

Al-Doped MoSe₂ Monolayer as a Promising Biosensor for Exhaled Breath Analysis: A DFT Study

Tun Liu, Ziwen Cui, Xin Li, Hao Cui, and Yun Liu*



Cite This: *ACS Omega* 2021, 6, 988–995



Read Online

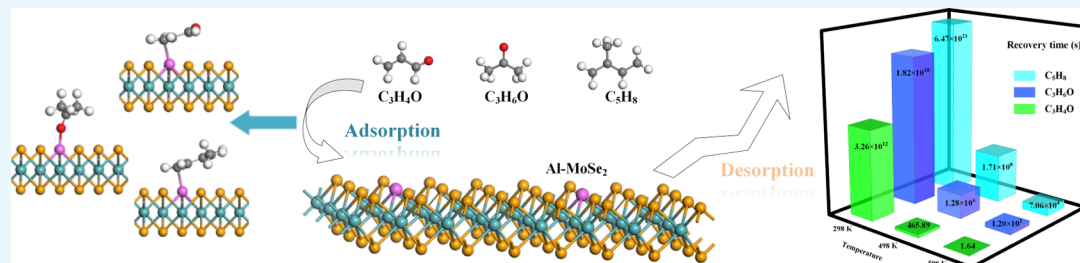
ACCESS |



Metrics & More



Article Recommendations



ABSTRACT: Exhaled breath analysis by nanosensors is a workable and rapid manner to diagnose lung cancer in the early stage. In this paper, we proposed Al-doped MoSe₂ (Al–MoSe₂) as a promising biosensor for sensing three typically exhaled volatile organic compounds (VOCs) of lung cancer, namely, C₃H₄O, C₃H₆O, and C₅H₈, using the density functional theory (DFT) method. Single Al atom is doped on the Se-vacancy site of the MoSe₂ surface, which behaves as an electron-donor and enhances the electrical conductivity of the nanosystem. The adsorption and desorption performances, electronic behavior, and the thermostability of the Al–MoSe₂ monolayer are conducted to fully understand its physicochemical properties as a sensing material. The results indicate that the Al–MoSe₂ monolayer shows admirable sensing performances with C₃H₄O, C₃H₆O, and C₅H₈ with responses of –85.7, –95.6, and –96.3%, respectively. Also, the desirable adsorption performance and the thermostability endow with the Al–MoSe₂ monolayer with good sensing and desorbing behaviors for the recycle detection of three VOCs. We are hopeful that the results in this paper could provide some guidance to the experimentalists fulfilling their exploration in the practical application, which can also broaden the exploration of transition-metal dichalcogenides (TMDs) in more fields as well.

1. INTRODUCTION

Lung cancer is recognized around the world as the second most prevalent cancers in adult men and women, and its morbidity and mortality rates are the highest among all cancers.¹ As reported, the tumors growing in the body will generate some specific substance, releasing volatile organic compounds (VOCs) into the blood and exchanging in the lung.² Besides, the exhaled VOCs of lung cancer patients are significantly more than those of the healthy people,³ which provides the possibility to clarify the possible patients and evaluate the severity of diagnosed ones. Therefore, exhaled breath analysis becomes an attractive, rapid, and workable method to diagnose lung cancer without trauma issue, and the characterized VOCs are accepted as the biomarkers to reflect the potential dysfunction of human lungs. These typical VOCs include hydrocarbons such as isoprene (C₅H₈) and methyl cyclopentane (C₆H₁₂), hydrocarbon derivatives such as acetone (C₃H₆O) and 2-propenal (C₃H₄O), and aromatic hydrocarbons such as benzene (C₆H₆) and ethylbenzene (C₈H₁₀).^{4–7}

In terms of VOC detection, a chemical resistance-type sensor is full of potential with advantages of rapid response,

high sensitivity, and low cost.^{8,9} Recently, many two-dimensional (2D) materials with favorable chemical reactivity and high electron mobility are demonstrated with strong interaction with the gas molecules,^{10,11} including transition-metal dichalcogenides (TMDs), III–IV compounds, and V group monolayer. Besides, metal-doping could significantly enhance the adsorption and sensing behaviors of the materials upon gas species due to the strong catalytic property of metal atom(s).^{12–14} This would be beneficial in guaranteeing their application in some harsh environment with good sensitivity. Specifically, the semiconducting MoSe₂ monolayer with a direct band gap of 1.55 eV has received great attention as a sensing material for small gases,^{15–17} which stimulates us to theoretically study its performance upon VOC sensing. Besides, aluminum (Al) is a common and inexpensive metal

Received: November 20, 2020

Accepted: December 11, 2020

Published: December 24, 2020



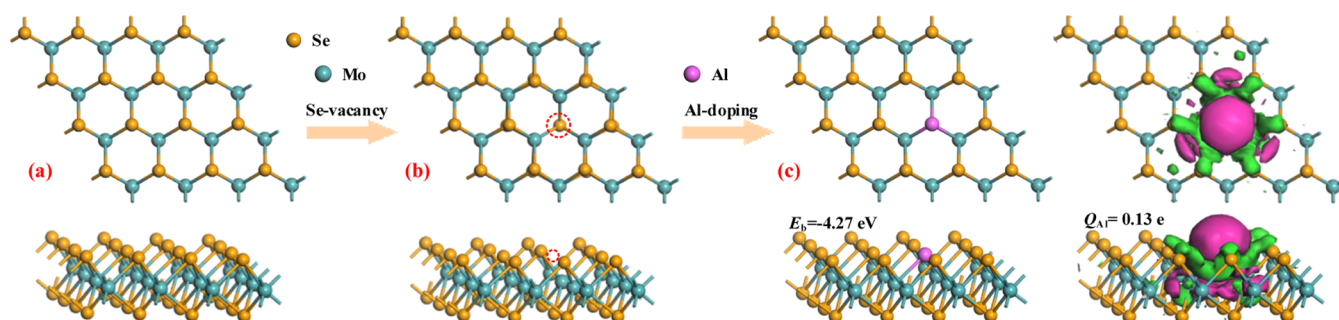


Figure 1. Formation process of the Al–MoSe₂ monolayer from (a) pure, (b) Se-defected, and (c) Al-doped MoSe₂ monolayers. In CDD, the green (rosy) area indicates electron accumulation (depletion). The isosurface is 0.01 eV/Å³.

