Understanding the adsorption behavior of small molecule in MoS₂ device based on first-principles calculations

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1. Introduction

Detection of industrial gas and environmental pollution is critical for public health. Thus, it is important to find new materials that have superior characteristics in gas sensing. Two-dimensional (2D) materials have inspired impressive passion in scientific community, their mechanical, electrical and optical properties are superior and strikingly different from their layered bulk counterparts. More important, because of the high surface-to-volume ratio and splendid sensing capability, 2D materials, such as graphene, two-dimensional (2D) transition metal dichalcogenides (TMDs), etc., are acting as a role for real-time detections of industrial processes and environment. MoS₂ is a typical TMDs material, that has been studied extensively as a candidate of various electronic applications [1–4]. For MoS₂ from bulk to atomic monolayer, a transition of bandgap from 1.2 to 1.8 eV will occur, crossing from indirect to direct one [5]. Due to the unique electrical properties, layered MoS₂ has spurred intense research interests towards the development of nano-electronic devices by utilizing these novel performances, such as field-effect transistors (FETs), photodetectors, and light-emitting diode (LEDs) [6–9], etc. Especially, layered MoS₂ have been regarded as a candidate of gas detection devices [10, 11]. For example, covalent functionalization was demonstrated experimentally and theoretically, which suggests that covalent adsorption can be achieved in the layered MoS₂ [12]. Currently, plenty of reports have proved the high sensing capability of pristine MoS₂ flakes as highly efficient gas sensors [13, 14], the adsorption behavior of small molecules is still ambiguous for layered MoS₂ under different effects, such as defect effect, doping and environment effect, etc.

In general, perfect layered MoS₂ exhibits excellent electrical properties as electrical devices (FETs), such as short-channel effect, better electrostatic control, relative higher mobility, and so on [15, 16]. However, in the applications of FETs, the existence of the intrinsic defect, such as sulfur and molybdenum vacancies, would greatly change the electric properties [17, 18]. Generally speaking, because chalcogen atoms are easy to volatilize, S vacancies are common in mechanical exfoliated and chemical vapor deposition MoS₂ sheets [19], and new
states below the conduction band edge caused by S vacancy leading to localization and undesirable electrons doping [20]. The localization and undesirable electrons doping could significantly influence the adsorption behavior of MoS2. Besides the intrinsic defect, the environmental effect is another important factor. It is well known that 2D materials are sensitive to the environment due to the inherent properties, which have been regarded as the impediment in stable and mass production of devices [21–23]. Therefore, such susceptibility to the environment may also ultimately affect the adsorption behavior of layered MoS2.

To clearly understand the adsorption characteristics of the layered MoS2, and then better design and fabricate gas sensor devices, an accurate prediction and determination of adsorption behavior for 2D semiconductor sensor devices is of fundamental importance especially for technological applications. Currently, first-principles calculations have become a core calculation method in materials, chemistry, biology, and other research fields due to their unique accuracy and the lack of empirical parameters. Based on the first-principles calculations, plenty of new materials with superior characteristics are predicted and discovered [24, 25]. In this work, we performed the first-principles calculations to systematically investigate the adsorption behavior of layered MoS2 with several kinds of absorbed small molecules, as well as the electronic properties. More important, the defect and environmental effect on the adsorbed small molecules have been discussed in detail. According to the results, some superior small-molecule gas sensors based on monolayer MoS2 are expected to be designed and fabricated.

