Adsorption Behavior of CH$_4$ Gas Molecule on the MoX$_2$(S, Se, Te) Monolayer: The DFT Study

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Abstract

We predict the CH$_4$-sensing performance of monolayer MoX$_2$(S, Se, Te) with X-vacancy, Mo-vacancy, and divacancy by the density functional theory (DFT). The results demonstrate that the combination of different sixth main group elements with Mo atom has different adsorption behaviors for CH$_4$ gas molecule. Compared with MoX$_2$, MV$_X$, MV$_{Mo}$, and MV$_{D}$ generally exhibit better adsorption properties under the same conditions. In addition, different defects will have different effects on adsorption behavior of the systems, the MV$_{D}$(MoTe$_2$) has the better adsorption, the better charge transfer, and the shortest distance in these systems. The results are proposed to predict the CH$_4$ gas molecule adsorption properties of MV$_{D}$(MoTe$_2$) and would help in guiding experimentalists to develop better materials based on MoX$_2$ for efficient gas detection or sensing applications.

Keywords: CH$_4$ gas molecule, Monolayer MoS$_2$, Band gap, DFT, Charge transfer, Adsorption energy, Sensor

Introduction

Methane (CH$_4$) is the simplest organic compound with colorless and tasteless gas [1–4], which is basically non-toxic to human beings, the oxygen content in the air will obviously decrease when the concentration of methane is too high, which makes people suffocate. When the concentration of methane reaches 25–30% in the air, it will cause headaches, dizziness, fatigue, inattention, rapid breathing and heartbeat, and ataxia [5–7]. Since the rise of graphene [8, 9] and the discovery of topological insulators [10], a lot of interesting physics have been found in systems with reduced dimensions. Other two-dimensional (2D) material, such as monolayers or few-layer systems (nanolayers) of transition-metal dichalcogenides (TMDs), gain importance because of their intrinsic band gap [11–15]. TMDs are MX$_2$-type compounds where r(S, Se, Te) [16–19]. These materials form layered structures in which the different X-M-X layers are held together by weak van der Waals forces [20–26]. Yi Li [27] studied that the adsorption energy of COF$_2$ on Ni-MoS$_2$ was better than CF$_4$, and Ni-MoS$_2$ acted as electron donor and obvious charge transfer was observed. Soumyajyoti Haldar [28] reported that structural, electronic, and magnetic properties of atomic scale defects in 2D transition metal dichalcogenides MX$_2$, and different vacancy had a great effect on different 2D dichalcogenides MX$_2$, it is likely that band gap, density of states, some properties, and so on. Janghwan Cha [29] used different functionals to show the relatively binding energies about gas molecule and MoX$_2$. The optPBE-vdW functionals showed relatively large binding energies. Furthermore, the TMDs are promising materials to realize gas sensors, so we study the effect of many defects on MoX$_2$(X=S, Se, Te) for structure, band gap [30–32], adsorption energy, charge transfer, etc. This paper studied the interaction of methane with monolayer MoX$_2$ by first-principle simulation (see Fig. 1). The green color ball is Mo atom, and the yellow color ball is X atom, the distance of d$_1$ for S-S, Se-Se, and Te-Te is 3.190 Å, 3.332 Å, and 3.559 Å, respectively, the distance of d$_2$ is the same as the three cases of d$_1$. This work was based on DFT, and the adsorption energy, charge transfer, adsorption distance, and density of states (DOS) of CH$_4$ gas molecule on MoX$_2$ were studied.
Method and Theory

A 4 × 4 supercell of MoX₂ (32 X atoms and 16 Mo atoms) and CH₄ gas molecule adsorbed onto it was built in Materials studio [33–36]. DMol³ [37] software was used for calculation. In this paper, the Perdew, Burke, and Ernzerhof (PBE) [38, 39] functions with generalized gradient approximation (GGA) were selected to describe the exchange energy Vxc. The Mo was generated in 4p⁶5s¹4d⁵ configuration and another was used for the generation of the valence electrons of X. The Brillouin zone of MoX₂ was sampled using a 6 × 6 × 1 k-point grid and Methfessel-Paxton smearing of 0.01 Ry. The cutoff energy was 340 eV with self-consistence-field (SCF) converged of 1.0 × 10⁻⁵ eV. All the atomic structures were relaxed until the maximum displacement tolerance of 0.001 Å and maximum force tolerance of 0.03 eV/Å [40, 41].