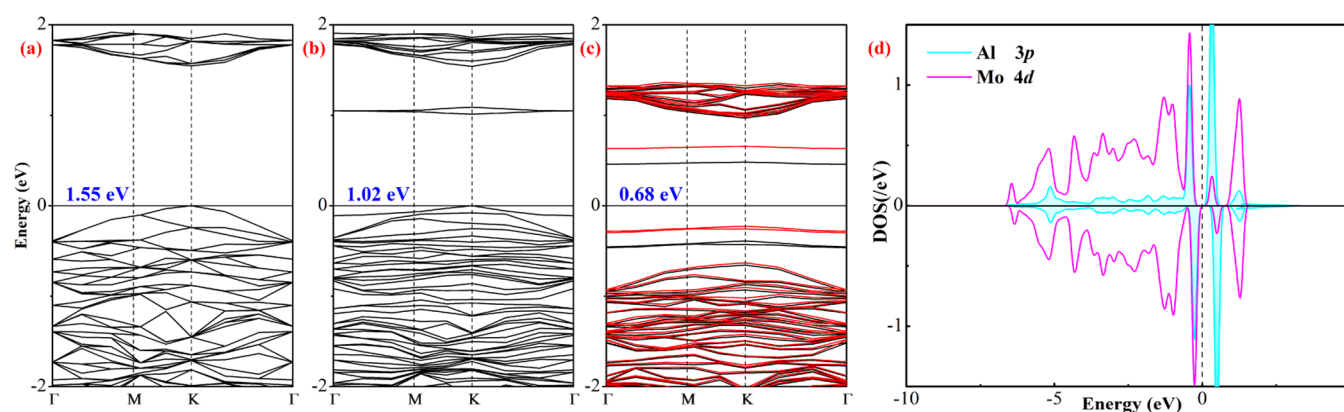


Figure 2. BS of (a) pure, (b) Se-defected, and (c) Al-doped MoSe₂ monolayers and (d) orbital DOS of Al and Mo. The Fermi level is set to 0. In BS, the black line is spin up and the red line is spin down.

with a superior catalytic behavior upon gas interactions, making it a frequently used dopant for the surface to promote the sensing behavior of the material.^{18,19}

In this work, we propose the Al-doped MoSe₂ (Al–MoSe₂) monolayer as a possible biosensor for sensing the VOCs of lung cancer based on density functional theory (DFT). Since the Se-vacancy inevitably exists in the MoSe₂ monolayer in the engineering synthesis, the Al–MoSe₂ monolayer is determined as the Al-doping on the Se-defected MoSe₂ monolayer to better meet the real condition, and we select C₃H₄O, C₃H₆O, and C₅H₈ as the typical VOCs to perform their adsorption behavior onto the Al–MoSe₂ surface. The sensing mechanism, desorption behavior, and thermostability of the Al–MoSe₂ monolayer are conducted as well to fully understand its property as a chemical sensor. Our results manifest the feasibility of the Al–MoSe₂ monolayer as a reusable sensor for the detection of VOCs, which provides the possibility for its further exploration in the diagnosis of lung cancer in daily life. From this aspect, our work can offer some guidance to the experimentalists and is important to broaden the application of TMDs in more fields.

2. RESULTS AND DISCUSSION

2.1. Al-Doping Behavior on the Se-Defected MoSe₂ Monolayer. Chalcogen vacancies in TMDs play a crucial role in their geometric and electronic behaviors.²⁰ Herein, we first analyze the Se-vacancy behavior on the MoSe₂ surface and then the Al-doping effect on the geometric and electronic property on the Se-defected monolayer. Figure 1 exhibits the process of establishing the Al–MoSe₂ monolayer based on the pristine MoSe₂ surface. The Se-defected MoSe₂ monolayer is

established by removing a Se atom from the upper layer of the pure MoSe₂ supercell. After full optimization, somewhat deformations could be identified compared with the pristine counterpart. Then, an Al dopant is adsorbed on the Se-vacancy of the Se-defected MoSe₂ monolayer to form the Al–MoSe₂ monolayer. Upon Al-doping on the Se-defected MoSe₂ surface, the binding force (E_b) is calculated to be -4.27 eV, which suggests the strong interaction between the Al dopant and the Se-defected MoSe₂ surface. Besides, the Al–Mo bonds are measured as 2.52 Å, slightly shorter than the original Se–Mo bond of 2.55 Å and the sum of the covalent radii of Se and Mo atoms (2.64 Å²¹), confirming the strong binding force between Al dopant and Mo atoms that leads to the formation of the chemical bonds of Al–Mo.²² In addition, the obtained E_b is much larger than the cohesive energy of the Al atom (3.39 eV), indicating the stable doping of Al dopant on the Se-vacancy without the clustering problem.^{23,24}

After doping, the Al adatom is positively charged by $0.13e$ according to the Hirshfeld method, meaning its electron-losing property on the Se-defected MoSe₂ surface. From the charge density difference (CDD) distribution, one can see that the Al adatom is surrounded by the electron depletion, whereas the neighboring Mo atoms are surrounded by electron accumulation. The evident electron overlaps on the Al–Mo bonds verify their ionic nature and a strong orbital interaction during Al-doping.

Figure 2 depicts the band structure (BS) of various systems and orbital density of state (DOS) of Al and Mo atoms to illustrate the deformation of the electronic behavior in the formation of the Al–MoSe₂ monolayer. First, in the pure MoSe₂ system, the BS implies that it shows direct semi-

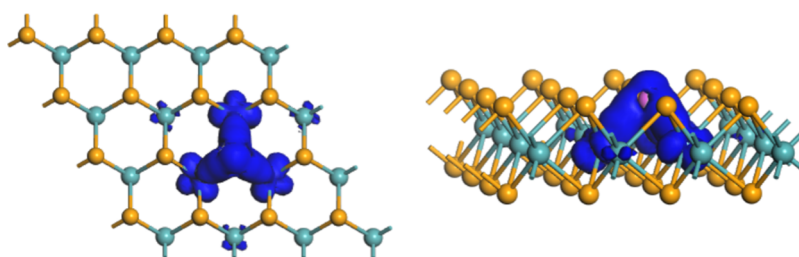


Figure 3. Spin density of the Al–MoSe₂ monolayer.

