A Comparative Study of Increasing Sensitivity Based on MoS$_2$ Gas Sensor

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A theoretical study of NO$_2$ sensing capability of MoS$_2$ doped with elements including Si and Fe is carried out. To understand the interaction effects between MoS$_2$ and NO$_2$ in consideration of electronic transport properties has been observed carefully. By bringing dopants and defects into the 2D sheets of MoS$_2$ have significant effects on transport properties which are observed from I-V curves. Finally, we conclude that MoS$_2$ can be used as potential gas sensor and the sensing properties of MoS$_2$ can be enhanced with Fe dopant.

**Keywords:** NEGF, Gas sensor, Electron density of states, Transport properties.

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1. **INTRODUCTION**

In recent years researchers have been focused on the material used in electronic devices considering on structural, mechanical and electronic properties. Two dimensional (2D) characteristics of graphene and MoS$_2$ hence therefore grabbed the attention of scientists and huge numbers of research have been conducted introducing these materials as sensing medium [1].

Moreover, the increment of uses these materials especially MoS$_2$ has been noticed as chemical vapor sensor, photo sensor, photo voltaic and photo detector [2]. The chemical and physical properties of MoS$_2$ have been analyzed with the interaction of different substances to increase its sensitivity and performance whereas the electronic properties of MoS$_2$ can have an impact to vary the performance of MoS$_2$-based devices [3]. So far the achievement of using MoS$_2$ as gas sensor is limited to the theoretical analysis of the interaction with small gas molecules [4]. However, the adsorption effects of CO$_2$, NH$_3$, NO$_2$ molecule on MoS$_2$ have been observed in the experiment [5]. The previous work suggests that the sensitivity of MoS$_2$ is highly depended on the introduction of the dopant into MoS$_2$ nanosheets [6]. Moreover, people have used monolayer MoS$_2$ as gas sensor in previous due to its functional changes in electronic properties by inducing with appropriate acceptors or donors [7]. In addition to the magnetic property of MoS$_2$ can be enhanced significantly by metal dopant or the deformity [8]. The study of sensing properties of MoS$_2$ to detect NO$_2$ can help tremendously towards human health and live as according to the US National Institute for Occupational Safety and Health (NIOSH) suggest that a level of 50 ppm or higher excessive amount of NO$_2$ is a great threat for human health [9].

It has been seen that the improvement of performance of NO$_2$ sensors by the surface adjustment of ZnO nanowires with Pd nanoparticles. However, in a real world the uses of carbon Nanotubes and graphene [10] as gas sensor has been increased tremendously but the effects of adsorption of gas molecule on MoS$_2$ has not been considered yet.

In addition to there is no research found concerning on the effect of NO$_2$ adsorption over current voltage (I-V) characteristics, Device Density of States (DDOS), electron density on the surface of MoS$_2$. We will provide a theoretical study of NO$_2$ sensing capability of MoS$_2$ doped with elements including Si and Fe.

To understand the interaction effects between MoS$_2$ and NO$_2$ has been observed carefully in consideration of electronic properties. By bringing dopants and defects into the 2D sheets of MoS$_2$ can leads an incredible effect on transport properties which is shown from I-V curves. In our experiment, we have made a conclusion that it can be possible to use MoS$_2$ as gas sensor and the sensing properties of MoS$_2$ can be enhanced with Fe dopant.

2. **CALCULATION METHOD AND MODEL**

The Non Equilibrium Green Function (NEGF) formalism was used to determine the transport properties i.e. current voltage characteristics and Device Density of states. The device configuration contains two periodic parts that characterizes the left and right electrodes and the middle portion between to electrode is acting as sensing medium where the adsorbates are supposed to adsorb.

The device density of states is computed via the spectral density matrix

$$\rho(E) = \rho^L(E) + \rho^R(E).$$  

By integrating the LDOS over all space, the device density of states is then obtained.

$$D(E) = \int dr D(E,r) = \sum_i \rho_{ii}(E) S_i,$$

where, $S_i = \int \Psi_i^*(r) \Psi_i(r) dr$ is the overlap matrix.

We have also calculated adsorption energy of NO$_2$ on MoS$_2$ surface which is calculated as:

$$E_{ad} = E_{(NO_2/MoS)} - E_{MoS} - E_{(NO_2)}.$$
For the NO\textsubscript{2}doped MoS\textsubscript{2} system, the adsorption energy was calculated as
\[ E_{\text{ad}} = E_{\text{(NO}_2\text{/doped-MoS}_2)} - E_{\text{(doped-MoS}_2)} - E_{\text{(NO}_2)} \] (1.4)

In the above equation, \( E_{\text{(NO}_2\text{/doped-MoS}_2)} \) is the energy of the optimized structure of gas adsorbed on MoS\textsubscript{2}, \( E_{\text{MoS}_2} \) is the energy of MoS\textsubscript{2} layer, \( E_{\text{(doped-MoS}_2)} \) is the energy of the optimized structure of gas absorbed on doped MoS\textsubscript{2} layer, \( E_{\text{(doped-MoS}_2)} \) is the energy of doped MoS\textsubscript{2}.

