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Functionalization of α-In$_2$Se$_3$ Monolayer via Adsorption of Small Molecule for Gas Sensing

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Based on first-principles calculations, the adsorption of NO and NO$_2$ gas molecules on the α-In$_2$Se$_3$ monolayer have been studied. The adsorption configuration, adsorption energy, electronic structure and charge transfer properties are investigated. It is found that the charge transfer processes of NO and NO$_2$ adsorbed on the surface of α-In$_2$Se$_3$ monolayer exhibit electron donor and acceptor characteristics, respectively. After the adsorption of the molecules, the α-In$_2$Se$_3$ monolayers have new states near the Fermi level induced by NO and NO$_2$, which can trigger some new effects on the conducting and optical properties of the materials, with potential benefits to gas selectivity. The present work provides new valuable results and theoretical foundation for potential applications of the In$_2$Se$_3$-based gas sensor.

Keywords: 2D materials, first-principles calculation, In$_2$Se$_3$, charge transfer, gas sensor

INTRODUCTION

In recent years, Layered two-dimensional (2D) materials have received tremendous research attention due to their unique physical and chemical properties (Miró et al., 2014; Bhimanapati et al., 2015; Xie et al., 2018). Because of their ultrahigh flexibility, strength and thickness-dependent electronic properties (Wang et al., 2012; Novoselov et al., 2016), the nanodevices based on 2D materials and tuning the properties of their heterostructures via defects engineering (Cervenka et al., 2009; Wang et al., 2011; Park et al., 2014; Sun et al., 2015) hold great promise for potential applications in nanoscale electronics, optoelectronics and spintronics (Wang et al., 2008, 2016; Geim and Grigorieva, 2013; Lan, 2018). Additionally, the high surface/volume ratio, weak electronic screening and ultrathin thickness of 2D materials induce that their structural stability and electronic properties are very sensitive to environmental molecules, and the relevant effects make them efficient for gas molecules sensing, catalysis, and energy storage technologies (Lightcap and Kamat, 2013; Yang et al., 2016; Zhang et al., 2018). Graphene has exhibited good performance in the field of gas sensor (Kemp et al., 2013). Previous reports have also shown that MoS$_2$-based nanosensors possess excellent sensing ability with high response value, and their molecule adsorption properties can be modulated by applying light, strain, and external electric field (Late et al., 2013; Ma et al., 2016). Recently, InSe monolayer has been found having tunable electronic properties via the molecule adsorption and promising for gas sensing application (Ma et al., 2017). All these studies clearly reveal that external factors can modulate the properties of 2D materials effectively and extend their application fields.

Indium selenide (In_2Se_3) is an interesting III-VI group layered chalcogenide compound with multiple phases and excellent properties (Shi et al., 2013), and have attracted extensive research interest for the applications in phase change memory (Yu et al., 2007), lithium batteries (Feng et al., 2016), optoelectronic and photovoltaic devices (Zhai et al., 2010; Jacobs-Gedrim et al., 2014). Among all the phases, 2D materials based on α-In_2Se_3 exhibit obvious thickness-dependent shift of band gap and promising prospects for tunable wavelength photodetection (Quereda et al., 2016). It is also reported that the strain sensor fabricated from 2D α-In_2Se_3 films possesses good stability, excellent sensitivity, and high spatial resolution in strain distribution, showing attractive properties for e-skin applications in wearable electronics (Feng et al., 2016). However, to best of our knowledge, the investigations on the adsorption of small gas molecules on atomically thin 2D In_2Se_3 materials and the related modification of their properties are still lacking so far. It is well-known that NO_2 and NO are common air pollutants and harmful to human health. The detection and control of them are very important for the environmental protection. Hence, in this work, we have made first-principles studies on the α-In_2Se_3 monolayers adsorbed by NO and NO_2, respectively. The adsorption configuration, structural stability, electronic structure and charge transfer properties have been investigated and discussed in detail.