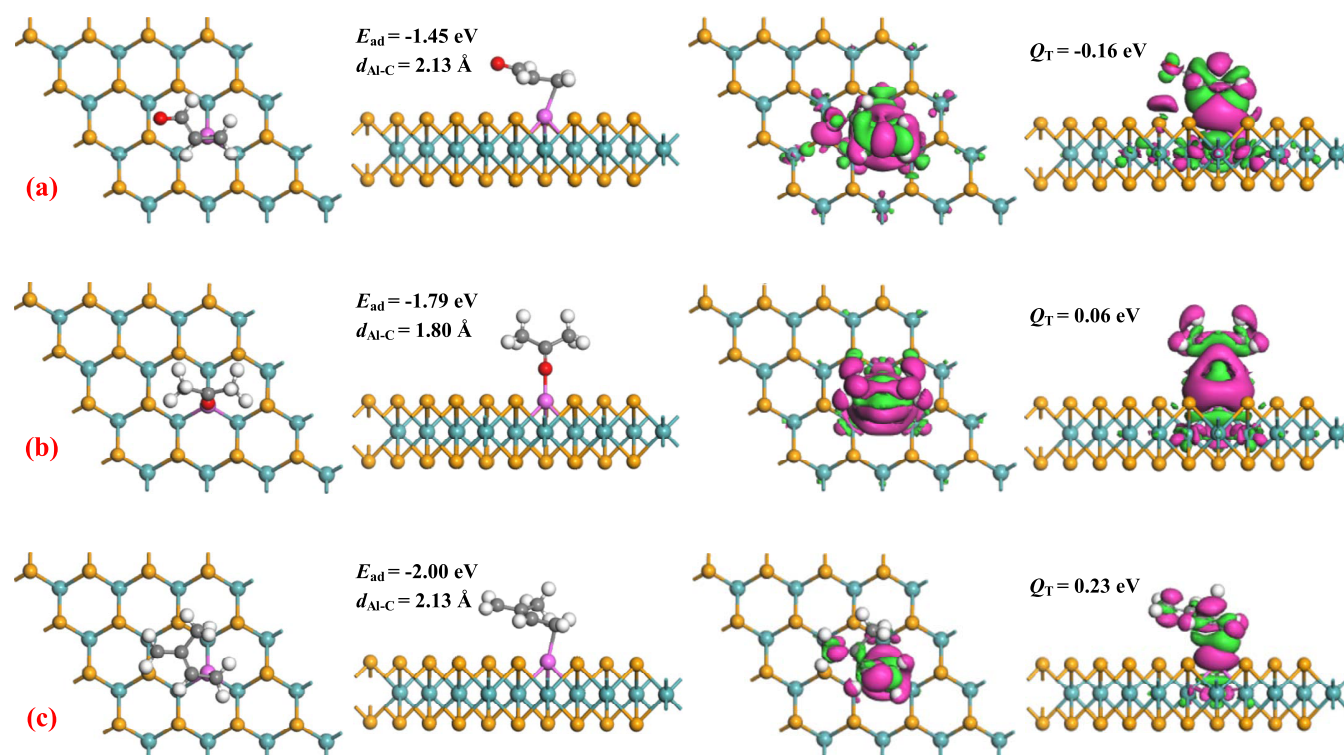


Figure 4. MSC and CDD for C₃H₄O (a), C₃H₆O (b), and C₅H₈ (c) adsorption on the Al–MoSe₂ monolayer. The characteristic of CDD are the same as in Figure 1.

conducting property with a band gap of 1.55 eV, in accordance with the previous work²⁵ manifesting the good accuracy of our calculations. After the removal of a Se atom, there exist several novel states within the band gap of the pure MoS₂ system, narrowing the band gap to 1.02 eV accordingly. At the same time, the BS states become much denser, suggesting the enhanced electron mobility in the Se-defected system. Both perfect and Se-defected MoSe₂ monolayers are nonmagnetic given the symmetric distribution of the BS states. However, the Al–MoSe₂ system has a magnetic moment of 1 μ_B according to our result. The spin up (black line) is not symmetric with a spin down (red line).

To explicitly expound the magnetic property of the Al–MoSe₂ monolayer, its spin density is plotted in Figure 3. It is found that the dipole moment is mainly localized on the Al dopant and the bonding Mo atoms, accounting for 0.148 and 0.509 μ_B , respectively. Apart from that, the spin up and spin down both shift to lower regions by about 0.12 and 0.46 eV, respectively. This finding not only supports the electron-losing property of the Al dopant causing n-doping in the system²⁶ but also evidences a decline in the band gap of 0.68 eV for the Al–MoSe₂ monolayer. In the atomic DOS, the Al 3p orbital is

highly overlapped with the Mo 3d orbital ranging at -0.5 to 1.2 eV, which confirms the orbital hybridizations and further verifies the strong binding force of the Al–Mo bonds. Moreover, the top of the valence band is occupied by the Mo atom, while the bottom of the conduction band is occupied by the Al dopant, agreeing with the charge-transfer path from the Al dopant to the Se-defected MoSe₂ surface according to the Hirshfeld analysis.²⁷

2.2. Adsorption Performance of the Al–MoSe₂ Monolayer. Figure 4 shows the most stable configurations (MSC) for (a) C₃H₄O, (b) C₃H₆O, and (c) C₅H₈ adsorption on the Al–MoSe₂ monolayer as well as related CDD distributions.

In the C₃H₄O system, one can see that the C₃H₄O molecule prefers to be adsorbed on the Al–MoSe₂ surface through the molecule-parallel position with a small slope to the plane, in which the C=C bond approaches the Al dopant, while the –CHO group does not. One C atom of the C=C bond is captured by the Al dopant with the Al–C bond length of 2.13 Å, which suggests the stronger chemical reactivity of the C=C bond than the –CHO group when interacting with the Al dopant. The E_{ad} in this system is -1.45 eV, indicating

