MSC. When the doping site is above the lower-layer Se, the binding energy is biggest, reaching -5.001 eV, indicating that Ti forms the MSC on the HfSe₂ surface. The structure of MSC is shown in Figure 3. The huge binding energy also makes Ti bond with the upper Se layer. Figure 4 shows the electron density difference (EDD) of Ti-HfSe₂, where the blue area indicates electron accumulation, and the yellow area indicates electron depletion. One can see that the electron depletion area is mainly concentrated around the Ti atom, and the electron accumulation area is mainly concentrated on the Ti-Se bond, which indicates that Ti transfers 1.034e of electrons to HfSe₂.

Doped Site	E_{bind}/eV	Distance/Å
Above the upper Se	-4.730	Ti-Se 2.450 Ti-Hf 2.838
Above the Hf	-4.730	Ti-Se 2.450 Ti-Hf 2.840
Above the lower Se	-5.001	Ti-Se 2.424 Ti-Hf 3.216

(b)

Table 1. Binding energy and distance for different doping positions.

Figure 3. MSC of Ti-HfSe₂. (**a**) Top view; (**b**) front view.

(a)



Figure 4. EDD of Ti-HfSe₂ with isosurface of 0.12e/Å³. (a) Top view; (b) front view.

The density of states (DOS) and partial density of states (PDOS) before and after Ti doping are shown in Figure 5. From Figure 5a, the DOS of the adsorbed material shifts to a lower energy overall, and the shape of the DOS of the adsorbed material is partially changed, with new peaks near -14eV and -5eV after Ti doping. Additionally, the Ti atoms have a great effect on the DOS in the part above the Fermi level, which leads to a higher peak of Ti $-HfSe_2$ at -1eV to 2eV than the peak of HfSe₂ pristine. Figure 5b shows the PDOS of the adsorbed material, where Ti 3d orbitals hybridize highly in the range of -6eV to 2eV, with Hf 6s, 5p, and 5d orbitals and Se 4p orbitals producing a strong hybridization. This also indicates that Ti forms a very stable structure with the HfSe₂ surface, and the strong electronic orbital hybridization also leads to the formation of chemical bonds between Ti and Se, which is consistent with the previous analysis.



Figure 5. DOS and PDOS of adsorption system. The dash line is Fermi level. (**a**) DOS of Ti–HfSe₂, Ti and HfSe₂; (**b**) PDOS of Ti–HfSe₂.

3.2. Adsorption Properties of Ti-HfSe₂ Monolayer

The CO₂, CH₄, and N₂O molecules are placed on the Ti–HfSe₂ surface in different ways, and these structures are geometrically optimized to finally find the MSC. Through several attempts, it can be found that the MSC exists when the gas molecule is located above the Ti atom. For the CO₂ gas molecule, two adsorption structures are selected: parallel and perpendicular close to the Ti–HfSe₂ surface. For the CH₄ molecule, two adsorption configurations are chosen: C atom perpendicular to the Ti atom and H atom perpendicular to the Ti atom. Due to the asymmetric structure of the N₂O gas molecule, there are three adsorption structures: parallel close to the Ti–HfSe₂ surface and perpendicular to the Ti–HfSe₂ surface with N and O atoms, respectively. Combined with the simulation results, the lowest energy adsorption structure can be obtained as shown in Figure 6.



Figure 6. MSC of each adsorption system. (**a**,**b**) CO_2 adsorption system; (**c**,**d**) CH_4 adsorption system; (**e**,**f**) N_2O adsorption system.

In order to further analyze the adsorption characteristics of the gas on the $Ti-HfSe_2$ monolayer, the energy change in the adsorption process of the gas molecules on the $Ti-HfSe_2$ surface is taken as the adsorption energy in this paper. The adsorption energy E_{ad} of the gas adsorption process is shown in Equation (2) [42]:

$$E_{ad} = E_{Ti-HfSe2/gas} - E_{Ti-HfSe2} - E_{gas}$$
⁽²⁾

in which $E_{Ti-HfSe2/gas}$, $E_{Ti-HfSe2}$, and E_{gas} denote the total energy of the system after gas adsorption, the energy of the layer Ti-HfSe2, and the total energy of the gas molecules, respectively.

The charge transfer ΔQ of the adsorption system is calculated by the Mulliken method, and the expression is as shown in Equation (3):

$$\Delta Q = Q_1 - Q_2 \tag{3}$$

in which Q_1 and Q_2 denote the charge of gas molecules after and before adsorption. If $\Delta Q > 0$, this indicates that the gas molecule loses electrons during the adsorption process; if $\Delta Q < 0$, this indicates that the gas molecule gains electrons during the adsorption process. The calculation results are shown in Table 2.

Distance/Å Gas E_{ad}/eV $\Delta Q/e$ C-Ti 2.057 CO_2 -0.813-0.483CH₄ -0.5200.107 H-Ti 2.357 -1.384N-Ti 1.916 N_2O -0.468

Table 2. Calculation result of CO₂, CH₄, and N₂O adsorption system.

