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DOI: https://doi.org/10.64388/IREV9I12-1719167

# First-Principles Investigation of $NH_3$ Adsorption and Sensing Behavior on Cu-Doped $MoSe_2$ Monolayer

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***Abstract- In this work, we use first-principles calculations to examine the potential of copper (Cu)-doped two-dimensional (2D) $MoSe_2$ monolayer for NH3 capture. Cu-doped $MoSe_2$ electronic properties in the context of NH3 sensing have been comprehensively investigated using Density Functional Theory (DFT). The negative formation and binding energy of -6.62 and -4.78 eV show the electronic stability of undoped Cu-doped MoSe2 ML. Band structure, sensitivity, recovery time, charge transfer, and adsorption energy of $SO_2$ molecules on the doped monolayer are all examined. Following NH3 adsorption, the results show significant alterations in the electromic and sensing properties of Cu-doped $MoSe_2$, highlighting its potential as a reliable and effective material for gas sensing applications.***

***Keywords: Adsorption, MoSe2 monolayer, Bandgap***

## I. INTRODUCTION

Air pollution is one of the most critical environmental challenges threatening human health and ecological systems worldwide. The rapid expansion of industrial, agricultural, and urban activities has significantly increased emissions of toxic and hazardous gases into the atmosphere [1]. Among these pollutants, Ammonia (NH3) is a highly toxic and volatile gas widely used in agriculture, refrigeration, chemical synthesis, and industrial processes [2]. Even at low concentrations, prolonged exposure can cause severe respiratory irritation, eye damage, and environmental pollution [3]. Due to the serious risks of ammonia exposure, real-time, reliable, and highly sensitive detection systems are urgently needed for industrial safety, environmental monitoring, and public health. Given these requirements, 2D nanomaterials stand out as ideal candidates for advanced gas sensors thanks to their large surface area, fast electron transport, and high sensitivity to surface interactions [4]. Unlike thicker materials, 2D structures expose all reactive sites directly to gases, causing clear changes in electrical behavior when molecules adsorb [5]. 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 [6]. Furthermore, research has revealed that the gas adsorption performance of two-dimensional (2D) $MoSe_2$ can be significantly enhanced through doping with transition metals [7,8]. Surface doping with elements such as Fe, Co, Ag, and Pt has been shown to improve the adsorption capacity of various materials [9]. 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 [10], while Chettri et al. studied the adsorption behavior of Fe-doped $MoS_2$ toward $CH_4N_2O$ and $CH_3OH$ molecules [11]. In the present study, Cu doping in 2D $MoSe_2$ is explored to enhance its gas adsorption efficiency, specifically for NH3 molecules. To understand the underlying mechanisms, first-principles calculations based on DFT are employed. For structural stability, Cu 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 NH3 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 Cu doping enhances the gas-sensing performance of 2D $MoSe_2$, offering valuable guidance for designing efficient gas sensor materials.

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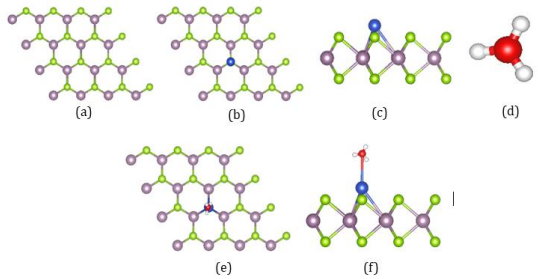


Figure 1 (a) $MoSe_2$ (b) Cu-$MoSe_2$ (Top View) (c) Cu-$MoSe_2$ (Side View) (d) $NH_3$ Gas Molecule (e) $NH_3$ adsorbed Cu-$MoSe_2$ (Top View) (f) $NH_3$ adsorbed Cu-$MoSe_2$ (Side View), (Mo-Indigo, Se-Green, Cu- Blur, N- Red, H-White)

## II. 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 perpendicular to the ML (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 [12]. Electronic and adsorption characteristics were computed using the SIESTA simulation package, employing an optimized configuration of the adsorbed $SO_2$ molecule [13]. 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 [41,15]. 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 [16]. Charge transfer between the $SO_2$ molecule and the $MoSe_2$ surface was quantified using Mulliken population analysis [17]. Additionally, Cu: 3d10 4s1, Mo: 4d5 5s1, and Se: 4s2 4p4 were used for investigating NH3 adsorption on Cu doped MoSe2.