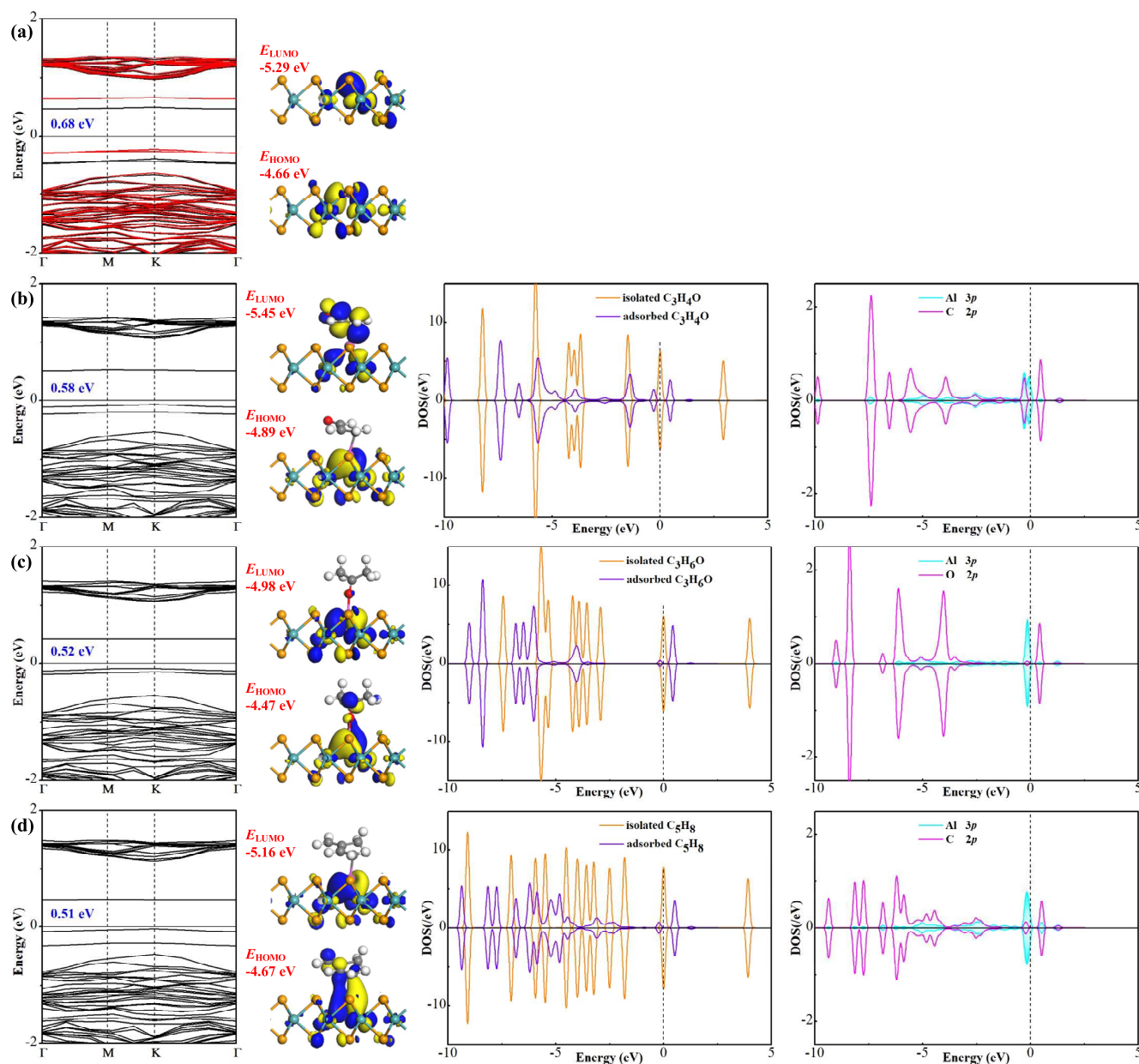


Figure 5. BS, FMO with related energies, and DOS of (a) Al-MoSe₂ system, (b) C₃H₄O system, (c) C₃H₆O, and (d) C₅H₈ system. The Fermi level is set to 0. In BS, the black line is spin up and the red line is spin down.

chemisorption for C₃H₄O adsorption on the Al-MoSe₂ monolayer.²⁸ According to the Hirshfeld analysis, the C₃H₄O molecule accepts 0.16e from the Al-doped surface, as verified by the CDD wherein the electron accumulation is mainly localized on the adsorbed gas molecule, while the electron depletion is mainly localized on the Al dopant. Besides, the electron hybridization could be observed on the Al-C bond identifying the formation of a chemical bond.

For the C₃H₆O system, we find that the preferred configuration for the C₃H₆O molecule adsorption on the Al-MoSe₂ surface is through the molecule-vertical position with the O atom oriented to the Al dopant. That is, the O atom in the ketone group is chemically active to interact with the Al dopant. The newly formed Al-O bond is measured as 1.80 Å, shorter than the sum covalent radii of Al and O atoms (1.89 Å²¹), confirming the strong binding force between them. The large E_{ad} of -1.80 eV also manifests the strong chemical

interaction between the Al-MoSe₂ monolayer and the C₃H₆O molecule. Different from that in the C₃H₄O system, the C₃H₆O molecule is positively charged by 0.06e after adsorption indicating its weak electron-donating property. From the CDD, one can see that for the trapped C₃H₆O molecule, the electron depletion is mainly on the ketone group, which accounts for the donated charge to the Al-MoSe₂ monolayer, while the overlaps between electron accumulation and electron depletion on the Al-O bond expound its chemical nature as well.

When it comes to the C₅H₈ system, the preferred configuration for the C₅H₈ adsorption is similar to that in the C₃H₄O system, in which the C₅H₈ molecule is almost parallel to the Al-MoSe₂ plane and one C atom in the C=C bond forms a new bond with the Al dopant with the equivalent bond length of 2.13 Å. These findings suggest the strong chemical reactivity of Al dopant upon C=C bond. The E_{ad}

(−2.00 eV) obtained in this system is the largest among the three adsorption configurations, which means the best adsorption performance of the Al–MoSe₂ monolayer upon C₅H₈ molecule compared with those of the C₃H₄O and C₃H₆O molecules. The Hirshfeld analysis indicates that 0.23e transfers from the C₅H₈ molecule to the Al–MoSe₂ surface. The largest value of Q_T for the C₅H₈ molecule also suggests the strongest electron redistribution for the whole system, which is supposed to change the electronic behavior of the Al–MoSe₂ monolayer to the maximum extent. From the CDD, one can see that the charge source mainly results from the trapped C=C bond of the C₅H₈ molecule, which is transferred by the Al–C bond mainly to the Al dopant. These findings explicate the charge-transfer path, the formation of the chemical Al–C bond, and the charge localization.

In short, the adsorption performance of the Al–MoSe₂ monolayer upon three VOCs are in the order of C₅H₈ > C₃H₆O > C₃H₄O. Based on their calculated E_{ad} , chemisorption could be identified in three systems. Furthermore, the morphologies of the adsorbed gas molecules also undergo different levels of deformations compared with their isolated structures, which indicates the geometric activation by the Al–MoSe₂ monolayer in adsorption. Besides, the magnetic behavior of the Al–MoSe₂ monolayer disappears after gas adsorption, which we assume attributes to the charge transfer that eliminates the effect of lone pair electron on the magnetic property of the whole system. At the same time, the electron redistribution caused by charge transfer could deform the electronic behavior of the Al–MoSe₂ system, which will be analyzed in Section 2.3.

2.3. Electronic Behavior of the Al–MoSe₂ Monolayer upon Gas Adsorptions. To comprehend the electronic behavior of the Al–MoSe₂ monolayer upon VOC adsorption, BS and DOS are conducted. Furthermore, the frontier molecular theory is also employed to obtain the distributions of frontier molecular orbitals (FMOs), including highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), and related energies, which is also an important method to analyze the sensing mechanism of the chemical resistance-type sensor.^{29,30} To perform the FMO calculations, the smearing is set to 10^{−4} Ha to guarantee the accuracy of their energies. The BS, FMO with related energies, and DOS of various systems are exhibited in Figure 5.

Initially, we focus on the BS and FMO analysis for the isolated Al–MoSe₂ system. As mentioned above, the Al–MoSe₂ monolayer shows magnetic property with a band gap of 0.68 eV. From the FMO, the HOMO and LUMO both distribute on the Al dopant, highlighting its strong chemical reactivity in the surroundings. The energy gap between HOMO and LUMO is calculated as 0.66 eV, close to the band gap in the BS implying the high accuracy of FMO calculations. In the C₃H₄O system, the band gap gets narrowed to 0.58 eV after gas adsorption, the energies of HOMO and LUMO are both down-shifted, with the energy gap calculated as 0.56 eV. The HOMO is mainly localized on the Al dopant, while the LUMO is mainly localized on the C₃H₄O molecule, which verifies the charge-transfer path from the C₃H₄O molecule to the Al–MoSe₂ monolayer. After adsorption, one can see that molecular DOS of isolated C₃H₄O is left-shifted and split into several small states in the lower region, which means the electronic activation behavior of Al dopant in adsorption. Besides, the Al 3p orbital is highly hybrid with the

C 2p orbital at −5.2 to 0 eV, which indicates the formation of the Al–C chemical bond.

