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First Principles Study on the Improved CO_2 Gas Sensing Behavior of Fe-Doped $MoSe_2$ Monolayer

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Abstract

This study investigates the potential of iron (Fe)-doped two-dimensional (2D) $MoSe_2$ monolayers for CO_2 capture using first-principles calculations. Understanding CO_2 capture is essential for advancing strategies aimed at converting CO_2 into hydrogen, a clean and sustainable fuel. Using Density Functional Theory (DFT), the electronic properties of Fe-doped $MoSe_2$ in the context of CO_2 sensing have been systematically examined. The analysis includes adsorption energy, charge transfer, band structure, sensitivity, and recovery time of CO_2 molecules on the doped monolayer. The findings indicate notable changes in the electronic and chemical characteristics of Fe-doped $MoSe_2$ upon CO_2 adsorption, underscoring its potential as a stable and efficient material for gas sensing applications.

Keywords:*Adsorption,$MoSe_2$monolayer,Bandgap,Recoverytime*

1. INTRODUCTION

Air pollution remains a critical challenge in modern society, primarily driven by human activities that release harmful substances into the atmosphere, posing serious risks to both the environment and human health. Developing efficient gas detection methods is therefore essential for protecting public health, ensuring safe working environments, and maintaining agricultural productivity [1–2]. Among various materials, $MoSe_2$ has shown heightened reactivity when exposed to air, indicating strong interactions with atmospheric components. This makes $MoSe_2$ a promising candidate for applications in energy storage, optoelectronics, and gas sensing technologies [3]. Furthermore, research has revealed that the gas adsorption performance of two-dimensional (2D) $MoSe_2$ can be significantly enhanced through doping with transition metals [4,5]. Surface doping with elements such as Fe, Co, Ag, and Pt has been shown to improve the adsorption capacity of various materials [6]. For instance, Wang et al. investigated the gas sensing capabilities of Sc-, Ti-, Cr-, and Mn-doped MoS_2 for phenol and N_2H_4 detection [7], while Chettri et al. studied the adsorption behavior of Fe-doped MoS_2 toward CH_4N_2O and CH_3OH molecules [8]. In the present study, Fe doping in 2D $MoSe_2$ is explored to enhance its gas adsorption efficiency, specifically for CO_2 molecules. To understand the underlying mechanisms, first-principles calculations

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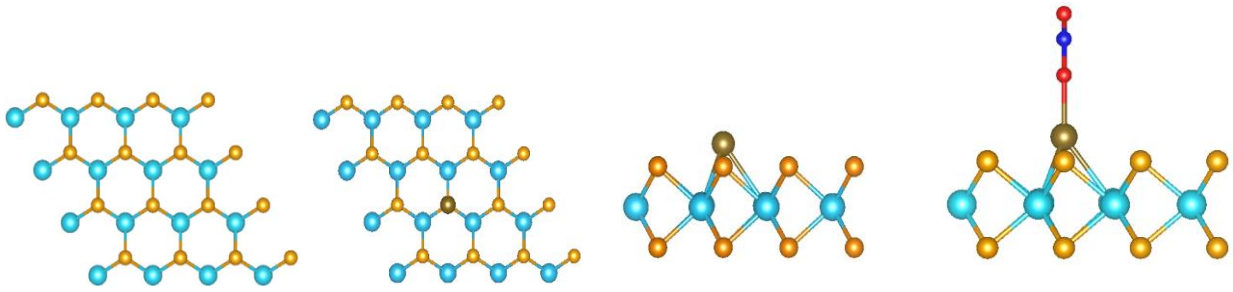
based on Density Functional Theory (DFT) are employed. For structural stability, Fe atoms are substituted at Se sites in the $MoSe_2$ lattice, and the corresponding formation energy is calculated. The investigation includes determining the most favorable adsorption site for the CO_2 molecule on the monolayer, followed by calculations of adsorption energy, charge transfer, and electronic band structure before and after doping. This theoretical analysis provides insight into how Fe doping enhances the gas-sensing performance of 2D $MoSe_2$, offering valuable guidance for designing efficient gas sensor materials.

