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Full Length Article

NO-sensing performance of vacancy defective monolayer MoS_2 predicted by density function theory

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ABSTRACT

Using density functional theory (DFT), we predict the NO-sensing performance of monolayer MoS_2 (MoS_2-MLs) with and without MoS3-vacancy/S-vacancy defects. Our theoretical results demonstrate that MoS3- and S-vacancy defective MoS_2-MLs show stronger chemisorption and greater electron transfer effects than pure MoS_2-MLs. The charge transfer analysis showed pure and defective MoS_2-MLs all act as donors. Both MoS3-vacancy and S-vacancy defects induce dramatic changes of electronic properties of MoS_2-MLs, which have direct relationship with gas sensing performance. In addition, S-vacancy defect leads to more electrons transfer to NO molecule than MoS3-vacancy defect. The H_2O molecule urges more electrons transfer from MoS3- or S-vacancy defective MoS2-MLs to NO molecule. We believe that this calculation results will provide some information for future experiment.

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1. Introduction

Molybdenum disulfide (MoS_2) with hexagonal structure had been extensively used in the field of field-effect transistor (FET), hydrogen production, solar cells, and gas sensor [1–8]. It had attracted considerable interest due to its unique physical and chemical properties in the past few decades [9]. The interest arisen from its high surface-to-volume ratio comparable to graphene, indirect-to-direct band-gap and layer-dependent tunable band-gap [10–12]. For example, the MoS_2-based field-effect transistor (FET) exhibited high room-temperature current on/off ratio up to 10^8 [13]; MoS_2-based gas sensor exhibited high sensitivity to NO gas with a detection limit down to 0.8 ppm [14]. Recently, monolayer MoS_2 (MoS_2-MLs) had been synthesized by mechanical exfoliation (ME) [15], physical vapour deposition (PVD) [16], chemical vapour deposition (CVD) [17,18], atomic layer deposition (ALD) [19] and molecular beam epitaxy (MBE) [20]. However, the vacancy defects were unavoidable during material's synthesis process, which were usually more reactive than perfect sites [21,22]. Vacancy defects also usually played an important role in tailoring the electric properties of MoS_2-MLs [23]. In 2013, Zhou et al. investigated the intrinsic defects in MoS_2-MLs grown by CVD method [21]. They found that monosulfur vacancy (S-vacancy) and vacancy complex of Mo and its nearby three sulfur (MoS3-vacancy) were frequently observed in the sample. Later, Hong et al. synthesized MoS_2-MLs by ME, CVD and PVD method [22]. They found that the most common defects were monosulfur vacancy (S-vacancy) for MoS_2-MLs grown by ME.

Detection of toxic gas, which caused environmental and public health problems, was extremely important and critical [24–27]. Experiment results showed that the MoS_2-based FET and films exhibited high sensitivity to NO [14] and NH_3 gas [25]. In theory, the interaction between pure MoS_2-MLs and gas molecules, such as CO, CO_2, NH_3, NO, O_2, and etc., had been studied [28–30]. The adsorption properties of NO_2 and NH_3 molecules on Al-, Si- and P-doped MoS_2-MLs had also been investigated [31]. However, they placed a little focus on vacancy defective MoS_2-MLs. In order to further exploit the possibilities of MoS_2-MLs as gas sensor, it was necessary to accomplish a systematic investigation on the adsorption properties of MoS_2-MLs, especially for vacancy defective MoS_2-MLs.

Nitrogen oxides like nitrogen monoxide (NO) and nitrogen dioxide (NO_2) are typical air pollutants that cause environmental problems [32,33]. Nitrogen monoxide (NO) can causes acid rains, photochemical smog and production of ozone [32]. Besides, NO also affects neuron operation such as transcriptional regulation and ion channel functions, thus causing neurodegenerative diseases [34,35]. The detection and the emission control of nitrogen oxides are crucial means to reduce their noxious effects on environmental and human beings [36,37]. Initial results have revealed that MoS_2 layers are extremely sensitive to NO_X [14].

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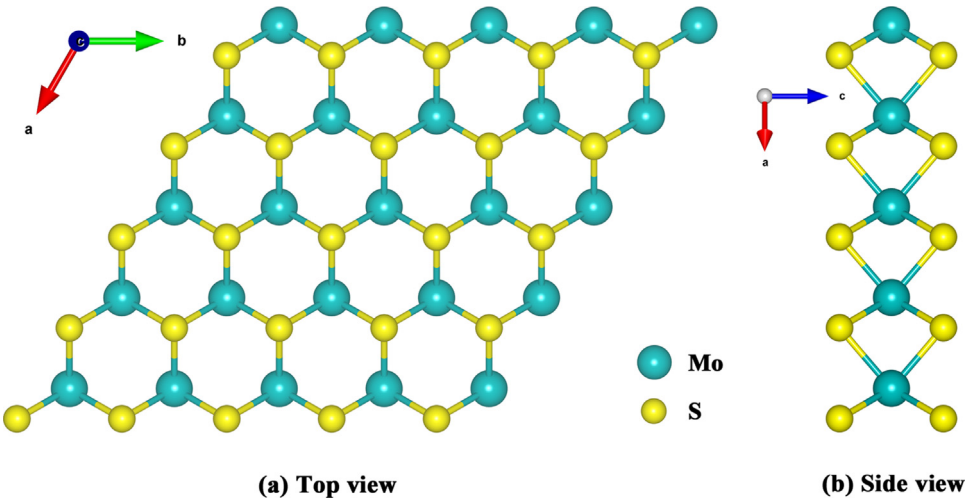