Whereas in the C₃H₆O and C₅H₈ systems, the band gaps are narrowed to 0.52 and 0.51 eV, respectively. The HOMO and LUMO distributions are afflicted with different deformations in contrast to the isolated Al–MoSe₂ system. Specifically, the HOMO is mainly localized on the bonding atoms (Al and O atoms for the C₃H₆O system, while Al and C atoms for the C₅H₈ system), and the LUMO is mainly localized on the Al dopant. These findings not only manifest the strong reactivity on the Al–O and Al–C bonds but also support the Hirshfeld analysis that C₃H₆O and C₅H₈ molecules show an electron-donating property. At the same time, the energies of HOMO and LUMO in such two systems experience remarkable up-shift, which is different from that in the C₃H₄O system. However, the energy gaps are similarly reduced to 0.51 eV for the C₃H₆O system and to 0.49 eV for the C₅H₈ system. Based on the molecular and orbital DOS of the C₃H₆O system, it is seen that there is little state deformation in the DOS of the adsorbed C₃H₆O compared with that of the isolated phase, and really weak orbital mixing between Al 3p and O 2p orbital is determined. These results may be attributed to the small charge transfer in the C₃H₆O adsorption that contributes not strong electron redistribution to the whole system. On the contrary, the state split could be identified in the DOS of the adsorbed C₅H₈ molecule, and there is obvious electron hybridization between the Al 3p and O 2p orbitals at −5.1 to 0.2 eV. These results illustrate the stronger interaction of Al dopant with the C₅H₈ molecule compared with that with the C₃H₆O molecule, in agreement with the largest E_{ad} and Q_T in the C₅H₈ system.

In short, the band gap and energy gap of the Al–MoSe₂ monolayer have identically declining trends after the adsorption of three VOCs, which confirms its increasing electrical conductivity with three VOCs adsorbed. We assume that the decline of the band gap and energy gap results from the DOS state contributions of the adsorbed molecules around the Fermi level within the band gap of the isolated Al–MoSe₂ system. The orbital overlap of the bonding atoms indicates their intensity of hybridization, reflecting the strength of the binding force. The charge-transfer path could be identified from the FMO analysis, which provides a workable manner to evaluate the chemical reactivity of typical species and judge the position where the reaction occurs.³¹

2.4. Sensing Explanation of the Al–MoSe₂ Monolayer. Based on the obtained results in Section 2.3, the sensing mechanism of the resistance-type gas sensor could be identified. As a chemical resistance-type sensor, the sensing response (S), determined by the change in the electrical resistance after and before gas adsorption, is important to evaluate its usability for detecting typical gas species, which could be assessed using the following formula^{32,33}

$$\sigma = \lambda \cdot e^{(-B_g/2kT)} \quad (1)$$

$$S = \frac{\frac{1}{\sigma_{\text{gas}}} - \frac{1}{\sigma_{\text{pure}}}}{\frac{1}{\sigma_{\text{pure}}}} \quad (2)$$

In formula 1, σ is the electrical conductivity, λ is a constant, B_g is the band gap of a certain system, k is the Boltzmann constant, and T is the working temperature; in formula 2, σ_{gas} and σ_{pure} , respectively, are the conductivity of the Al–MoSe₂

monolayer after and before gas adsorption, respectively. On the basis of these two equations, the responses for the sensing $\text{C}_3\text{H}_4\text{O}$, $\text{C}_3\text{H}_6\text{O}$, and C_5H_8 molecules are calculated to be -85.7 , -95.6 , and -96.3% , respectively. In other words, the Al–MoSe₂ monolayer has desirable negative responses to such three VOCs, and the decreased electrical resistance of the Al–MoSe₂ monolayer upon exhaling gas is the basic sensing mechanism and evidence of the possible lung cancer in real clinic diagnosis.

The recovery property, meanwhile, is another important parameter to evaluate the reusability of a chemical gas sensor. To this end, the recovery time (τ), the minimum time for the adsorbed gases desorption from the Al–MoSe₂ surface, is defined based on the van't-Hoff–Arrhenius³⁴

$$\tau = A^{-1}e^{(-E_a/k_B T)} \quad (3)$$

where A is the attempted frequency (10^{12} s^{-1} ³⁵), T is the temperature, and k_B is the Boltzmann constant ($8.318 \times 10^{-3} \text{ kJ}/(\text{mol}\cdot\text{K})$). E_a is the potential barrier of desorption which in this work is determined to be equal to E_{ad} . From this formula, it could be inferred that the recovery time is related to the working temperature of the sensor. Based on this, we plot the recovery time of the Al–MoSe₂ monolayer at three typical temperatures in Figure 6. One can see from this figure that

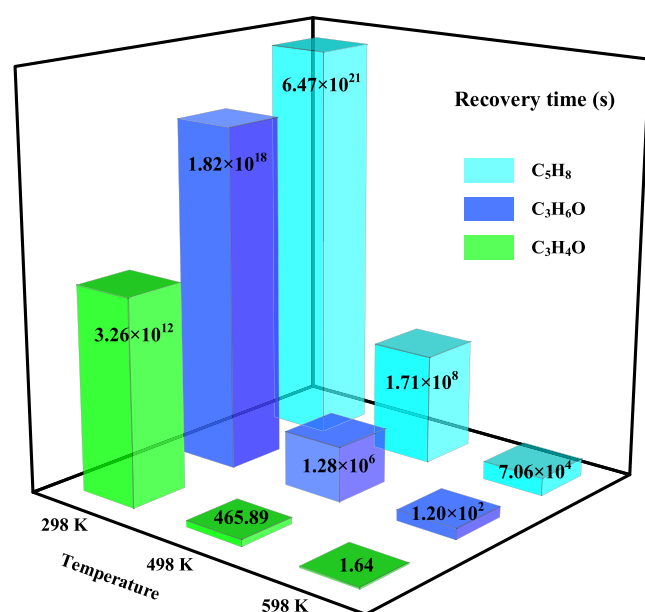


Figure 6. Recovery property of the Al–MoSe₂ monolayer upon VOC desorption.