2. Theoretical method

The small molecule gas sensor is usually based on the diode or FETs. Here, the diode is selected as the prototype device. Figure 1 shows a structure of gas sensors based on layered MoS2. The first-principles calculations were utilized based on density functional theory (DFT) [26] with the CASTEP code [27]. The generalized gradient approximation (GGA) functional of Perdew, Burke and Ernzerhof (PBE) was used to treat the exchange and correlation potentials [28]. The van der Waals interactions were corrected using Tkatchenko-Scheffler method [29]. All the atomic positions and lattice parameters were optimized with the maximum Hellmann–Feynman forces of 0.01 eV/Å, which leads to obtaining relaxed structures. A 4 × 4 × 2 Monkhorst-Pack k-point grid was employed and the plane wave energy cutoff was set to 450 eV [30], self-consistent field (SCF) tolerance was
converged to $5 \times 10^{-7}$ eV/atom, which confirms a reasonable calculated result [31]. We adopted a $5 \times 5 \times 1$ supercell containing 75 atoms (25 Mo and 50 S atoms). The distance between the neighboring interface was set to be 25 Å to minimize the interaction between layers [32]. Figures 1(b)–(d) displays the configurations for subsequent calculations. Here, the lattice parameters and Mo-S bonds in the MoS$_2$ monolayer were firstly optimized with the values of 3.166 Å and 2.403 Å, respectively, in good agreement with the reported values (lattice parameter: 3.16 Å, Mo-S bond length: 2.41 Å) [33]. The band gap calculated is about 1.721 eV, which is in good line with the previous experimental and theoretical data [34].

Adsorption energy of gas molecule on pristine and defective MoS$_2$ was calculated using [35].

$$E_{ad} = E_{MoS_2/gas} - E_{MoS_2} - E_{gas}$$

where $E_{MoS_2/gas}$ is the total energy of the MoS$_2$/gas system, $E_{MoS_2}$, and $E_{gas}$ are the energies of layered MoS$_2$ and the gas molecule, respectively.

In terms of a similar method, the adsorption energy of gas molecule on the layered MoS$_2$ in different environments can be determined as,

$$E_{ad} = E_{(MoS_2+gas1)/gas2} - E_{MoS_2+gas1} - E_{gas2},$$

where $E_{(MoS_2+gas1)/gas2}$ is the total energy of the system, $E_{gas2}$ is the energy of the isolated small molecule, $E_{MoS_2+gas1}$ is the total energy of MoS$_2$ with environmental gas.

The charge transfer between gas molecules and MoS$_2$ defined as [36].

$$\Delta Q = Q_{MoS_2/gas} - Q_{MoS_2},$$

where $Q_{MoS_2/gas}$ and $Q_{MoS_2}$ are the charge of MoS$_2$/gas system and pristine MoS$_2$, respectively.
3. Results and discussion

3.1. Small molecule adsorption on perfect MoS$_2$

To investigate the adsorption behavior, firstly, we examined the configurations and electronic properties of pristine MoS$_2$ and different gas molecule-MoS$_2$ systems. Figure 2 displays the energy gaps of the pristine MoS$_2$ and small molecules adsorbed MoS$_2$. Our results show that the band gap of the pristine monolayer MoS$_2$ is about 1.721 eV, which is similar as the experimental and theoretical results (1.7 eV $\sim$ 1.8 eV) $^{[34, 37]}$. As compared with the pristine sample with the larger energy gap, the energy gaps of layered MoS$_2$ with different small molecules are almost similar, except for N-based small molecules (especially NO and NO$_2$) which have been remarkably decreased. To explain the phenomenon, we have calculated the density of states (DOS). Figure 3 shows the DOS and partial DOS (PDOS) of pristine monolayer MoS$_2$ and MoS$_2$ with adsorbed N-based small molecules, respectively. As compared with DOS of pristine MoS$_2$, the DOS of MoS$_2$ with adsorbed small molecules (NO and NO$_2$) overall move to lower energy levels. More important, a new peak has appeared near the Fermi level. Based on the PDOS, one can find that the new peak derives from the p state of NO (NO$_2$) molecule. Therefore, the decrease of bandgap for N-based small molecules adsorbed on monolayer MoS$_2$ is attributed to the introduction of p state from NO (NO$_2$) molecule.