We calculated the adsorption energy (E_ad) in the adsorbed systems, which was defined in the following equation:

\[ E_a = E_{MoX₂+CH₄ \text{ gas molecule}} - (E_{MoX₂} + E_{CH₄ \text{ gas molecule}}) \]

Where, \( E_{MoX₂+CH₄ \text{ gas molecule}} \), \( E_{MoX₂} \) and \( E_{CH₄ \text{ gas molecule}} \) represent the energies of the monolayer MoX₂ adsorbed system, monolayer MoX₂, and a CH₄ gas molecule, respectively. All energies achieve the best optimization after structural optimization. We used Mulliken’s population analysis to study the charge transfer.

Results and Discussion

Firstly, we discussed the geometric and electric structures of the four MoX₂ substrates (ee in Fig. 2). The bond length of Mo-S, Mo-Se, and Mo-Te were 2.426 Å, 2.560 Å, and 2.759 Å, which were in good agreement with experimental value of 2.410 Å (MoS₂) [42, 43], 2.570 Å (MoSe₂) [44] and 2.764 Å (MoTe₂) [45], the four structures MoX₂ were in this paper, pristine MoX₂, MVX(one X atom vacancy), MVMo(one Mo atom vacancy), and MV_D(one X atom and one Mo atom vacancy) respectively. Full structural relaxation showed that the stretching X-Mo bond length from 2.420 Å to
2.394 Å (MV₃), 2.420 Å to 2.398 Å (MV_Mo), and the main reason was that the absence of atoms enhanced the interaction between the adjacent Mo atoms and other S atoms, the chemical bond became stronger and the bond length became shorter.

Figure 3a–c displayed the calculated adsorption energy, charge transfer, and adsorption distance of CH₄/MoX₂ system. Before the adsorption, the distance between the CH₄ gas molecules and the molybdenum disulfide was 3.6 Å. The CH₄ gas molecule obtained about −0.001 e to −0.009 e from the four systems of MoS₂ sheet, −0.009 e to −0.013 e from the four systems of MoSe₂ sheet and −0.014 e to −0.032 e from the four systems of MoTe₂ sheet, respectively, which means that CH₄ acted as an acceptor. Inclusion of the van der Waals correction enhances the adsorption energies of CH₄ gas molecule by −0.31 eV to −0.46 eV on the four systems of MoS₂ systems, by −0.07 eV to −0.50 eV on the four systems of MoSe₂ systems, and by −0.30 eV to −0.52 eV on the four systems of MoTe₂ system, and 0.01 eV was usually thought within the error range. It was obvious that the adsorption distance was the shortest in the case of S atom defects and divacancy defects. To sum up the above data, we saw that the adsorption effect was the best under the condition of divacancy defected.

Adsorption of CH₄ Gas Molecule on Monolayer MoS₂

In order to have a clear understanding about the bonding mechanism of CH₄ gas molecule on pure and defected MoS₂ (including MV₃, MV_Mo, and MV_D), we analyzed the corresponding density of states (DOS) for adsorbed CH₄ gas molecule in adsorption structures. Comparing four systems, the adsorption effect of CH₄ gas molecule on pure and defected MoS₂ (including MV₃, MV_Mo, and MV_D) were further investigated. The DOS (Fig. 4) showed that there was a certain change in the vicinity of the Fermi level, which was the same as the general DOS form. The energy band gap of four systems was observed along the gamma point (G) noticed to be 1.940 eV (MoS₂), 1.038 eV (MV₃), 0.234 eV (MV_Mo), and 0.209 eV (MV_D). Moreover, the observed energy band gap of MoS₂ nanosheet was in good agreement with other reported theoretical work (1.78 eV [39], 1.80 eV [40]) and experimental work (1.90 eV [41], 1.98 eV [42]). Meantime, monolayers MoS₂ had five peak values, the peak was −12.2 eV, −5 eV, −4 eV, −2 eV, and −1 eV which were ascribed to the S atom in MoS₂ and the Mo atom in MoS₂. However, the DOS of four systems (Fig. 4) showed that the electronic level of CH₄ gas molecule has a peak for about −3 eV which was closed to Fermi level. It was contributed to the conduction band in the system and affects the conductivity of CH₄ gas molecule on MoS₂.
the system. Comparing four systems, the peak of −12.5 eV MVs was obviously much lower than MoS$_2$ because of the defect of the S atom in the MoS$_2$. And the defects of the Mo atom do not have much effect; however, the contribution at the conduction zone was still decreasing. As shown in Fig. 3 b, obviously, the band around the 0 eV was getting smaller and smaller, and the curve was more and more stable. In summary, there was no bond between CH$_4$ gas molecule and MoS$_2$, and the electron transfer and adsorption energy were small, and the adsorption was not very strong, which was obviously physical adsorption.