Fig. 1. Top (a) and side (b) view of pure MoS_2-ML. Green and yellow balls represent Mo and S atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In this work, we report the adsorption properties and gas sensing mechanisms of NO molecule on most common MoS3-vacancy and S-vacancy defective MoS_2-MLs, using density functional theory (DFT) method. The stabilities of NO molecule on defective MoS_2-MLs (including MoS3-vacancy and S-vacancy defects) are investigated according to their adsorption energies. Our calculation results reveal that defective MoS_2-MLs show stronger chemisorption and more transferred electrons than pure MoS_2-MLs. MoS3-vacancy and S-vacancy defects can effectively improve the adsorption and gas sensing performance of NO molecule on MoS_2-MLs. The Bader charge analysis shows that the electrons transfer from pure and defective MoS_2-MLs to NO molecule. The transferred electrons lead to appearance of hole-carrier in pure MoS_2-ML, which leads to p-type conductivity behavior of pure MoS_2-MLs. The resistances (R_P) of gas sensors based on pure MoS_2-MLs decrease with the increasing of hole-carrier concentration. However, the transferred electrons result in a decrease in the electron-carrier concentration in defective MoS_2-MLs because of their n-type semiconductor characteristics. The resistances (R_N and R_M) of gas sensors based on defective MoS_2-MLs increase with the decreasing of electron-carrier concentration. The adsorption properties and gas-sensing mechanisms of pure and defective MoS_2-MLs are investigated in detail. In addition, the effects of H_2O molecule on NO-sensing performance of defective MoS_2-MLs are also studied in this research.

2. Computational details

2.1. Calculation methods

Density functional theory (DFT) calculations were employed using the projector augmented wave (PAW) pseudopotential in *Vienna ab initio simulation package* (VASP) [38,39]. The electron–electron exchange and correlation energy were described by the generalized gradient approximation (GGA) pseudopotential with Perdew-Burke-Ernzerhof (PBE) formation [40]. In order to describe the van der Waals (vdw) interaction, we adopt the DFT-D3 method proposed by Grimme [41]. The plane-wave cutoff energy was set to 400 eV. A vacuum thickness of 15 Å between adjacent monolayers was used to avoid the coupling of the interlayer. The Monkhorst-pack k point meshes of $5 \times 5 \times 1$ were employed for geometry and calculation of density of states [42]. All the structures were fully relaxed using the conjugated-gradient algorithm [43]. The convergence criterion in progress of geometry optimization was set to 1.0×10^{-4} eV per atom for energy. All calculations were spin-polarized. The Bader charge analysis was used to analyze the valence electron distribution [44].

In the work, adsorption energy (E_{ads}) between the NO molecule and MoS_2-MLs was defined as [45]:

$$E_{ads} = E_{substrate} + E_{adsorbate} - E_{substrate\text{-}adsorbate}$$

Where $E_{substrate\text{-}adsorbate}$ was the total energy of adsorbate-substrate system in the equilibrium state, $E_{substrate}$ and $E_{adsorbate}$ were the total energies of substrate and adsorbate, respectively. By this definition, a position value, corresponding to an exothermic process, indicated stable adsorption. In addition, the net electron-transfer (ΔQ) between the NO molecule and MoS_2-MLs was defined as:

$$\Delta Q = Q_{ads\text{-}NO} - Q_{iso\text{-}NO}$$

Where $Q_{ads\text{-}NO}$ and $Q_{iso\text{-}NO}$ were the valence electrons of NO molecule in adsorbed state and isolated state, respectively. By this definition, a positive value indicates that the electrons transfer from NO molecule to MoS_2-MLs.

2.2. Calculation models

MoS_2 with space group P63/mmc was chosen as our object. Its crystal structure parameters come from experiment [46]. The lattice constants were $a = b = 3.168$ Å, $c = 12.322$ Å and $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$. After optimization, (0 0 1) surface was cleaved off. Subsequently, a $5 \times 5 \times 1$ super-cell along a–c directions with 25 Mo atoms and 50 S atoms was built and a 15 Å vacuum layer was added to the super-cell. Fig. 1 displays the top and side view of pure MoS_2-MLs. The calculated distances of Mo—S bonds, Mo—Mo bonds, and S—S bonds in monolayer MoS_2 are 2.41 Å, 3.19 Å and 3.17 Å, respectively. These computational bond lengths are consistent with previous report [37].

3. Results and discussion

3.1. Results of relaxed defective MoS_2-MLs

In this work, we investigate two types of vacancies, sulfur vacancy (S-vacancy) and vacancy complex of Mo and its nearby three sulfur vacancy (MoS3-vacancy). After fully relaxed, the structures with two vacancies are shown in Fig. 2. From Fig. 2a, we can see that the MoS3-vacancy induces structural reconstruction.

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