## III. RESULTS AND DISCUSSION

### *A. Structure optimization of MoSe2 and Cu-doped MoSe2*

Figure 1(a) showss the optimized structure of pristine $MoSe_2$, where each molybdenum (Mo) atom makes bonds with neighboring 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 [18]. 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 [18].

The electronic properties of pristine $MoSe_2$ were also calculated, revealing a direct bandgap of 1.40 eV, which is consistent with values reported in the literature [19]. Prior studies suggest that Cu atoms suitable to be positioned on Se sites during doping [20]. Based on this, Cu substitutional doping was performed by replacing a Se atom in the optimized 4×4×1 $MoSe_2$ supercell. The doped Cu atom forms stable bonds with three adjacent Mo atoms at distances of 4.096 Å, 4.097 Å, and 4.098 Å, slightly sticking out ~2 Å above the Se atomic plane due to its relatively larger atomic radius.

To measure the structural stability of both pristine and Cu-doped systems, formation energy (Ef) and binding energy (Eb) were calculated using equations (1) and (2), resulting values of –6.62 and -4.78 eV, respectively. These negative values authorize the thermodynamic stability of the Cu-doped $MoSe_2$ system with a Se vacancy, consistent with previous findings [21,22].

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

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

In equation (1), the terms E_Moand E_Serepresent the energy of isolated Mo and Se atoms, respectively, while E_(MoSe_2 )denote the ground-state energy of MoSe2. In equation (2), E_(Cu-MoSe_2 ) indicates the energy of the Cu doped MoSe2, where E_Cu and E_vacstand for the total energy of individual Cu and undoped MoSe2 with Se vacancy on the ML. x and y

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show the numbers of Mo and Se atoms, respectively, and N represents entire number of atoms in MoSe2. Additionally, examined the interaction between a single metal atom and MoSe2. It was obtained that there is a charge transfer from the Cu atom to the ML MoSe2 of 0.23e, which is likely crucial for the chemical activity and sensitivity of the doped ML MoSe2. To further explore the effects introduced by doping metal atoms into defective MoSe2, the research conducted additional investigations on the band gap of Cu-doped MoSe2, revealing a decrease.

*B. Adsorption properties MoSe2 and Cu-doped MoSe2 system*

In this study, the Cu-doped MoSe2 gas detection performance mechanism with NH3 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 MoSe2 is indicated by the adsorption energy value, which is defined as follows:

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

Where E_(Cu-MoSe_2+Gas) represents the total energy of NH3 absorbed Cu-MoSe2, and E_Gas denotes the energy of isolated NH3. The greater negative value of the adsorption energy, the more vigorous the gas molecule's attachment to the substrate [23]. The adsorption energy of 2-D MoSe2 for NH3 before adding Cu-atom is lower than -0.5 eV, as indicated in Table1, suggesting physical adsorption. The adsorption energy does, however, approach -1eV following doping, indicating that Cu doping does, in fact, improve the 2-D MoSe2's ability to adsorb gas molecule and, consequently, the electron interaction between gas molecule and MoSe2.

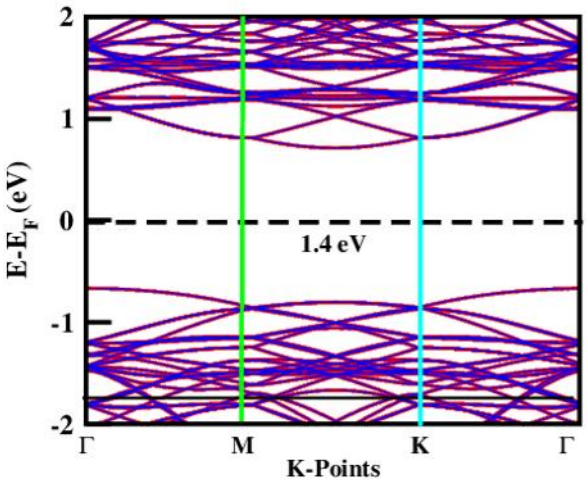
Table 1 Calculated parameters of undoped MoSe2 and Cu-MoSe2 adsorption structure.