C_5H_8 is the hardest to desorb from the Al–MoSe₂ surface, while $\text{C}_3\text{H}_4\text{O}$ is the easiest to adsorb. Even so, the desorption of three VOCs at room temperature is somewhat unrealistic. On the other hand, the desorption of $\text{C}_3\text{H}_4\text{O}$ become feasible as the temperature increases to 498 K; furthermore, as the temperature increases to 598 K, the recovery time of the Al–MoSe₂ monolayer for the desorption of all three VOCs becomes acceptable. In that case, the Al–MoSe₂ monolayer becomes reusable as a gas sensor for sensing VOCs from the exhaled breath, and the related devices based on the Al–MoSe₂ monolayer will have a longer lifespan in real applications.

When it comes to the enhanced desorption performance through heating at high temperatures, the stability of the Al–

MoSe₂ monolayer becomes another issue. Therefore, we conduct the molecular dynamic simulation in a period of 1 ps (1000 fs) at 500 and 800 K for the Al–MoSe₂ monolayer to verify its thermostability. The obtained configurations of the Al–MoSe₂ monolayer after simulation are displayed in Figure 7. From this figure, one can see that the Al–MoSe₂ surface suffers somewhat deformation in the high temperatures. However, these slight distortions have not impacted the morphology of the whole system, and the Al dopant experiencing tiny displacement remains its original doping site on the Se-vacancy MoSe₂ monolayer. These findings imply the desirable thermostability of the Al–MoSe₂ monolayer at 500 and 800 K. Meanwhile, the vibrational analysis suggests that the calculated frequency of the Al–MoSe₂ monolayer ranges from 80.54 to 840.39 cm^{-1} , in which the nonincluded virtual frequency further confirms the chemical stability of the Al–MoSe₂ monolayer. From all these aspects, it could be inferred that the Al–MoSe₂ monolayer possesses desirable thermostability and desorption of gas species from its surface is completely feasible without impairing its morphology.

3. CONCLUSIONS

In this paper, we theoretically investigate the adsorption and sensing performance of the Al–MoSe₂ monolayer upon three characteristic VOCs of exhaled breath to explore its potential as a resistance-type chemical sensor for an early diagnosis of lung cancer. The desorption behavior and the thermostability of Al–MoSe₂ are also performed to fully understand its property as a gas sensor. The main conclusions are as follows:

- Al dopant behaves as an electron-donor, leading to 1 μ_B of magnetic moment and narrowing the band gap for the whole system.
- The adsorption performance of the Al–MoSe₂ monolayer upon three VOCs are in the order of $\text{C}_5\text{H}_8 > \text{C}_3\text{H}_6\text{O} > \text{C}_3\text{H}_4\text{O}$, with sensing responses calculated as -85.7 , -95.6 , and -96.3% , respectively.
- The Al–MoSe₂ monolayer with desirable adsorption performance and thermostability offers good sensing and desorbing behaviors for the recycle VOC detection.

Our work can provide guidance for experimentalists to explore its practical use in the diagnosis of lung cancer and is important to broaden the further application of TMDs in more fields.

4. COMPUTATIONAL DETAILS

The spin-polarized calculations were implemented using DMol3 package³⁶ to obtain the results below. The Perdew–Burke–Ernzerhof (PBE) function within the generalized gradient approximation (GGA) was employed to deal with the electron exchange–correlation terms.³⁷ In terms of van der Waals force and long-range interactions, the Grimme method based on DFT-D2 was adopted.³⁸ Double numerical plus polarization (DNP) was selected as the atomic orbital basis set,³⁹ and DFT semicore pseudopotential (DSSP) method was selected to resolve the relativistic effect.⁴⁰ We adopted the Monkhorst–Pack k -point mesh of $6 \times 6 \times 1$ for the supercell geometry optimizations and of $9 \times 9 \times 1$ for electronic structure calculations.⁴¹ The energy tolerance accuracy, maximum force, and displacement were set as 10^{-5} Ha, 2×10^{-3} Ha/Å, and 5×10^{-3} Å,⁴² respectively. Self-consistent loop energy of 10^{-6} Ha, global orbital cutoff radius of 5.0 Å, and

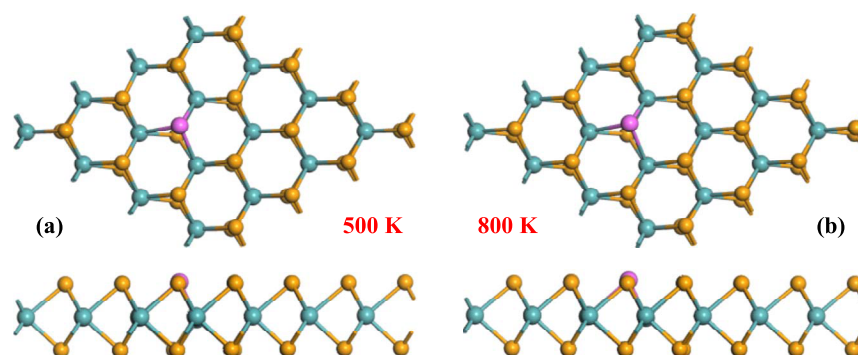


Figure 7. Configurations of the Al–MoSe₂ monolayer at (a) 500 K and (b) 800 K.

smearing of 0.005 Ha were applied to ensure the accuracy of the total energy.⁴³

We established a $4 \times 4 \times 1$ pure MoSe₂ supercell with a vacuum region of 15 Å to perform the calculations throughout this work, which contains 16 Mo and 32 Se atoms. It has been proved that a 4×4 supercell is large enough to conduct the gas adsorption process,⁴⁴ while a 15 Å slab is proper to prevent the interaction between adjacent units.⁴⁵ The lattice constant of the relaxed MoSe₂ configuration here was 3.30 Å, which is in agreement with other theoretical work (3.31 Å⁴⁶). The binding force (E_b) for Al-doping on the Se-vacancy MoSe₂ monolayer is calculated as

$$E_b = E_{\text{Al-MoSe}_2} - E_{\text{vac-MoSe}_2} - E_{\text{Al}} \quad (4)$$

where $E_{\text{Al-MoSe}_2}$, $E_{\text{vac-MoSe}_2}$, and E_{Al} are the energies of the Al–MoSe₂ monolayer, the isolated Se-vacancy MoSe₂ monolayer, and Al dopant, respectively. Besides, the adsorption energy (E_{ad}) was calculated by the following formula⁴⁷

$$E_{\text{ad}} = E_{\text{Al-MoSe}_2/\text{gas}} - E_{\text{Al-MoSe}_2} - E_{\text{gas}} \quad (5)$$

where $E_{\text{Al-MoSe}_2/\text{gas}}$, $E_{\text{Al-MoSe}_2}$, and E_{gas} are the energies of the adsorbed system, pure Al–MoSe₂ monolayer, and gas molecule, respectively. The Hirshfeld method was used to consider the atomic charge of Al (Q_{Al}) and molecular charge of the adsorbed molecule (Q_{T}) in every system. The positive charge meant the electron-donating property of the analytes and vice versa. Only the most favorable adsorption configurations were plotted and analyzed in this work.