COMPUTATIONAL METHODS

All calculations are carried out using the Vienna *ab initio* simulation package (VASP)(Kresse and Furthmüller, 1996), with the core electrons described by the projected augmented wave (PAW) method. For the exchange-correlation term, the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) scheme is employed. The cutoff energy for plane-wave basis is set as 450 eV. For simulating the adsorption of the molecules, a $4 \times 4 \times 1$ supercell of the α-In_2Se_3 monolayer is built with one NO or NO_2 molecule adsorbed on its surface, and a vacuum space of more than 15 Å is set up to prevent the interactions between the repeated monolayers. The Monkhorst-Pack of $2 \times 2 \times 1$ ($4 \times 4 \times 2$) k-point grid is adopted

for the Brillion zone sampling in geometry optimization (total energy calculation). The convergence criterion of energy is taken as 10^{-5} eV. Structure relaxation is performed until the force on each atom is smaller than 0.02 eV/Å. To estimate the adsorption stability of gas molecules on the surface of α-In_2Se_3 monolayer, the adsorption energy (E_{ad}) is calculated by the formula: $E_{ad} = E_M + E_G - E_{M+G}$, where E_M, E_G, and E_{M+G} denote the total energy of the α-In_2Se_3 monolayer, the free gas molecule, and the α-In_2Se_3 monolayer adsorbed by gas molecules, respectively. According to this definition, a positive value of E_{ad} represents the adsorption is energetically favorable.

## RESULTS AND DISCUSSION

Firstly, the geometry optimizations of free gas molecules were performed. The obtained bond lengths of NO and NO_2 are 1.17 and 1.21 Å, respectively, and the O-N-O bond angle of NO_2 is 133.39°. The band gap of the clean α-In_2Se_3 monolayer has been calculated to be 0.77 eV (see **Figure 3A**). All these results are in line with the data of previous reports (Debbichi et al., 2015; Ma et al., 