| Monolayers | $E_{ads}$ (eV) | $Q_t$ (e) |
|---|---|---|
| $NH_3/MoSe_2$ | -0.46 | 0.09e |
| $NH_3/Cu\text{-}MoSe_2$ | -1.42 | -0.19e |

*C. Electronic properties MoSe2 and Cu-doped MoSe2 system*

In $MoSe_2$ ML, it is observed that there is a no energy level region near the Fermi level (shifted to zero), indicating semiconducting behavior, as shown in Figure 2(a). However, after Cu doping, impurity states are introduced into the system, altering the region near the Fermi level, as depicted in Figure 2(c). These impurity-induced states contribute to changes in the electronic structure, enhancing conductivity of the Cu-doped $MoSe_2$ ML and bandgap reduces to 0.98 eV. All the estimated value of bandgaps for both systems are close agreement with the published work [24,22].

The adsorption of gas molecules onto the Cu-doped $MoSe_2$ monolayer (ML) significantly influences its gas sensing performance. The interaction with NH3 molecules modifies the electronic band structure of the Cu-$MoSe_2$ ML, resulting in a reduced bandgap of 0.72 eV. This reduction suggests an enhancement in electrical conductivity upon gas adsorption. Figure 2 presents (BS), highlighting the effects of NH3 adsorption on both undoped and Cu-doped $MoSe_2$ MLs.




(a)

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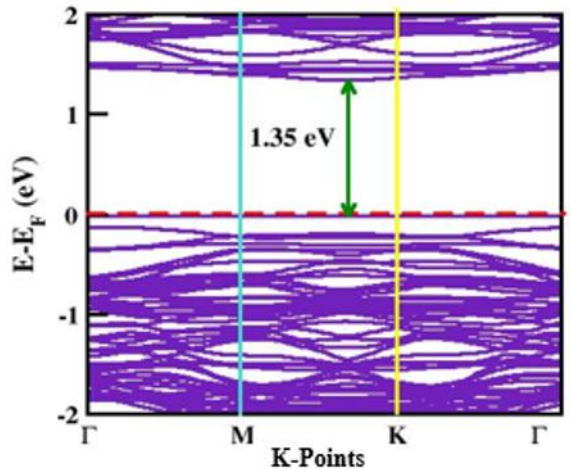
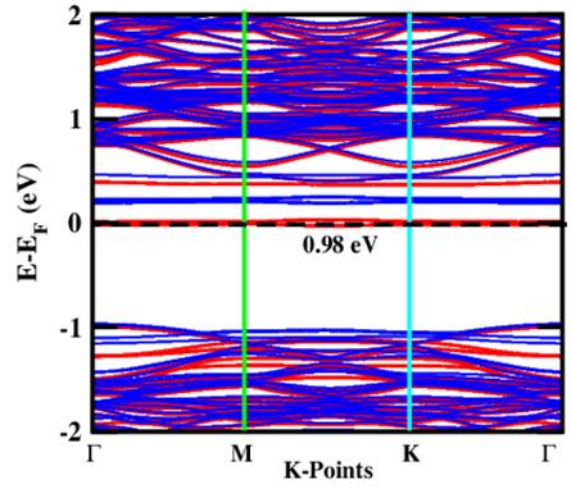
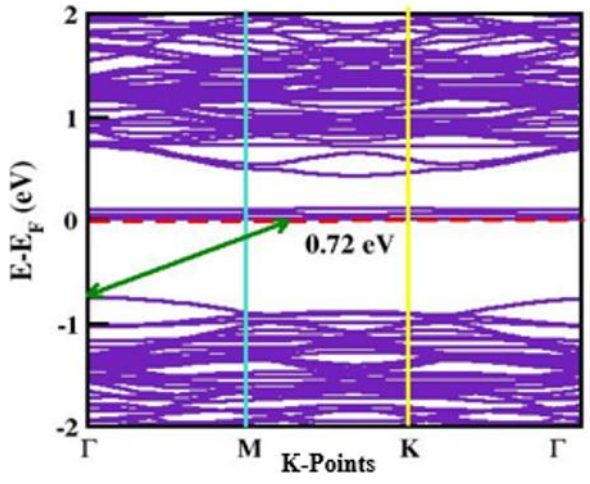