AUTHOR INFORMATION

Corresponding Author

Yun Liu – College of Artificial Intelligence, Southwest University, Chongqing 400715, China; orcid.org/0000-0002-9567-5531; Email: yunliu@swu.edu.cn

Authors

Tun Liu – School of Traffic and Transportation Engineering, Central South University, Changsha 410083, China

Ziwen Cui – College of Mobile Telecommunications, Chongqing University of Posts and Telecommunications, Chongqing 401520, China

Xin Li – School of Management and Economics, Tianjin Vocational Institute, Tianjin 300410, China

Hao Cui – State Key Laboratory of Power Transmission Equipment & System Security and New Technology, Chongqing University, Chongqing 400044, China

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acsomega.0c05654>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work is supported by the Natural Science Foundation of Chongqing (Nos. cstc2020jcyj-msxmX0324 and cstc2020jcyj-msxmX0500) and the Fundamental Research Funds for the Central Universities (No. SWU119044).

REFERENCES

- (1) Cui, H.; Yan, C.; Jia, P.; Cao, W. Adsorption and sensing behaviors of SF₆ decomposed species on Ni-doped C₃N monolayer: A first-principles study. *Appl. Surf. Sci.* **2020**, *512*, No. 145759.
- (2) Lu, N.; Zhuo, Z.; Guo, H.; Wu, P.; Fa, W.; Wu, X.; Zeng, X. C. CaP₃: a new two-dimensional functional material with desirable band gap and ultrahigh carrier mobility. *J. Phys. Chem. Lett.* **2018**, *9*, 1728–1733.
- (3) Liu, H.; Neal, A. T.; Zhu, Z.; Luo, Z.; Xu, X.; Tománek, D.; Ye, P. D. Phosphorene: an unexplored 2D semiconductor with a high hole mobility. *ACS Nano* **2014**, *8*, 4033–4041.
- (4) Wan, Q.; Xu, Y.; Chen, X.; Xiao, H. Exhaled gas detection by a novel Rh-doped CNT biosensor for prediagnosis of lung cancer: a DFT study. *Mol. Phys.* **2018**, *116*, 2205–2212.
- (5) Buszewski, B.; Ligor, T.; Jezierski, T.; Wenda-Piesik, A.; Walczak, M.; Rudnicka, J. Identification of volatile lung cancer markers by gas chromatography–mass spectrometry: comparison with discrimination by canines. *Anal. Bioanal. Chem.* **2012**, *404*, 141–146.
- (6) Itoh, T.; Nakashima, T.; Akamatsu, T.; Izu, N.; Shin, W. Nonanal gas sensing properties of platinum, palladium, and gold-loaded tin oxide VOCs sensors. *Sens. Actuators, B* **2013**, *187*, 135–141.
- (7) Hakim, M.; Broza, Y. Y.; Barash, O.; Peled, N.; Phillips, M.; Amann, A.; Haick, H. Volatile organic compounds of lung cancer and possible biochemical pathways. *Chem. Rev.* **2012**, *112*, 5949–5966.
- (8) Phillips, M.; Altorki, N.; Austin, J. H.; Cameron, R. B.; Cataneo, R. N.; Greenberg, J.; Kloss, R.; Maxfield, R. A.; Munawar, M. I.; Pass, H. I.; et al. Prediction of lung cancer using volatile biomarkers in breath. *Cancer Biomarkers* **2007**, *3*, 95.
- (9) Zhao, G.; Li, M. Ni-doped MoS₂ biosensor: a promising candidate for early diagnosis of lung cancer by exhaled breathe analysis. *Appl. Phys. A* **2018**, *124*, No. 751.
- (10) Cui, H.; Zhang, X.; Li, Y.; Chen, D.; Zhang, Y. First-principles insight into Ni-doped InN monolayer as a noxious gases scavenger. *Appl. Surf. Sci.* **2019**, *494*, 859–866.
- (11) Zhang, D.; Zong, X.; Wu, Z.; Zhang, Y. Ultrahigh-performance impedance humidity sensor based on layer-by-layer self-assembled tin disulfide/titanium dioxide nanohybrid film. *Sens. Actuators, B* **2018**, *266*, 52–62.