Then, by using equations (1) and (3), we have calculated the adsorption energies and charge transfer between MoS$_2$ and small molecules, as presented in Table 1. It is found that perfect layered MoS$_2$ exhibits a strong sensitivity to N-based gas molecules, especially for NO and NO$_2$. However, it is worth noting that, lower adsorption energies mean that the elementary molecule (such as H$_2$ and N$_2$) are weakly adsorbed on perfect MoS$_2$. The calculated adsorption energies and charge transferred are consistent with the reported results, at which for NH$_3$ and NO$_2$, $E_{ad}$ is $-0.149$ eV and $-0.258$ eV, and $\Delta Q$ is $-0.009$ e and $-0.097$ e, respectively $^{[38]}$.
3.2. Small molecule adsorption on defective MoS2

Since perfect MoS2 exhibits the strong sensitivity to N-based gases, we then studied the adsorption behavior of the N-based molecules on defective MoS2. Here, S vacancy and Mo vacancy are the two main intrinsic defects for defective MoS2. The calculated adsorption energies for different conditions are summarized in Table 2. One can see that in Table 2, the adsorption energies of NO and NO2 adsorbed on defective MoS2 with Mo vacancy increase remarkably (larger than 5 times), as compared with that on perfect MoS2. While on the defective MoS2 with S vacancy, the adsorption energy changes of NO2 and NH3 is not that notable — almost unchanged, especially for NH3. In order to uncover the different adsorption behavior for the defective MoS2 with Mo vacancy and S vacancy, we have further analyzed the electron localization function (ELF), as shown in Figure 4. From the ELF, we deem that for NO and NO2 small molecules adsorbed on defective MoS2, the different adsorption behaviors are attributed to that whether or not bonds can be formed between the small molecules and MoS2. In terms of our calculated results, O-S bond has formed between NO2 and MoS2 with Mo vacancy, as well as N-S bond between NO and MoS2. Similarly, N-Mo bond has formed between NO and MoS2 with S vacancy. Thus, the significant increase of adsorption stability of the defective MoS2 originates in the formation of the chemical bond. As a result, in the layered MoS2, covalent adsorption of N-based functional groups has been achieved.

To further understand the adsorption behavior, we also utilized the charge density difference ($\Delta \rho$) to analyze the charge transfer. Figure 5 shows the plane-averaged $\Delta \rho$ and side view of charge density difference plots. Our results show that for NO2 adsorbed on defective MoS2, $\Delta \rho$ near MoS2 interface region displays a negative charge value, which suggests that the charge will transfer from NO2 to MoS2. However, $\Delta \rho$ for defective MoS2 with different defects is notably different. For example, $\Delta \rho$ of NO2 adsorbed on MoS2 with Mo vacancy is about $-6.9 \times 10^{-4} \text{ e/Å}$, which is twice larger than that of NO2 adsorbed on MoS2 with S vacancy ($-3.2 \times 10^{-4} \text{ e/Å}$). Otherwise, based on equation (3), the value of the transfer charge has been obtained, that is, the charge transfer from NO2 to MoS2 is $-0.32$ and $-0.12 \text{ e}$ for NO2 on Mo vacancy-MoS2 and S vacancy-MoS2, respectively. As for the adsorption of NO on defective MoS2, $\Delta \rho$ near the MoS2 interface shows a positive charge value, which suggests that the charge will transfer from MoS2 to NO. That is, $\Delta \rho$ of NO on Mo vacancy-MoS2 is about $4.24 \times 10^{-4} \text{ e/Å}$, while $\Delta \rho$ of NO on S vacancy-MoS2 is about $9.72 \times 10^{-4} \text{ e/Å}$. The charge transfer from MoS2 to NO is $-0.11$ and $-0.64 \text{ e}$ for the adsorption of NO on Mo vacancy-MoS2 and S vacancy-MoS2, respectively. Thus, these results indicate that the stronger the charge transfer is, the larger the adsorption energy is. In general, as two materials forming a covalent bond, $\Delta \rho$ will change significantly. Therefore, the larger change of $\Delta \rho$, accompanying with the charge transfer, confirms the formation of O-S bond, N-S bond and N-Mo bond, respectively.

