Interactions of Gas Molecules with Monolayer $MoSe_2$: A First Principle Study

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Abstract. We present a first principle study of interaction of toxic gas molecules (NO, NO_2 and SO_2) with monolayer $MoSe_2$. The predicted order of sensitivity of gas molecule is $NO_2 > SO_2 > NO$. Adsorbed molecules strongly influence the electronic behaviour of monolayer $MoSe_2$ by inducing impurity levels in the vicinity of Fermi energy. NO and SO_2 is found to induce p-type doping effect while semiconductor to metallic transitions occur on NO_2 adsorption. Our findings may guide the experimentalist for fabricating sensor devices based on $MoSe_2$ monolayer.

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INTRODUCTION

Sensing of harmful and toxic gases by developing sensor devices and studying the materials for the sensor applications is one of the important areas of research. Conventionally, metal oxides are commonly used in sensing devices [1-2], however, lack of their poor activity and high temperature operation is pushing the researcher's to investigate new materials such as CNT, MoS_2 etc. for sensing applications [3-4]. Two dimensional (2D) layered transition metal dichalcogenides (TMDs) offers high surface-to-volume ratio and semiconducting properties which are essential for sensing applications [5]. Recently TMDs based sensor for sensing NO_2 and NH_3 have been realized experimentally [6-7]. Particularly, MoS_2-based TMDs monolayers remain a testing ground for sensing applications. However, $MoSe_2$ also offers another alternative having semiconducting nature and high surface-to-volume ratio which makes $MoSe_2$ a candidate for gas sensing applications. In the present study, our aim is to explore structural and electronic properties of monolayer $MoSe_2$ on the adsorption of three toxic gases NO, NO_2 and SO_2 (Figure 1).

COMPUTATIONAL DETAILS

Our calculations have been performed within the framework of Density Functional Theory (DFT) using SIESTA code [8-9]. In this work, we have used well tested Troullier Martin, norm conserving, relativistic pseudopotentials in fully separable Kleinman and Bylander form for N, O, S, Se and Mo [10, 11]. The Generalized Gradient Approximation (GGA) according to the Perdew, Burke, Ernzerhof (PBE) parameterization has been used to treat electron-electron interaction. A 4x4x1 supercell has been used to model monolayer $MoSe_2$. A large vacuum of ~25 Å along the z-direction has been taken to prevent the interaction between the adjacent replicas of monolayer. A 250 Ry mesh cutoff has been used for the reciprocal space expansion of the total charge density. Brillion zone has been sampled by using 15×15×3 Monkhorst-Pack of k points. Localized atomic orbitals basis set has been used with confinement energy of 0.02 Ry.

RESULTS AND DISCUSSIONS

Structural Properties

The calculated structural parameters, band gap and adsorption energy for pristine and gas molecule (NO, NO_2 and SO_2) adsorbed on $MoSe_2$ monolayer have been tabulated in Table 1. Structural parameters for pristine $MoSe_2$ monolayer are found to be in close agreement with the other reported values elsewhere

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[12]. Our calculated results show that $d_{Mo\text{-}Se}$ bond length does not changes on gas molecule adsorption (table 1).

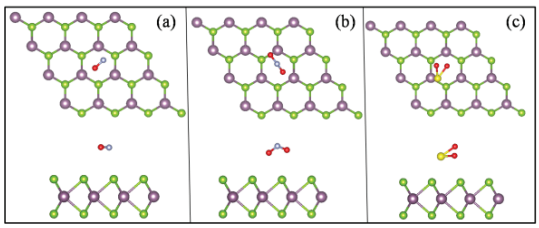

FIGURE 1. Top view and side view of optimized configuration of (a) NO on $MoSe_2$, (b) NO_2 on $MoSe_2$ and (c) SO_2 on $MoSe_2$.

To gauge the sensitivity of $MoSe_2$ towards the gas molecules we have calculated the adsorption energy (E_{ads}) as

$$E_{ads} = E_{MoSe_2-molecule} - E_{MoSe_2} - E_{molecule}$$

Where $E_{MoSe_2-molecule}$ is total energy of molecule adsorbed $MoSe_2$, E_{MoSe_2} and $E_{molecule}$ is the total energy of $MoSe_2$ and gas molecule (NO, NO_2 and SO_2) as obtained from converged SIESTA runs. The adsorption energy is found to be -0.20 eV, -0.33 eV and -0.23 eV for NO, NO_2 and SO_2 respectively. Our calculated adsorption energy of -0.33 eV for NO_2@$MoSe_2$ is in close agreement with the other reported value of -0.26 eV [13]. The negative adsorption energies indicate the exothermic process. Higher the value of adsorption energy more is the binding of gas molecules, hence the sensitivity of monolayer. The predicted order of sensitivity of $MoSe_2$ is: NO_2>SO_2>NO.

Electronic Properties

The electronic band structures of molecule adsorbed $MoSe_2$ has been calculated along highly symmetric Γ-M-K-Γ directions. A modulation in band gap has been observed on adsorbing the different molecules on $MoSe_2$ (Figure 2).