The equation for the EDD is shown in Equation (4):

$$\Delta \rho = \rho_{gas/Ti-HfSe2} - \rho_{gas} - \rho_{Ti-HfSe2}$$
(4)

in which $\rho_{gas/Ti-HfSe2}$, ρ_{gas} , and $\rho_{Ti-HfSe2}$ denote the electron density of the adsorption system after adsorption of gas molecules, individual gas molecules, and Ti-HfSe₂, respectively. The EDD is shown in Figure 7 based on the calculated results, where the blue area indicates electron accumulation, and the yellow area indicates electron depletion.

For the CO_2 adsorption system, the large adsorption energy leads to a significant change in the structure of CO₂, with the C-O bond length elongated from 1.178 Å to 1.207 Å and 1.350 Å, and with the angle changed to 132.734° . The Ti-Se bond in Ti-HfSe₂ increased by about 0.126 Å, following adsorption. In the CH_4 adsorption system, the C-H bond in CH_4 near Ti-HfSe₂ increased by 0.009 Å, and the Ti-Se bond length changed by 0.001 Å. The whole system is almost unchanged, which also indicates that CH₄ adsorption on Ti-HfSe₂ surface is not effective. There are no bonds formed during the adsorption process, indicating that the adsorption process is a physical adsorption and the main force is Van der Waals (VDW). From the EDD of the CH_4 adsorption system, the electron depletion region is concentrated on the surface of H atoms in CH_4 , and the electron accumulation region is concentrated near the C atoms. The trace electron transferring amount of 0.107e also confirms the weak interaction between CH₄ and Ti-HfSe₂. The N₂O adsorption system changes significantly during the adsorption process, with the Ti-Se bond elongating by 0.032 Å to 0.130 Å, attracted by N_2O . From the EDD, it can be seen that a large electron accumulation region is formed near N and O atoms, and a large electron depletion region exists near Ti atoms, indicating that there is a large amount of charge transfer during the adsorption process, further verifying the strong adsorption performance of Ti–HfSe₂ on N_2O . The CO_2 and N_2O adsorption systems have large adsorption energies and transfer charges, and both create new bonds during the adsorption process, indicating that these adsorption processes are chemical adsorptions, rebuilding the electron arrangement.

3.3. DOS of Adsorption System

To further analyze the interaction between gas molecules and the surface of the adsorbent material, the DOS and PDOS of three gas adsorption systems are investigated in this section, and the results are shown in Figure 8.



Figure 7. EDD of adsorption system. (**a**,**b**) EDD of CO₂ with isosurface of 0.04e/Å³; (**c**,**d**) EDD of CH₄ with isosurface of 0.02e/Å³; (**e**,**f**) EDD of N₂O with isosurface of 0.04e/Å³.

From Figure 8, the DOS and PDOS change to different degrees after the adsorption of gas by $Ti-HfSe_2$. The CO₂ adsorption system is shown in Figure 8a. The structure of CO_2 is changed after adsorption and the positions of the different peaks of the DOS of CO₂ are changed, which leads to three new peaks at -21 eV, -8.5 eV, and -6.5 eVfor $CO_2/Ti-HfSe_2$. In addition, in the range from -1eV to 0eV, the Ti 3d orbitals, and the C 2p orbitals and O 2p orbitals overlap highly, forming a strong hybridization. This also confirms the bonding between Ti atoms and C and O atoms, respectively, making the structure of CO2 gas molecules change. The adsorption effect is obvious; the adsorption is a chemical adsorption. Figure 8b shows the DOS and PDOS of the CH₄ adsorption system. It can be seen that the DOS of CH_4 is changed in position and peaks during the adsorption process, which leads to two new peaks in the DOS of the adsorption system at -15 eV and -7.5 eV. It can also be seen that the other parts almost overlap with the DOS of before adsorption, indicating that the interaction between CH_4 molecules and the $Ti-HfSe_2$ surface is weak, and only a small amount of charge is transferred during the adsorption process. Meanwhile, the Ti 3d orbitals only have a small overlap with the C 2p and H 1s orbitals. The trace amount of hybridization also indicates that Ti-HfSe₂ is less effective in the adsorption of CH₄. In the N₂O adsorption system, the DOS of the system changed significantly after adsorption, generating new peaks at -20 eV, -10 eV, -7.5 eV, -6.5 eV, and -3 eV, and the newly generated peaks were caused by the adsorbed N₂O. There is an obvious overlap between the Ti 3d orbitals and the N 2p and O 2p orbitals near the Fermi

level, indicating a strong hybridization between these orbitals and a strong adsorption of N_2O by $Ti-HfSe_2$, an adsorption which is sufficient to change the structure of N_2O . It also indicates that Ti is bonded to N and O atoms. The adsorption is chemisorption, and the main force is an intermolecular force.



Figure 8. DOS and PDOS of adsorption system. (a) CO_2 adsorption system; (b) CH_4 adsorption system (b); (c) N_2O adsorption system.

3.4. Gas sensor Analyzation of Ti-HfSe₂

The sensitivity of this material and the recovery time after adsorption of each gas are analyzed to evaluate the possibility of $Ti-HfSe_2$ as a resistive gas sensor.