3.3. Small molecule adsorption on MoS2 in different environments

Since layered MoS2 are sensitive to the environment due to the inherent properties, understanding the adsorption behavior of layered MoS2 in different environments can provide crucial input in the development of sensing technology based on layered MoS2. Here, we focus on the adsorption of N-based small molecules in different environments. Table 3 shows the adsorption energies of NH3, NO2 and NO molecules adsorbed on the layered MoS2 in CO2, N2, and H2O environments, respectively. The calculated results display that the adsorption...
stability of N-based small molecules adsorbed on the layered MoS2 will increase under the environmental influence, as compared with that on perfect layered MoS2. However, the adsorption behavior in different environments is much weaker than that on defective MoS2, which implies that the adsorption of small molecules in different environments belongs to physical absorption. ELF analysis also displays that chemical bonds are not formed between the N-based small molecules and MoS2. To clearly understand the environmental effect on the adsorption behavior, we also calculated the $\Delta \rho$. Figure 6 shows the calculated plane-averaged $\Delta \rho$ and side view of plots. In which, the charge accumulation is represented in red and charge depletion is in blue, respectively.

Table 3. The adsorption energies (meV) of N-based small molecules in different environments.

|           | $E_{ad}$ (meV) |
|-----------|----------------|
| NH$_3$    | $-208.28$      |
| NO$_2$    | $-313.76$      |
| NO        | $-229.92$      |
| CO$_2$    | $-241.00$      |
| H$_2$O    | $-256.79$      |
|            | $-324.81$      |
|            | $-256.84$      |
|            | $-279.02$      |

Figure 6. Plane-averaged differential charge density ($\Delta \rho$) and charge density difference plots for the adsorption of (a) NH$_3$, (b) NO$_2$, and (c) NO on MoS$_2$ with CO$_2$, N$_2$, and H$_2$O environments. Inset: Side view of charge density difference plots. In which, the charge accumulation is represented in red and charge depletion is in blue, respectively.

Figure 7. Schematic diagram of adsorption behavior of small molecules adsorbed on perfect MoS$_2$ (a), MoS$_2$ with gas environment (b), and defective MoS$_2$ (c).
3.4. Small molecule adsorption mechanism on MoS$_2$

It is well known that the adsorption behavior of small molecules mainly includes physical and chemical adsorptions. Here, the forming of covalent bonds between gas small molecules and monolayer MoS$_2$ means chemical adsorption, otherwise it is physical adsorption [39]. According to the description above, one can tell that physical and chemical adsorptions coexist for small molecules adsorbed on the layered MoS$_2$. For small molecules adsorbed on perfect MoS$_2$, it is mainly embodied in physical absorption. For this adsorption behavior, the outer-shell electrons between small molecules and MoS$_2$ are going to overlap, which induces a small amount of charge transfer among them. For small molecules adsorbed on defective MoS$_2$, it is mainly manifested in chemical absorption, at which a covalent chemical bond may be formed between small molecules and MoS$_2$. At the same time, a great deal of charge transfer will occur among them. For small molecules adsorbed on MoS$_2$ in different environments, it is also embodied in physical absorption. However, due to the influence of environment gas, except the outer-shell electrons are going to overlap, a larger amount of charge transfer will occur among them, as compared with that on perfect MoS$_2$. Figure 7 shows the schematic diagram of the adsorption behavior of small molecules adsorbed on MoS$_2$.

4. Conclusions

To understand the adsorption behavior of small molecules in MoS$_2$ device, the adsorption of small molecules on MoS$_2$ under different conditions has been investigated based on the first-principles calculations. We demonstrate that, as compared with small molecules adsorbed on perfect MoS$_2$, adsorption behaviors on defective MoS$_2$ and MoS$_2$ with environmental gases have remarkably changed. On perfect MoS$_2$, gas molecules are all physically adsorbed, whereas, NO ad NO$_2$ can be chemically adsorbed on Mo vacancy-MoS$_2$, at which O-S and N-S covalent bonds are formed between NO and MoS$_2$, NO$_2$ and MoS$_2$, respectively. Meanwhile, NO can also be chemically adsorbed on S vacancy-MoS$_2$ owing to the N-Mo covalent bond between NO and S vacancy-MoS$_2$. The forming of covalent bonds can be demonstrated by the electron localization function. Adsorption energies of gas molecules on perfect MoS$_2$, MoS$_2$ with gas environment, and defective MoS$_2$ increase gradually. As a result, the environmental gas can improve the adsorption stability to a certain extent, and defects can remarkably enhance the stability but extend the recovery time of sensor.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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