Adsorption of CH$_4$ Gas Molecule on Monolayer MoSe$_2$

We studied the adsorption of CH$_4$ gas molecule on four systems of MoSe$_2$, it could be seen from the DOS (Fig. 5) that the electron energy levels of CH$_4$ gas molecule in the four adsorption orientations were close to the Fermi level, which had a certain influence on the conductivity of the system, and the band gap system was so small, same as adsorption of MoS$_2$. Meantime, the DOS (Fig. 5) also showed that the Se atoms in MoSe$_2$ had five peak values, the peak was −12 eV, −5 eV, −4 eV, −3 eV, and −2 eV, the Mo atom in MoSe$_2$ had overlapping peaks at about 0.5 eV and 2 eV. Compared with MoS$_2$, Se contributed more to the system than S in MoS$_2$ below the fermi level, and the energy band gaps of four systems were observed along the gamma point (G) that was noticed to be 1.680 eV (MoSe$_2$), 1.005 eV (MV$_{Se}$), 0.094 eV (MV$_{Mo}$), and 0.024 eV(MV$_D$). The band was narrower and more stable around the 0 eV. Therefore, it could be confirmed that the adsorption properties and the CH$_4$ gas molecule on the four systems were physisorption.

Adsorption of CH$_4$ Gas Molecule on Monolayer MoTe$_2$

We studied the adsorption of CH$_4$ gas molecule on four systems of MoTe$_2$, the DOS (Fig. 6) of CH$_4$ gas molecule on the MoTe$_2$ were analyzed. As shown in Fig. 6, the

Fig. 4 The structure and DOS of CH$_4$ gas molecule on four systems (MoS$_2$, MV$_{S}$, MV$_{Mo}$, and MV$_D$)
The electronic levels of CH$_4$ in the four MoTe$_2$ systems were short with CH$_4$/MoS$_2$ systems and CH$_4$/MoSe$_2$ systems, and the energy band gap of four systems were observed along the gamma point (G) was noticed to be 1.261 eV (MoTe$_2$), 0.852 eV (MV$_{Te}$), 0 eV (MV$_{Mo}$), and 0.316 eV (MV$_{D}$). One of the strangest things of all was the defect of the Mo atom, which allowed the system to be transformed from semiconductor to metal. Meanwhile, the DOS (Fig. 6) also showed that the Te atoms in MoTe$_2$ had four peaks value, the peak was $-10$ eV, $-5$ eV, $-3$ eV, and $-1$ eV and the Mo atom in MoSe$_2$ had overlapping peaks at about 1 eV.

In general, on the basis of the adsorption behaviors of CH$_4$ gas molecule in different systems, the CH$_4$ gas molecule adsorbed by the MV$_X$ could have two peaks near the Fermi level. The DOS between the two spikes was not zero but very wide, which reflected the strong covalent property of the system. To summarize all the data, the MV$_{Te}$ might become an ideal sensing material for the detection of CH$_4$ gas molecule.

**Conclusions**

We carried out density-functional-GGA studies to study the interaction of an isolated CH$_4$ gas molecule on MoX$_2$ (X=S, Se, Te). The results indicated that the different defects changed the electrical properties of MoX$_2$ greatly, and our results revealed a weak interaction between the CH$_4$ gas molecules and MoX$_2$ monolayer, which indicated the physical nature of the adsorption. The total electron density plots confirmed the physisorption of gas molecules on the MoX$_2$ surface, as the material weakly interacts with the CH$_4$ gas molecules without the formation of covalent bonds at the interface region. Furthermore, the structure of MV$_{D}$ has a good band
gap, semiconductor property, the best adsorption energy, and the stronger charge transfer for the CH₄ gas molecule. Besides, the electronic band structures of the sensing system were altered upon the adsorption of gas molecules. MoTe₂ had the highest adsorption energy (−0.51 eV), the shortest intermolecular distance (2.20 Å), and the higher charge transfer (−0.026 e). At last from the analysis of these three materials, it could be seen that MV₃ (MoTe₂) had the best adsorption effect on CH₄ gas molecule. The calculated results thus suggested a theoretical basis for the potential application of MV₃(MoTe₂) monolayers in the CH₄ based gas sensor devices.

Abbreviations
CH₄: Methane; DOS: Density of states; Ea: Adsorption energy

Acknowledgements
We also thank the College of Materials Science and Engineering, Anhui University of Science and Technology, for its assistance with the MS simulations.

Authors’ Contributions
JR and YX designed and carried out the experiments and drafted the manuscript. JR, HL, and LW participated in the work to analyze the data. HL participated in the revision of the manuscript. All authors read and approved the final manuscript.

Authors’ information
Not applicable

Funding
The financial supports for this work from the Natural science fund for colleges and universities in Jiangsu Province (17KJB510007, 17KJB535001, 18KJB510005).

Availability of Data and Materials
All data are fully available without restriction.

Competing Interests
The authors declare that they have no competing interests.

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