The impact of adsorption over transport properties of NO\textsubscript{2}/defect-MoS\textsubscript{2}, NO\textsubscript{2}/Fe-MoS\textsubscript{2}, NO\textsubscript{2}/Si-MoS\textsubscript{2} and NO\textsubscript{2}/MoS\textsubscript{2} are investigated in this paper by taking consideration of device density of states, charge density and current-voltage characteristics. Ballistic current through doped-, pristine- MoS\textsubscript{2} considering self-consistent field imposed by the adsorbate molecules is calculated using Launder’s Equation.

\[ I = \frac{2q^2}{h} \int [dET(E)(f_R^+-f_L^+)] \] (1.5)

where, \( q \) = charge of the electrons and \( h \) = Planck’s constant, \( f_E^+ \) is the Fermi function of the left electrode and \( f_R^+ \) is the Fermi function of the right electrode [11].

3. RESULT AND DISCUSSION

In order to get all the information regarding to the orientations of adsorbate (NO\textsubscript{2}) and the binding energy between MoS\textsubscript{2} and NO\textsubscript{2} molecule, twelve different configurations of adsorption were need to be considered.

It is to be noted that we are mainly concentrated on the effects of adsorption over electronic structure instead of giving on the importance of adsorbate’s orientation in charge transfer mechanism. However, it is found that the electronic structure is independent of the adsorption sites and orientations of adsorbate. A weak adsorption is observed due to the adsorption of CO, CO\textsubscript{2} and NH\textsubscript{3} molecule on MoS\textsubscript{2} surface suggesting weak adsorption energy [12]. However, the adsorption of paramagnetic molecules such as NO\textsubscript{2} and NO shows high adsorption energy, indicating a strong binding between MoS\textsubscript{2} surface and adsorbate.

Thus, the adsorption energy becomes useful parameter to determine a material for the possibility of performing as gas sensor. Here, we have made a comparison of adsorption energy between MoS\textsubscript{2} and graphene since graphene has been demonstrated to hold excellent sensing properties. For NO\textsubscript{2}, the \( E_{\text{ad}} \) values on MoS\textsubscript{2} is determined to be 35.8 meV which appears to be larger than that on graphene with 11-29 meV while \( E_{\text{ad}} \) values for NO\textsubscript{2} on MoS\textsubscript{2} is smaller than that on graphene (55-67 meV) [13]. But, in our observation, we see that in case of adsorbed NO\textsubscript{2} on Fe doped MoS\textsubscript{2} (Fe-MoS\textsubscript{2}) and Si doped MoS\textsubscript{2} (Si-MoS\textsubscript{2}) exhibit high adsorption energy than graphene. Moreover, adsorption of NO\textsubscript{2} on Fe-MoS\textsubscript{2} and Si-MoS\textsubscript{2} show higher sensitivity rather than pristine-, defect MoS\textsubscript{2} as the strong binding energy between NO\textsubscript{2} molecules and doped – MoS\textsubscript{2}. However, this strong binding energy may lead the distortion of NO\textsubscript{2}, and the device may suffer from longer recovery time [14].

The total charge density illustrates that a weak physisorption takes place between NO\textsubscript{2} molecule and pristine MoS\textsubscript{2}, where a strong chemisorptions occurs between NO\textsubscript{2} adsorbed Fe-, Si- and defect- MoS\textsubscript{2}. However, in case of the adsorption of NO\textsubscript{2} molecule on Fe-MoS\textsubscript{2} shows the strongest orbital overlap, resulting the significant changes in electronic properties. Thus, it is safe for us to conclude that the Fe-MoS\textsubscript{2} is the most suitable for sensing NO\textsubscript{2} compared to defect-pristine- and Si-MoS\textsubscript{2}.

It was found that the charge density from total SCF density of NO\textsubscript{2}/MoS\textsubscript{2} is 0.163 a.u, HOMO energy is −0.02 a.u and LUMO energy is 0.02 a.u. and HOMO-LUMO energy gap is 0.04 a.u. Charge density of NO\textsubscript{2}/Fe/defect-MoS\textsubscript{2} is 0.143 a.u, HOMO energy is −0.01 a.u, LUMO energy is 0.01 a.u and HOMO-LUMO energy gap is −0.02 a.u. Again, it was found that the charge density of NO\textsubscript{2}/Fe-MoS\textsubscript{2} is 0.173 a.u, HOMO energy is −0.02 a.u and LUMO energy is 0.04 a.u and HOMO-LUMO energy gap is −0.06 a.u. NO\textsubscript{2}/Si-MoS\textsubscript{2} charge density was found which is 0.293 a.u, HOMO energy is 0.02 a.u and LUMO energy is −0.05 a.u. and HOMO-LUMO energy gap is 0.07 a.u. The eventual charge transfer interaction is explained by the lower in the HOMO and LUMO energy gap taking place within the molecules. However, in the adsorption process, NO\textsubscript{2} molecule acts as the electron donor. In NO\textsubscript{2}/Fe-MoS\textsubscript{2}, high adsorption energy and large electron density overlap have been observed as a result of the coordination bond placed between NO\textsubscript{2} molecule and Fe atom.