- (12) Wei, H.; Gui, Y.; Kang, J.; Wang, W.; Tang, C. A DFT Study on the Adsorption of H₂S and SO₂ on Ni Doped MoS₂ Monolayer. *Nanomaterials* **2018**, *8*, No. 646.
- (13) Cui, H.; Liu, T.; Zhang, Y.; Zhang, X. Ru-InN Monolayer as a Gas Scavenger to Guard the Operation Status of SF₆ Insulation Devices: A First-Principles Theory. *IEEE Sens. J.* **2019**, *19*, 5249–5255.
- (14) Cui, H.; Jia, P. Doping effect of small Rhn (n = 1–4) clusters on the geometric and electronic behaviors of MoS₂ monolayer: A first-principles study. *Appl. Surf. Sci.* **2020**, 526, No. 146659.
- (15) Choi, S. Y.; Kim, Y.; Chung, H. S.; Kim, A. R.; Kwon, J. D.; Park, J.; Kim, Y. L.; Kwon, S. H.; Hahm, M. G.; Cho, B. Effect of Nb Doping on Chemical Sensing Performance of Two-Dimensional Layered MoSe₂. *ACS Appl. Mater. Interfaces* **2017**, *9*, 3817–3823.
- (16) Cui, H.; Zhang, H.; Zhang, X.; Tang, J. Rh-doped MoSe₂ as toxic gas scavenger: A first-principles study. *Nanoscale Adv.* **2019**, *2019*, 772–780.
- (17) Late, D. J.; Doneux, T.; Bougouma, M. Single-layer MoSe₂ based NH₃ gas sensor. *Appl. Phys. Lett.* **2014**, *105*, No. 233103.
- (18) Su, Y.; Ao, Z.; Ji, Y.; Li, G.; An, T. Adsorption mechanisms of different volatile organic compounds onto pristine C₂N and Al-doped C₂N monolayer: A DFT investigation. *Appl. Surf. Sci.* **2018**, *450*, 484–491.
- (19) Pashangpour, M.; Peyghan, A. A. Adsorption of carbon monoxide on the pristine, B- and Al-doped C₃N nanosheets. *J. Mol. Model.* **2015**, *21*, No. 116.
- (20) Ma, D.; Wang, Q.; Li, T.; He, C.; Ma, B.; Tang, Y.; Lu, Z.; Yang, Z. Repairing sulfur vacancies in the MoS₂ monolayer by using CO, NO and NO₂ molecules. *J. Mater. Chem. C* **2016**, *4*, 7093–7101.
- (21) Pyykkö, P.; Atsumi, M. Molecular single-bond covalent radii for elements 1–118. *Chem. – Eur. J.* **2009**, *15*, 186–197.
- (22) Giovanni, M.; Poh, H. L.; Ambrosi, A.; Zhao, G.; Sofer, Z.; Šaněk, F.; Khezri, B.; Webster, R. D.; Pumera, M. Noble metal (Pd, Ru, Rh, Pt, Au, Ag) doped graphene hybrids for electrocatalysis. *Nanoscale* **2012**, *4*, 5002–5008.
- (23) Ao, Z. M.; Yang, J.; Li, S.; Jiang, Q. Enhancement of CO detection in Al doped graphene. *Chem. Phys. Lett.* **2008**, *461*, 276–279.
- (24) Cui, H.; Chen, D.; Zhang, Y.; Zhang, X. Dissolved gas analysis in transformer oil using Pd catalyst decorated MoSe₂ monolayer: A first-principles theory. *Sustainable Mater. Technol.* **2019**, *20*, No. e00094.
- (25) Tongay, S.; Zhou, J.; Ataca, C.; Lo, K.; Matthews, T. S.; Li, J.; Grossman, J. C.; Wu, J. Thermally driven crossover from indirect toward direct bandgap in 2D semiconductors: MoSe₂ versus MoS₂. *Nano Lett.* **2012**, *12*, 5576–5580.
- (26) Qi, L.; Wang, Y.; Shen, L.; Wu, Y. Chemisorption-induced n-doping of MoS₂ by oxygen. *Appl. Phys. Lett.* **2016**, *108*, No. 063103.
- (27) Jiang, Q.; Zhang, J.; Ao, Z.; Huang, H.; He, H.; Wu, Y. First Principles Study on the CO Oxidation on Mn-Embedded Divacancy Graphene. *Front. Chem.* **2018**, *6*, No. 187.
- (28) Zhou, X.; Chu, W.; Zhou, Y.; Sun, W.; Xue, Y. DFT simulation on H₂ adsorption over Ni-decorated defective h-BN nanosheets. *Appl. Surf. Sci.* **2018**, *439*, 246–253.
- (29) Yao, Z.; Yang, M. A fast response resistance-type humidity sensor based on organic silicon containing cross-linked copolymer. *Sens. Actuators, B* **2006**, *117*, 93–98.
- (30) Ma, D.; Jing, Z.; Li, X.; He, C.; Lu, Z.; Lu, Z.; Yang, Z.; Wang, Y. C₃N monolayers as promising candidates for NO₂ sensors. *Sens. Actuators, B* **2018**, *266*, 664–673.
- (31) Cui, H.; Liu, Z.; Jia, P. Pd-doped C₃N monolayer: A promising low-temperature and high-activity single-atom catalyst for CO oxidation. *Appl. Surf. Sci.* **2021**, 537, No. 147881.
- (32) Zhang, X.; Yu, L.; Wu, X.; Hu, W. Experimental Sensing and Density Functional Theory Study of H₂S and SOF₂ Adsorption on Au-Modified Graphene. *Adv. Sci.* **2015**, *2*, No. 1500101.
- (33) Cui, H.; Jia, P.; Peng, X.; Li, P. Adsorption and sensing of CO and C₂H₂ by S-defected SnS₂ monolayer for DGA in transformer oil: A DFT study. *Mater. Chem. Phys.* **2020**, *249*, No. 123006.
- (34) Zhang, Y.-H.; Chen, Y.-B.; Zhou, K.-G.; Liu, C.-H.; Zeng, J.; Zhang, H.-L.; Peng, Y. Improving gas sensing properties of graphene by introducing dopants and defects: a first-principles study. *Nanotechnology* **2009**, *20*, No. 185504.
- (35) Peng, S.; Cho, K.; Qi, P.; Dai, H. Ab initio study of CNT NO₂ gas sensor. *Chem. Phys. Lett.* **2004**, *387*, 271–276.
- (36) Delley, B. J. From molecules to solids with the DMol³ approach. *J. Chem. Phys.* **2000**, *113*, 7756–7764.
- (37) Cui, H.; Zhang, X.; Chen, D.; Tang, J. Adsorption mechanism of SF₆ decomposed species on pyridine-like PtN₃ embedded CNT: A DFT study. *Appl. Surf. Sci.* **2018**, *447*, 594–598.
- (38) Tkatchenko, A.; DiStasio, R. A., Jr.; Head-Gordon, M.; Scheffler, M. Dispersion-corrected Møller-Plesset second-order perturbation theory. *J. Chem. Phys.* **2009**, *131*, No. 094106.
- (39) Zhang, D.; Wu, J.; Li, P.; Cao, Y. Room-temperature SO₂ gas-sensing properties based on a metal-doped MoS₂ nanoflower: an experimental and density functional theory investigation. *J. Mater. Chem. A* **2017**, *5*, 20666–20677.
- (40) Delley, B. Hardness conserving semilocal pseudopotentials. *Phys. Rev. B* **2002**, *66*, No. 155125.
- (41) Chen, D.; Zhang, X.; Tang, J.; Cui, H.; Li, Y. Noble metal (Pt or Au)-doped monolayer MoS₂ as a promising adsorbent and gas-sensing material to SO₂, SOF₂ and SO₂F₂: a DFT study. *Appl. Phys. A* **2018**, *124*, No. 194.
- (42) Cui, H.; Zhu, H.; Jia, P. Adsorption and sensing of SO₂ and SOF₂ molecule by Pt-doped HfSe₂ monolayer: A first-principles study. *Appl. Surf. Sci.* **2020**, 530, No. 147242.
- (43) Ju, W.; Li, T.; Su, X.; Li, H.; Li, X.; Ma, D. Au cluster adsorption on perfect and defective MoS₂ monolayers: structural and electronic properties. *Phys. Chem. Chem. Phys.* **2017**, *19*, 20735–20748.
- (44) Cui, H.; Zhang, X.; Zhang, J.; Zhang, Y. Nanomaterials-based gas sensors of SF₆ decomposed species for evaluating the operation status of high-voltage insulation devices. *High Voltage* **2019**, *4*, 242–258.
- (45) Wu, P.; Yin, N.; Li, P.; Cheng, W.; Huang, M. The adsorption and diffusion behavior of noble metal adatoms (Pd, Pt, Cu, Ag and Au) on a MoS₂ monolayer: a first-principles study. *Phys. Chem. Chem. Phys.* **2017**, *19*, 20713–20722.
- (46) Ma, Y.; Dai, Y.; Guo, M.; Niu, C.; Lu, J.; Huang, B. Electronic and magnetic properties of perfect, vacancy-doped, and nonmetal adsorbed MoSe₂, MoTe₂ and WS₂ monolayers. *Phys. Chem. Chem. Phys.* **2011**, *13*, 15546.
- (47) Cui, H.; Jia, P.; Peng, X. Adsorption of SO₂ and NO₂ molecule on intrinsic and Pd-doped HfSe₂ monolayer: A first-principles study. *Appl. Surf. Sci.* **2020**, 513, No. 145863.