The sensitivity of gas-sensitive materials can be obtained by detecting the change in conductivity of the material before and after adsorption of gas, and the band gap is the main

factor that determines the conductivity of the material. Furthermore, there is a quantitative relationship between conductivity (σ) and band gap (B_g), as in Equation (5) [43,44]:

$$\sigma = A \times e^{\left(\frac{-Bg}{2kT}\right)} \tag{5}$$

in which A is a constant, k is Boltzmann constant, and T(K) denotes the thermodynamic temperature.

The relationship between sensitivity (*S*) and conductivity (σ) of the gas-sensitive material is shown in Equation (6):

$$S = \begin{vmatrix} \frac{1}{\sigma_{gas}} - \frac{1}{\sigma_{pure}} \\ \frac{1}{\sigma_{pure}} \end{vmatrix}$$
(6)

in which σ_{gas} and σ_{pure} denote the conductivity of the adsorption system and Ti–HfSe₂, respectively. The change in conductivity of Ti–HfSe₂ after adsorbing different gases can be approximated by calculating the change in band gap of each system. When the band gap of the material increases, it is more difficult to excite electrons in the material from the valence band to the conduction band, leading to a decrease in the conductivity of the material; conversely, the conductivity of the material increases.

The band structures of CO₂, CH₄, and N₂O after adsorption are shown in Figure 9. From Equations (5) and (6), the sensitivities of Ti-HfSe₂ for CO₂, CH₄, and N₂O at room temperature are 73.34, 123.63, and 1013.97, respectively, which indicates that the conductivity of Ti-HfSe₂ has changed significantly after adsorbing three gases above with a high sensitivity. Therefore, Ti-HfSe₂ can meet the application requirements of gas detection.



Figure 9. Band structures of Ti–HfSe₂ and each adsorption system. (**a**) Ti–HfSe₂; (**b**) CO₂; (**c**) CH₄; (**d**) N₂O.

In addition, the desorption performance is also an important index for evaluating gas sensors and is often expressed in terms of the recovery time (τ), which is the time for the gas to desorb from the material surface, and is expressed as shown in Equation (7) [45,46]:

$$\tau = A^{-1} \times e^{\left(-\frac{Lg}{kT}\right)} \tag{7}$$

in which *A* is the attempt frequency with a value of 10^{12} s⁻¹, *k* is the Boltzmann constant, *T*(K) denotes the thermodynamic temperature, and $E_g(eV)$ denotes the potential barrier; the value of the potential barrier of the desorption process can be considered as the absolute value of the adsorption energy E_{ad} . When the potential barrier is large, the desorption process on the material surface becomes very difficult, and heating is often used to speed up the desorption process.

The recovery time for different gases at different temperatures is shown in Table 3. The recovery times for CO₂, CH₄, and N₂O at room temperature are 38.024 s, 4.852×10^{-4} s, and 1.312×10^{11} s, respectively. CO₂ has a fast recovery time at room temperature, which

allows Ti–HfSe₂ to be recycled quickly to meet the practical use requirements of gas sensors. Therefore, Ti–HfSe₂ has significant advantages in terms of gas-sensitive properties and practicality. For the CH₄ adsorption system, the recovery time reaches milliseconds at room temperature due to its weaker adsorption energy, and the recovery time is too fast for the gas sensor to detect the gas. The recovery time of N₂O at room temperature is longer, at 1.312×10^{11} s. Even when heated to 398 K, the recovery time is still long, indicating that N₂O is strongly adsorbed and Ti–HfSe₂ can be used as an adsorbent for this gas to reduce its emission.

6	Recovery Time/s		
Gas	298 K	398 K	498 K
CO ₂	38.024	0.015	1.626×10^{-4}
CH_4	$4.852 imes10^{-4}$	$2.834 imes10^{-6}$	$1.786 imes10^{-7}$
N_2O	$1.312 imes 10^{11}$	$1.490 imes 10^5$	95.109

Table 3. Recovery time of gas at different temperatures.

4. Conclusions

In this paper, the doping model of Ti on the HfSe₂ surface is constructed and CO₂, CH₄, and N₂O are adsorbed by Ti-HfSe₂. The results show that the MSC of Ti-HfSe₂ is when Ti is located above the upper-layer Se atoms of HfSe₂ and that Ti-HfSe₂ has a good adsorption performance for CO₂ and N₂O. Furthermore, the sensitivity and recovery time of Ti-HfSe₂ to CO₂ are great, which allows Ti-HfSe₂ to be used to detect CO₂. Conversely, Ti-HfSe₂ is not suitable for detecting CH₄, due to its fast recovery time. Due to the excellent adsorption and excessive recovery time of N₂O, Ti-HfSe₂ can be considered as an adsorbent for N₂O.

Author Contributions: Conceptualization, Y.W. and B.L.; methodology, R.F.; software, B.L.; formal analysis, Y.W. and P.W.; data curation, L.J. and P.W.; writing—original draft preparation, Y.W. and S.T.; writing—review and editing, B.L. and S.T.; visualization, L.J.; supervision, Y.W.; project administration, P.W.; funding acquisition, S.T. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

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