To get the physical insight about the changes in electronic structure rises by the adsorption of NO\textsubscript{2} molecule, the density of states (DOS) are calculated for the system of pristine-, defect-, Fe-and Si-MoS\textsubscript{2}. Fig. 1 illustrates the DOS of representative system. Again, from the DOS curve (Fig. 1a), we see that a small change after the adsorption of NO\textsubscript{2} molecule, suggesting the weak interaction between MoS\textsubscript{2} and NO\textsubscript{2}.

Compared to the pristine-MoS\textsubscript{2}, the DOS of defect-MoS\textsubscript{2} shows the dramatically changes after the adsorption of NO\textsubscript{2} molecule, revealing a strong interaction between defect-MoS\textsubscript{2} and NO\textsubscript{2} molecule. In contrast to the pristine-MoS\textsubscript{2}, the defect-MoS\textsubscript{2} exhibits a large peak appearing just before the Fermi level, which indicates the system is strongly metallic and the increment of significant conductivity. After the chemisorption of NO\textsubscript{2} molecule on defect-MoS\textsubscript{2}, the systems acts more likely a semiconductor and a drop of DOS is observed near the Fermi level. A shifting of Fermi level towards the lower energy is observed after the adsorption of NO\textsubscript{2} molecule on defect-MoS\textsubscript{2}. Furthermore, such strong interaction of NO\textsubscript{2} and defect-MoS\textsubscript{2} can leads the rearrangement of the sheet structure [15, 17]. In case of NO\textsubscript{2}/Si-MoS\textsubscript{2}, there is a peak before Fermi levels indicating the adsorption sites of NO\textsubscript{2} molecule, and this indicates that the system can exhibits semiconductive behavior. Fe-MoS\textsubscript{2} is more suitable than Si, defect-, MoS\textsubscript{2} is shown by the result of electron density which is discussed before but in case of DOS Si-MoS\textsubscript{2}
behaves more for sensing property than others are shown in Fig. 1c. If we consider the strong magnetic property of Fe atom, both Fe-MoS$_2$ and NO$_2$/Fe-MoS$_2$ could be also magnetic. Fig. 1d illustrates the spin up channel of the Fe-MoS$_2$ shows two new states, one near $-1.0$ eV in the valence band and the other near $0.3$ eV in the conduction band. However, there is no shift observed in the upper spin DOS, which suggest that after the adsorption of NO$_2$ molecule on Fe-MoS$_2$ system; the system become non-magnetic. The partial DOSs (PDOSs) is shown in Fig. 1e.

The s orbitals of Fe in Fe-MoS$_2$ contribute to the states near $-1.21$ eV and $0.74$ eV. The p orbitals contribute to the states $-1.01$ eV below the Fermi level and between $0.15$ eV and $0.75$ eV above the Fermi level. As the magnetic property is mainly depend on the d orbital of Fe-MoS$_2$, therefore much stronger intensity is found then. In the spin-up channel of the Fe-MoS$_2$, the d orbitals give one major peak below the Fermi level near $0.5$ eV and another two major peaks near $0.95$ eV and $1.57$ eV.

Magnetic moment occurring is clearly indicated by
The I-V curve is another parameter to investigate the feasibility of using MoS$_2$ as sensing medium to detect gas molecules. The effects of NO$_2$ molecule adsorption on the transport properties of electronic devices based on MoS$_2$ are further investigated. The I-V curve of pristine MoS$_2$ exhibits nonlinear behaviour shown in Fig. 2a. It shows highest sensitivity at bias voltage 1.9. The sensitivity arises quickly at 1.6 bias voltage and increase continuously before reaching the highest sensitivity. The sensitivity of Fe-MoS$_2$ to NO$_2$ is found to be dependent on the bias voltage. After adding Fe in MoS$_2$ layer the sensitivity changes dramatically. The difference sensitivity after and before adding Fe in MoS$_2$ is clearly shown in Fig. 2b. the NO$_2$/Fe–MoS$_2$ shows a sensitivity of nearly twice times higher than that of the MoS$_2$ at the bias voltage of 1.9 V.

4. CONCLUSION

In summary, it has been found that MoS$_2$ with Fe and defect exhibit highly enhanced NO$_2$ sensing behaviors, compared to that of pristine MoS$_2$ when exposed to gaseous NO$_2$ molecule. In addition, doping with N or B doesn’t act any promising role for sensing NO$_2$ molecule in MoS$_2$. In contrast, with the presence of lattice defect, or doping Si, Fe into the MoS$_2$ layer exhibits strong interaction between NO$_2$ molecule and MoS$_2$. It is found from electron density that metal doped on MoS$_2$ layer especially Fe shows high sensitivity with NO$_2$. Again from DOS, it is found that NO$_2$-Si/MoS$_2$ has shown high sensitivity rather that NO$_2$ on Fe-, defect-MoS$_2$. The changes of DOS by varying gate voltage shows a negotiable effect on NO$_2$/Fe-MoS$_2$, NO2/Si-MoS$_2$ and NO2/defect-MoS$_2$ and have a little bit effect on NO2-MoS$_2$.

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