(b)




(c)




(d)

Figure 2 Bandstructure of (a) MoSe2 (b) NH3 adsorbed MoSe2(c) Cu-MoSe2 (d) NH3 adsorbed Cu-MoSe2

*D. Exploring Sensors Based on Resistance Characteristics*

When gas adsorption (NH3) is introduced to the Cu-doped MoSe2 ML, the band structure of the MoSe2 ML is modulated, which further changes the conductivity (σ). Equations 5 and 6 [25], which are provided below, are used to empirically estimate the change in electronic conductivity and sensitivity:

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

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

Here, λ constant, KB is the Boltzmann constant, and T is the temperature in K. The relationship between bandgap and conductivity is inverse. In our study, the bandgap of the Cu-MoSe2 reduces to 0.72 eV during NH3 adsorption. The results indicate that Cu doping markedly enhances the NH3 sensing performance of $MoSe_2$, increasing its sensitivity from 62.36% to 99.37%. These significant changes in conductivity of the Cu-MoSe2 ML demonstrate the material's potential as a liable resistance-type gas sensor for NH3 detection through the use of a resistance detection-based apparatus.

Table 2 Calculated Bandgap and sensitivity of undoped MoSe2 and Cu-MoSe2 adsorption structure.

| Monolayers | Bandgap (eV) | Sensitivity (%) |
|---|---|---|
| $MoSe_2$ | 1.4 | - |
| Cu-$MoSe_2$ | 0.98 | 62.36 |
| $NH_3$/$MoSe_2$ | 1.35 | - |
| $NH_3$/Cu-$MoSe_2$ | 0.72 | 99.37 |

*E. Recovery Time*

This section reports the desorption ability of Cu-MoSe2 ML towards NH3 in terms of recovery time (τ). The Arrhenius equation and transition state theory serve as the foundation to estimate recovery time [26].

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

A is known as attempt frequency, taken 10-12 s-1 according to previous reports [22]. A number of factors, such as temperature (T) and Ea (magnitude of the same as Eads), can affect the recovery time in desorption processes. Gas desorption would be more difficult at higher Eads, and this process can be efficiently accelerated by raising the temperature. The recovery time for the desorption of gase at different temperatures was calculated using the Ea values (as stated in table 3). It may be concluded that at room temperature, NH3 desorption from the Cu-MoSe2 ML would be quite simple. The desorption time from the ML reduces with increasing temperature. As a result, using Cu-MoSe2 ML as the sensing material for NH3 detectionwould be suitable since gas sensors would function effectively.

Table 3 Recovery time of NH3 gas molecule on Cu-MoSe2 as a function of temperature

| ML | Temperature (in K) | Recovery Time (in sec) |
|---|---|---|
| $NH_3$/Cu-$MoSe_2$ | 298 | $3.34\times10^{10}$ |
| | 398 | $5.78\times10^{4}$ |
| | 498 | 26.59 |

## IV. CONCLUSION

This paper investigated the adsorption of NH3 gas molecules on a Cu-doped MoSe2 monolayer using the SIESTA under the DFT relationships. Using the theoretical simulation, the adsorption energy, bandgap, recovery time, total charge transfer, and sensitivity were all investigated. The adsorption characteristics of the Cu-MoSe2 monolayer were improved, according to the results. Because of the high adsorption energy, the NH3 molecules and Cu-MoSe2 have a tight bond. The conductivity of the bandgap increases significantly after Cu doping and NH3 molecule adsorption.

The magnetic behaviour was seen after doping of Cu atom in the MoSe2 ML. Furthermore, the Cu-MoSe2 monolayer has an outstanding sensitivity of 99.37% for adsorbing NH3 molecules. The NH3 configuration was shown to have a shorter desorption time of 26.59s at 498K, which reduced as the temperature rise. For a resistance-type sensor that can detect NH3 molecule, Cu-MoSe2 monolayer is a practicable choice.

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