2017). In order to find the most stable adsorption configuration, four typical adsorbing sites on the Se atom plane of one side have been considered including the top of Se atom, the center of a Se-In bridge and two centers of the hexagonal void (see **Figure 1A**). Because of the different coordination structures of the Se atom plane on the other side, four similar adsorbing sites were also investigated on the other side (see **Figure 1B**).

For the adsorption of NO molecule, besides the eight adsorbing sites mentioned above, we also considered two different orientations of the molecule with the N-O bond perpendicular or parallel to the surface of α-In_2Se_3 monolayer. Therefore, 16 configurations have been examined. **Figure 2A** presents the top and side views of the most stable configuration obtained, where the O atom of NO molecule points away from the α-In_2Se_3 surface and the N atom of NO molecule points toward the surface with the smallest distance between the adsorbed NO and the surface atom is 2.65 Å. The N-O bond is a little shortened to 1.16 Å compared with that (1.17 Å) of free NO molecule. The adsorption energy was calculated
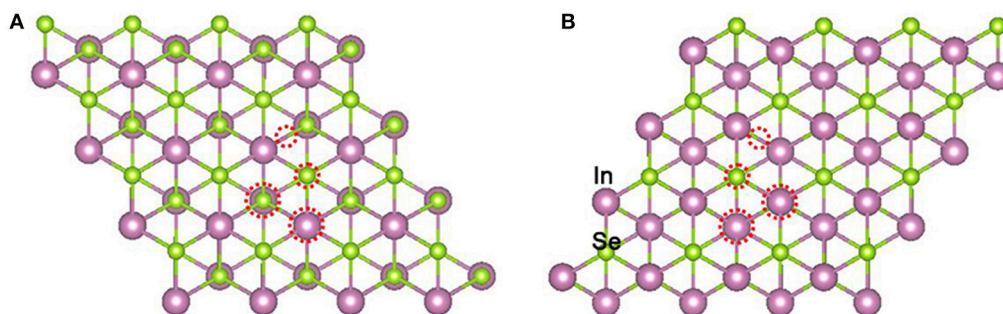
FIGURE 1 | Top views of typical adsorbing sites on the Se atom planes of one side **(A)** and the other side **(B)** of the α-In_2Se_3 monolayer. The adsorbing sites are denoted by red dotted circles.
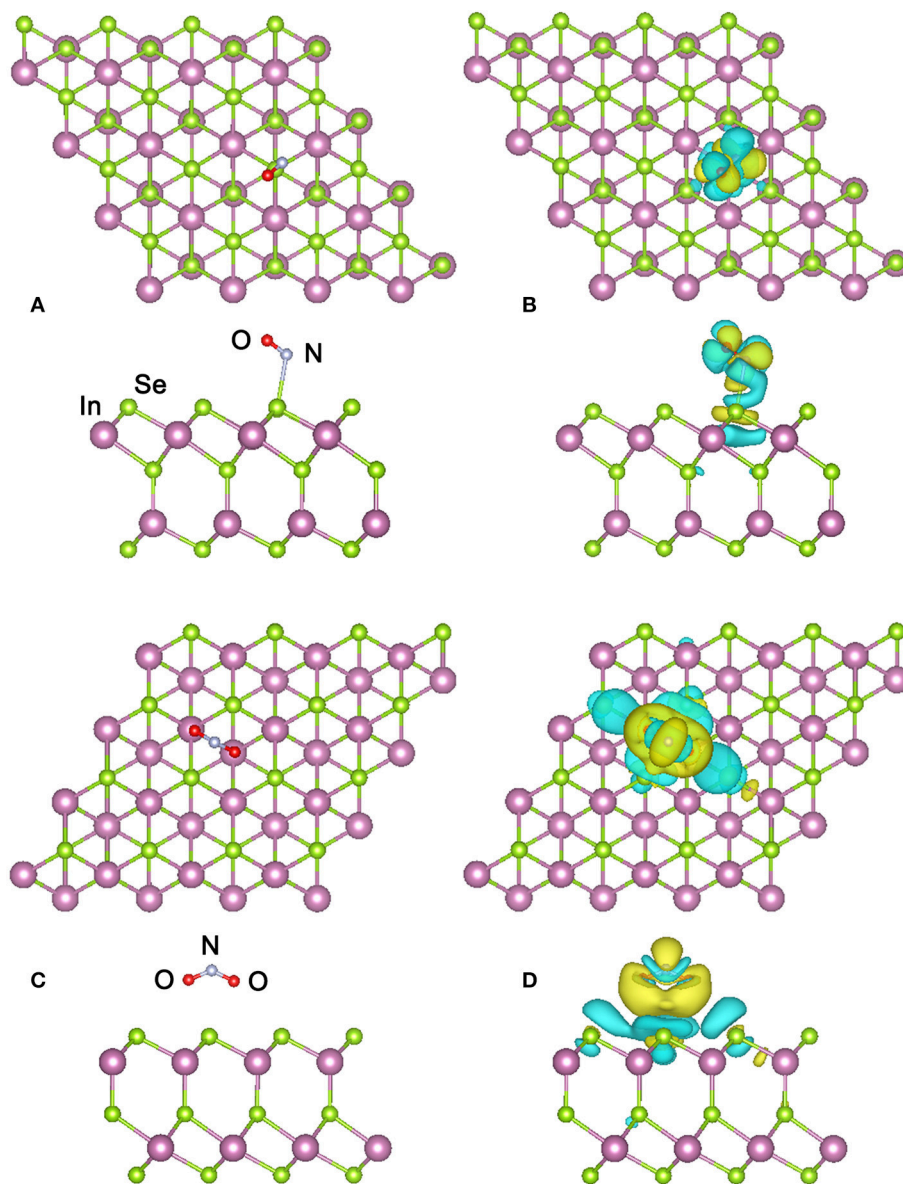
FIGURE 2 | (A) Top and side views of the most stable configuration of the α-In$_2$Se$_3$ monolayer adsorbed by NO and **(B)** its charge density difference. **(C)** Top and side views of the most stable configuration of the α-In$_2$Se$_3$ monolayer adsorbed by NO$_2$ and **(D)** its charge density difference. The cyan and yellow isosurfaces denote the electron depletion and accumulation, respectively. The isosurface value is set as 0.0001 e/bohr^3.