2. METHODS

To evaluate the adsorption capability of the $MoSe_2$ monolayer (ML), a 4×4×1 supercell structure was constructed with a vacuum spacing of 15 Å along the z-axis to prevent interlayer interactions. The optimized lattice constant of $MoSe_2$ was determined to be 3.31 Å, which aligns well with previously reported values [9]. Electronic and adsorption characteristics were computed using the SIESTA simulation package, employing an optimized configuration of the adsorbed CO_2 molecule [10]. A double-zeta polarized (DZP) basis set was applied to ensure an accurate representation of atomic orbitals, along with the generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) functional for exchange-correlation interactions [11,12]. The force and energy convergence criteria were set to 0.01 eV/Å and 10^{-5} eV, respectively. A mesh cutoff energy of 650 eV was used, and Brillouin zone sampling was performed using an 8×8×1 Monkhorst-Pack k-point grid for the structural relaxation of the $MoSe_2$ monolayer [13]. Charge transfer between the CO_2 molecule and the $MoSe_2$ surface was quantified using Mulliken population analysis [14]. Additionally, relativistic norm-conserving pseudopotentials were employed, with valence electron configurations of Fe: $3s^2\ 3p^6\ 4s^2\ 3d^6$ and Se: $4s^2\ 4p^4$, to study CO_2 adsorption on Fe-doped $MoSe_2$.



3. RESULTS AND DISCUSSION

Figure 1 (a) $MoSe_2$(b) Fe-$MoSe_2$ (Top View)(c) Fe-$MoSe_2$(Side View) (d) CO_2adsorbed Fe-$MoSe_2$

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3.1 Structure and properties of $MoSe_2$ and Fe-doped $MoSe_2$

Figure 1(a) displays the optimized structure of pristine $MoSe_2$, where each molybdenum (Mo) atom forms bonds with surrounding selenium (Se) atoms at a bond length of 2.504 Å. The Se–Mo–Se and Mo–Se–Mo bond angles are approximately 82.7°, aligning well with previously reported data. The Mo–Mo and Se–Se interatomic distances are 3.314 Å and 3.317 Å, respectively (with an alternate Se–Se distance of 3.231 Å in another direction), and the Mo–Se bond measures approximately 2.505 Å. These structural parameters are in good agreement with earlier studies [15].

The electronic properties of pristine $MoSe_2$ were also examined, revealing a direct bandgap of 1.39 eV, which is consistent with values reported in the literature [16]. Prior studies suggest that Fe atoms prefer to be positioned above Se sites during doping [17]. Based on this, Fe substitutional doping was performed by replacing a Se atom in the optimized 4×4×1 $MoSe_2$ supercell. The doped Fe atom forms stable bonds with three neighboring Mo atoms at distances of 4.096 Å, 4.097 Å, and 4.098 Å, slightly protruding ~2 Å above the Se atomic plane due to its relatively larger atomic radius.

To assess the structural stability of both pristine and Fe-doped systems, formation energy (E_x) and binding energy (E_b) were calculated using equations (1) and (2), yielding values of –6.62 eV and –7.65 eV, respectively. These negative values confirm the thermodynamic stability of the Fe-doped $MoSe_2$ system with a Se vacancy, consistent with previous findings [18,19].

$$E_f = \frac{1}{n}\left[E_{MoSe_2} - xE_{Mo} - yE_{Se}\right] \quad (1)$$

$$E_b = E_{Fe-MoSe_2} - E_{Fe} - E_{vac} \quad (2)$$

In equation (1), the terms E_{Mo} and E_{Se} represent the energy of isolated Mo and Se atoms, respectively, while E_{MoSe_2} denote the ground-state energy of $MoSe_2$. In equation (2), $E_{Fe-MoSe_2}$ indicates the energy of the Fe doped $MoSe_2$, where E_{Fe} and E_{vac} stand for the total energy of individual Fe and undoped $MoSe_2$ with Se vacancy on the ML. x and y show the numbers of Mo and Se atoms, respectively, and n represents entire number of atoms in $MoSe_2$. Additionally, examined the interaction between a single metal atom and $MoSe_2$. It was found that there is a charge transfer from the Fe atom to the ML $MoSe_2$ of 0.23e, which is likely crucial for the chemical activity and sensitivity of the metal-doped ML $MoSe_2$. To further explore the effects introduced by doping metal atoms into defective $MoSe_2$, the research conducted additional investigations on the band gap of Fe-doped $MoSe_2$, revealing a decrease.