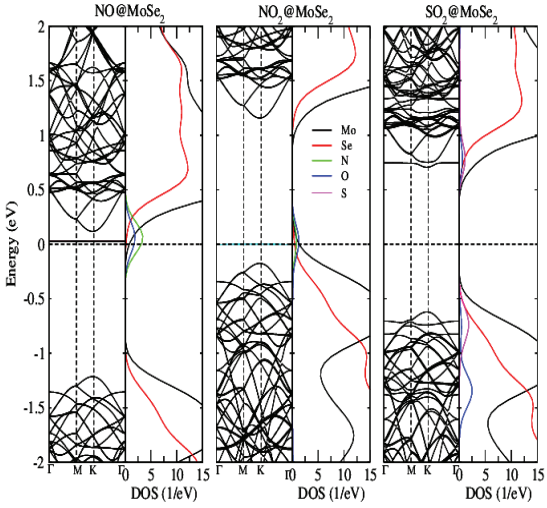

FIGURE 2. Band structure and Partial Density of States (PDOS) for (a) NO on $MoSe_2$, (b) NO_2 on $MoSe_2$ and (c) SO_2 on $MoSe_2$.

It is clear from Figure 2 that the NO and SO_2 adsorption leads to appearance of impurity like energy level in vicinity of Fermi level and conduction band minima (CBM) respectively, resulting in deacrese of effective electronic band gap. Interestingly adsorption. level in vicinity of Fermi level and conduction band minima (CBM) respectively, resulting in deacrese of effective electronic band gap. Interestingly adsorption of NO_2 results in appearnace of an energy level exactly at the Fermi level leading $MoSe_2$ to be metalic. Thus we can say that $MoSe_2$ offers a platform for sensing application according to their need in electronic devices

The right side of band structures in Figure 2 shows the partial density of states (PDOS) for all the atomic species in the simulation model. We can see that the peaks of PDOS in the vicinity of Fermi energy in case of NO@$MoSe_2$ and NO_2@$MoSe_2$ are mainly due to N-*2p* and *O-2p* states which lead to appearance of a discrete energy level in the vicinity of Fermi level. In

TABLE 1. Calculated structural parameters (Mo-Se and O-X average bond lengths (X=N,S) $<d_{Mo\text{-}Se}>$, and $<d_{O\text{-}X}>$; Se-Mo-Se, O-X-O bond angles $\Theta_{Se\text{-}Mo\text{-}Se}$, $\Theta_{C\text{-}Si\text{-}C}$; intra-planer distance between molecule and $MoSe_2$,$R_{molecule\text{-}MoSe2}$; adsorption energy,$E_{Ads}$ and band gap for pristine and molecule adsorbed $MoSe_2$.

System	$<d_{Mo\text{-}S}>$ (Å)	$<d_{O\text{-}X}>$ (Å)	$\Theta_{S\text{-}Mo\text{-}S}$ (degree)	$\Theta_{O\text{-}X\text{-}O}$ (degree)	$R_{molecule\text{-}MoSe2}$ (Å)	E_{ads} (eV)	Band Gap (eV)
$MoSe_2$	2.57, 2.51 [12]	-	82.23	-	-	-	1.49, 1.33 [12]
NO@$MoSe_2$	2.59	1.17	82.27	-	3.10	-0.20	1.21
NO_2@$MoSe_2$	2.59	1.24	82.21	128.60	2.68	-0.33, -0.26 [13]	metallic
SO_2@$MoSe_2$	2.59	1.77	82.23	50.76	2.65	-0.23	1.25

case of SO_2 adsorption, an energy level in the vicinity of CBM appears due to S-*3p* states. Thus, NO and SO_2 adsorption induce p-type doping effect whereas NO_2 adsorption leads to semiconductor-to-metal transition indicating $MoSe_2$ to be a potential candidate for sensing NO_2 with more sensitivity as compared to NO and SO_2.

To get further insight into the change in band structure, we have also analyzed the charge density difference profile. We define the charge density difference as difference between the total charge density of composite system ($\rho_{molecule@MoSe2}$) and sum of isolated charge density of gas molecule (NO, NO_2,SO_2) and monolayer $MoSe_2$ ($\rho_{molecule}$, ρ_{MoSe2}) i.e.

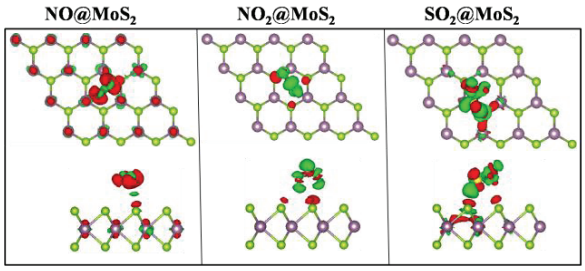

FIGURE 3. Charge density difference plots for NO, NO_2 and SO_2 adsorption on monolayer $MoSe_2$. (molecule@$MoSe_2$). The isosurface value is set at the one eighth of the maximum value.

$\Delta\rho = \rho_{molecule@MoSe2} - (\rho_{molecule} + \rho_{MoSe2})$. Figure 3 gives the charge density difference plots. The green and red regions show positive and negative charge respectively. Green color on NO_2 in case of NO_2@$MOSe_2$ indicates the charge transfer from $MoSe_2$ to NO_2 indicating NO_2 as acceptor. While in case of NO@$MoSe_2$ NO act as donor as the charge depletion occurs from NO. Charge redistribution in SO_2 and $MoSe_2$ has been also observed in case of SO_2@$MoSe_2$. The charge redistribution occurring on gas molecule on adsorption indicates its role in appearance of p-type doping effects as reflected in PDOS analysis (figure 2).

Conclusions

In conclusion, we have performed a first principle calculations to study the interaction of three gas molecules (NO, NO_2 and SO_2) with monolayer $MoSe_2$. We find that NO_2 has large adsorption energy as compared to NO and SO_2 indicating the more sensitivity of $MoSe_2$ towards NO_2. NO and SO_2 adsorption leads to p-type doping effects in $MoSe_2$ upon adsorption. Our results may be useful for the fabrication of devices based of $MoSe_2$ monolayer.

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