to be 208 meV, which is comparable to those of NO adsorptions on the monolayers of InSe, GaSe, and MoS$_2$ (Yue et al., 2013; Ma et al., 2017; Zhou et al., 2017). This low adsorption energy indicates the NO adsorption capability of α-In$_2$Se$_3$ monolayer is not very strong, which is applicable for the gas detection since the adsorption-desorption of NO molecule on α-In$_2$Se$_3$ monolayer can be easily achieved.

For further investigating the interactions and electron transfers between the adsorbed NO molecule and the α-In$_2$Se$_3$ monolayer, the charge density difference (CDD) is calculated from the formula: $\Delta\rho = \rho_{M+G} - \rho_M - \rho_G$, where ρ_{M+G},

ρ_M and ρ_G represent the total charge densities of the α-In$_2$Se$_3$ monolayer adsorbed by gas molecules, the α-In$_2$Se$_3$ monolayer, and the isolated gas molecule, respectively. The ρ_M and ρ_G are obtained with each atom at the same position as the adsorption configuration. In the NO$_2$ adsorption case, the similar calculation has also been performed. As shown in **Figure 2B**, it can be seen that the adsorption make the redistribution of charges around the NO molecule. In the space between the adsorbed NO and the α-In$_2$Se$_3$ surface, the depletion of electrons is dominant. Based on the Bader charge analysis, the charge transfer has been quantitatively calculated. It is demonstrated that the NO
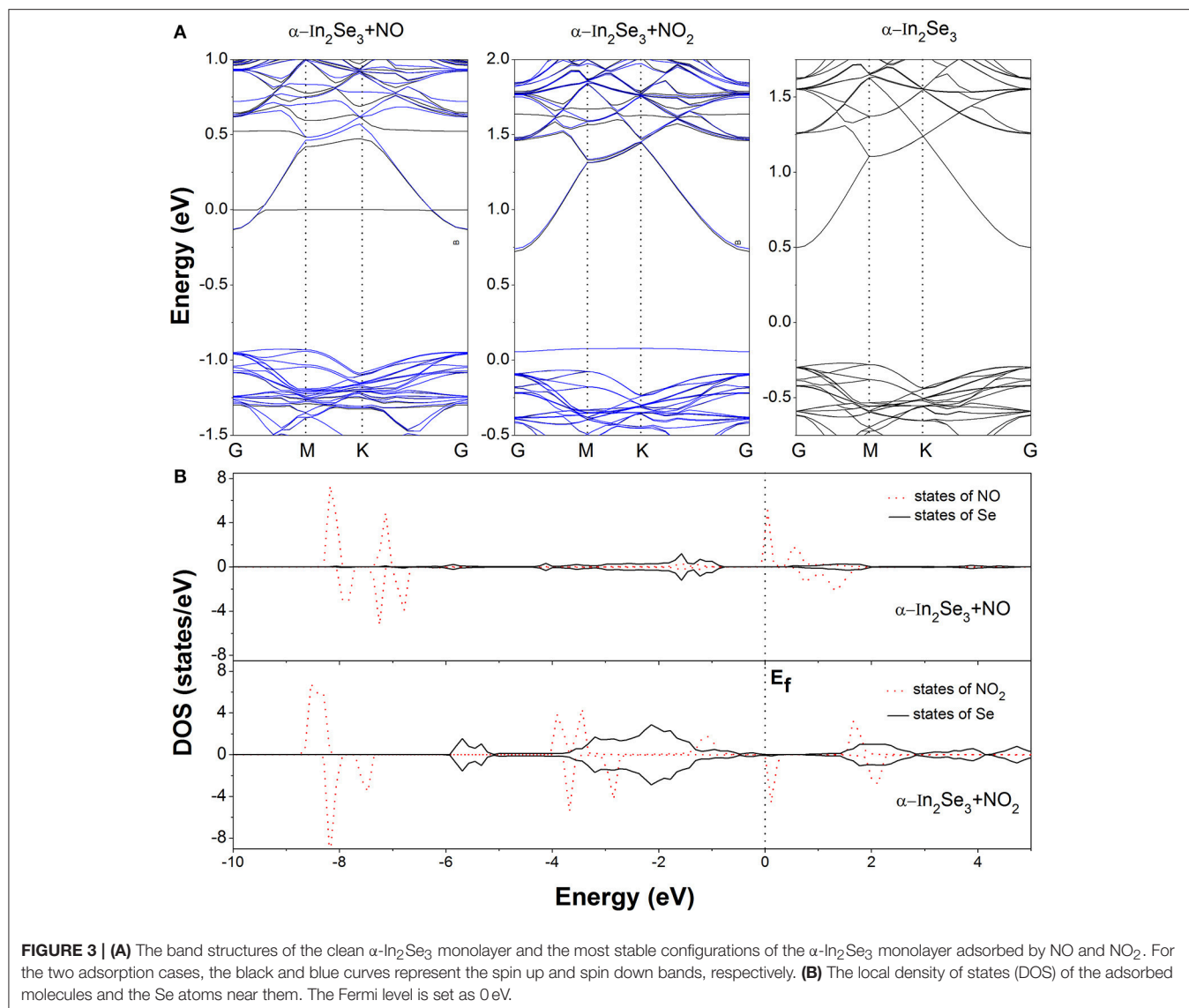
FIGURE 3 | (A) The band structures of the clean α-In₂Se₃ monolayer and the most stable configurations of the α-In₂Se₃ monolayer adsorbed by NO and NO₂. For the two adsorption cases, the black and blue curves represent the spin up and spin down bands, respectively. **(B)** The local density of states (DOS) of the adsorbed molecules and the Se atoms near them. The Fermi level is set as 0 eV.