3.2 Adsorption properties $MoSe_2$ and Fe-doped $MoSe_2$ system

In this study, the Fe-doped $MoSe_2$ gas detection performance mechanism with CO_2 gas molecule, it is computed the adsorption energy of the surface for both systems (undoped and doped). The strength of gas molecule adsorption on the surface of 2-D $MoSe_2$ is indicated by the adsorption energy value, which is defined as follows:

$$E_{ads} = E_{Fe-MoSe_2+Gas} - E_{Fe-MoSe_2} - E_{Gas} \quad (3)$$

Where $E_{Fe-MoSe_2+Gas}$ represents the total energy of Fe-$MoSe_2$ with CO_2 absorbed, and E_{Gas} denotes the energy of CO_2 gas. The greater the absolute value of the adsorption energy, the more robust the gas molecule's attachment to

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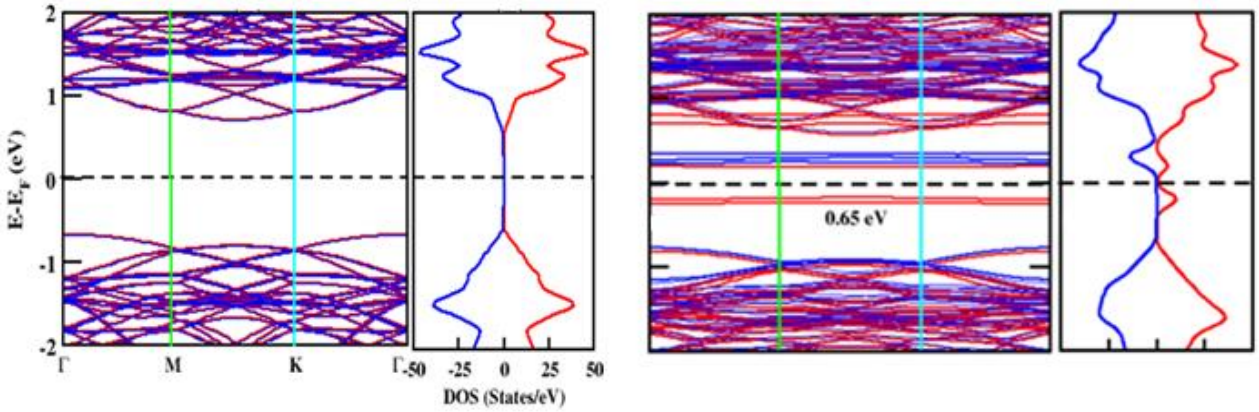
the substrate [20]. The adsorption energy of two-dimensional $MoSe_2$ for CO_2 before doping is lower than -0.5 eV, as indicated in Table1, suggesting physical adsorption. The adsorption energy does, however, approach 1eV following doping, indicating that Fe doping does, in fact, improve the two-dimensional $MoSe_2$'s ability to adsorb gas molecule and, consequently, the electron interaction between gas molecule and $MoSe_2$.

Table 1 Calculated parameters of undoped $MoSe_2$ and Fe-$MoSe_2$ adsorption structure.

Monolayers	E_{ads} (eV)	Q_t (e)	Bandgap (eV)
$MoSe_2$	-	-	1.39
CO_2/$MoSe_2$	-0.331	-0.07e	1.33
Fe-$MoSe_2$	-	-0.23e	0.65
CO_2/Fe-$MoSe_2$	-0.965	-0.08e	0.60



3.3Electronic properties $MoSe_2$ and Fe-doped $MoSe_2$ system

The adsorption of gas molecules onto the Fe-doped $MoSe_2$ monolayer (ML) significantly influences its gas sensing performance. The interaction with CO_2 molecules modifies the electronic band structure of the Fe-$MoSe_2$ ML, resulting in a reduced bandgap of 0.65 eV. This reduction suggests an enhancement in electrical conductivity upon gas adsorption. Figure 2 presents the density of states (DOS), highlighting the effects of CO_2 adsorption on both pristine and Fe-doped $MoSe_2$ monolayers.

In the pristine $MoSe_2$ ML, a flat region near the Fermi level (shifted to zero) is observed, indicating semiconducting behavior, as shown in Figure 2(a). However, after Fe doping, impurity states are introduced into the system, altering the flat region near the Fermi level, as depicted in Figure 2(b). These

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impurity-induced states contribute to changes in the electronic structure, enhancing conductivity and introducing magnetic characteristics into the Fe-doped $MoSe_2$ ML. Consequently, a net magnetic moment emerges, indicating the development of magnetic behavior due to Fe incorporation.

3.4Exploring Sensors Based on Resistance Characteristics

The impact of gas adsorption (CO_2) on the Fe-doped $MoSe_2$ monolayer shows the modulation in the band structure of the $MoSe_2$ monolayer, which further alters the electronic conductivity (σ). The change in the electronic conductivity and sensitivity is estimated empirically using equations 5 and 6 [21] given below:

$$\sigma = \lambda e^{\frac{-E_g}{2K_BT}} \quad (4)$$

$$S = \frac{{}^{1}/_{\sigma_{Gas}} - {}^{1}/_{\sigma_{pure}}}{{}^{1}/_{\sigma_{pure}}} \quad (5)$$

Here, λ denotes proportionality constant, K_B is the Boltzmann constant, and T is the temperature in K.

Figure2 Bandstructureand DOS of(a)$MoSe_2$(b)FedopedMoSe$_2$

Conductivity and bandgap are inversely proportional to each other. In our study, the bandgap of the Fe-$MoSe_2$ decreases to 0.086 eV during CO_2 adsorption. Later, the sensitivity of Fe-$MoSe_2$ for CO_2 detection is computed to be 84.4%. These significant changes in the Fe-$MoSe_2$ ML's electrical conductivity highlight the material's potential as a susceptible resistance-type gas sensor for CO_2 recognition using a resistance detection-based device.

3.5 Recovery Time

The recovery time (τ) of the CO_2adsorbed Fe- $MoSe_2$monolayer is reported in this section. The aboveanalysis is based on the transition state theory and the Arrhenius equation [41]. The activation energy (E_a) required for desorption and the desorption rate are crucial parameters in determining the recovery time.

$$\tau = Ae^{-\frac{E_g}{K_BT}} \quad (6)$$

A is known as attempt frequency, taken $10^{-12}s^{-1}$ according to previous reports [22]. The recovery time in desorption processes can be influenced by various factors, including temperature (T) and E_a(magnitude of the same as E_{ads}). A higher E_{ads}would make gas desorption more challenging,and increasing the temperature can effectively accelerate this process. Using the $E_a$values, the recovery time for the desorption of various gases at different temperatures was obtained (as shown in table 3). It can be inferred that desorption of CO_2 from the Fe-$MoSe_2$ ML would be very easy at room temperature. As the temperature increases, the desorption time from the surface decreases. Therefore, utilizing Fe-$MoSe_2$ ML as the sensing material for CO_2 detection would be appropriate, as the operation for gas sensors would be efficient.

Table 3 Recovery time of CO_2 gas molecule on Fe-$MoSe_2$ as a function of temperature

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S.No	ML	Temperature (in K)	Recovery Time (in pico sec)
1	CO_2-Fe-$MoSe_2$	298	10563.614
		398	1032.77
		498	254.68

4. CONCLUSION

In this paper, the adsorption of CO_2 gas molecule on a Fe-$MoSe_2$ monolayer was investigated using the SIESTA under the flag-ships of DFT. The theoretical simulation was used to investigate the adsorption energy, total charge transfer, bandgap, recovery time and sensitivity. The obtained results demonstrated an improvement in the adsorption property of the Fe-$MoSe_2$ monolayer. Because of the high adsorption energy, the CO_2 molecules are adsorbed with Fe-$MoSe_2$, and their bonding is strong. The bandgap shows a significant increase in conductivity after doping with Fe and adsorbing the CO_2 molecules. The magnetic property was observed after Fe atom substitution in the MoS2 monolayer. Furthermore, for adsorbing CO_2 molecules, the Fe-MoS2 monolayer has an excellent sensitivity of 84.4%. For the CO_2 configuration, the shorter desorption time was calculated to be 0.0 012 μs at 298K and reduces with temperature. As a result, Fe-MoS2 monolayer is a promising candidate for use as a spintronic sensor for detecting urea and methanol molecules.

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