molecule provides 0.054 e electrons to the α-In₂Se₃ surface and acts as an electron donor. This behavior is different from the situation of the NO adsorption on InSe monolayer, where the NO molecule acts as an electron acceptor with the amount (0.018 e) of transferred charges (Ma et al., 2017) smaller than that (0.054 e) between NO and α-In₂Se₃ monolayer. The band structure of the most stable configuration is depicted in **Figure 3A**, it is shown that after the NO adsorption the Fermi level (E_f) of the system moves upwards to the bottom of the conduction bands compared with that of the clean α-In₂Se₃ monolayer (see **Figure 3A**), demonstrating an n-type conducting property of the materials with NO adsorption, which is similar to the situation of property modification in the NO-adsorbed MoS₂ monolayer (Shokri and Salami, 2016). This property changes can be useful to the detection of NO molecule. In addition, some new states are found to be located at the E_f. To better understand the adsorption effect of NO molecule on the α-In₂Se₃ monolayer,

the local density of states (DOS) of the adsorbed NO and its nearest Se atom are illustrated in **Figure 3B**. It is clearly shown the new states at the E_f are from the adsorbed NO, and there is little hybridization between the states of NO molecule and the states of the surface Se atom near it, which is similar to the NO adsorption behavior on InSe monolayer, further confirming that the interaction between the adsorbed NO molecule and the α-In₂Se₃ monolayer is not strong.

In the NO₂ adsorption case, two orientations of NO₂ molecule have been considered. One is the two O atoms point toward the α-In₂Se₃ surface, and the other is that they point away from the α-In₂Se₃ surface. The obtained most stable adsorption configuration is displayed in **Figure 2C**, in which the NO₂ is adsorbed on the Se atom plane of the other side different from that of the NO adsorption case and the two O atoms of NO₂ molecule point toward the α-In₂Se₃ surface. The smallest distance between the NO₂ molecule and the α-In₂Se₃ surface is

3.57 Å, and the N-O bond is a little elongated to 1.22 Å with the O-N-O angle reduced to 131.89°. The adsorption energy was calculated to be 59 meV, suggesting the adsorption of NO$_2$ on α-In$_2$Se$_3$ monolayer is weak, which is comparable to that of the NO$_2$ adsorption on graphene (Leenaerts et al., 2008).

The CDD of the most stable configuration for NO$_2$ adsorption is displayed in **Figure 2D**. It is shown that the charge redistribution of NO$_2$ molecule is apparent. The electrons accumulate in the vicinity of the adsorbed NO$_2$ with a little electron depletion in its core region. The depletion of electrons mainly occurs for the Se atoms around the NO$_2$ molecule. From the Bader analysis, it is indicated that the NO$_2$ molecule is an electron acceptor and obtains 0.081 e electrons from the α-In$_2$Se$_3$ monolayer, which is similar to the situation of NO$_2$ adsorption on InSe monolayer, and their amounts of transferred charges are comparable (Ma et al., 2017). The band structure of the discussed configuration is shown in **Figure 3A**. It can be seen that there is a new impurity band lying just above the top of the valence bands and the E$_f$, which can modify the optical and conducting properties of the materials, benefiting the detection of NO$_2$ molecule. As shown in **Figure 3B**, the local DOS distributions demonstrate that the impurity states just above the E$_f$ are from the adsorbed NO$_2$ molecule, and there are some overlaps of states between the NO$_2$ molecule and the Se atoms near it.

CONCLUSION

To explore the gas sensing applications of 2D materials based on In$_2$Se$_3$, the effects of the adsorbed NO and NO$_2$ molecules on α-In$_2$Se$_3$ monolayer have been studied using first-principles calculations. When the NO and NO$_2$ are adsorbed on the surface of the α-In$_2$Se$_3$ monolayer, the calculated adsorption

energies of positive value indicate their adsorption processes are exothermic and energetically favorable. Their low adsorption energies demonstrate the α-In$_2$Se$_3$ monolayer is applicable for the gas molecules detection. In the most stable configurations, the gas molecules are adsorbed on different Se atom planes for NO and NO$_2$, respectively, and the smallest distance (3.57 Å) between the adsorbed NO$_2$ and the α-In$_2$Se$_3$ monolayer is larger than that (2.65 Å) of NO adsorption case. NO provides 0.054 e electrons to the α-In$_2$Se$_3$ monolayer as the donor gas molecule, while NO$_2$ acts as the acceptor gas molecule and gains 0.081 e electrons from the α-In$_2$Se$_3$ monolayer. Both of the adsorbed molecules induce new electronic states near the Fermi level compared with the electronic structure of clean α-In$_2$Se$_3$ monolayer. These changes of electronic properties can modify the conducting and optical properties of the materials and benefit gas sensing. The theoretical findings of this work suggest the 2D α-In$_2$Se$_3$ materials hold great promise for the application of gas sensor.

AUTHOR CONTRIBUTIONS

ZX and FY performed the calculations and analyzed the data with the help of XX, RL, and LC. ZX and FY wrote the manuscript with input from all authors. All authors read and approved the manuscript.

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