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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 senor, 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 2*D* sheets of MoS_2 can leads a 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

$$\rho(E) = \rho^L(E) + \rho^R(E). \tag{1.1}$$

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

$$D(E) = \int dr D(E,r) = \sum \rho_{ij}(E) S_{ij}, \tag{1.2}$$

where, $S_{ij} = \int \varnothing_i(r) \varnothing_j(r) dr$ is the overlap matrix.

We have also calculated adsorption energy of NO_2 on MoS_2 surface which is calculated as as:

$$E_{ad} = E_{(NO_2/MoS_2)} - E_{MoS_2} - E_{(NO_2)}. \tag{1.3}$$

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For the NO_2/doped MoS_2 syste, the adsorption energy was calculated as

$$E_{ad} = E_{(NO_2/doped-MoS_2/)} - E_{(doped-MoS_2)} - E_{(NO_2)} \quad (1.4)$$

In the above equation, $E_{(NO_2/MoS_2)}$ is the energy of the optimized structure of gas adsorbed on MoS_2, $E_{(MoS_2)}$ is the energy of MoS_2 layer, $E_{(NO_2/doped-MoS_2)}$ is the energy of the optimized structure of gas absorbed on doped MoS_2 layer, $E_{(doped-MoS_2)}$ is the energy of doped MoS_2.

The impact of adsorption over transport properties of NO_2/defect-MoS_2, NO_2/Fe-MoS_2, NO_2/Si-MoS_2 and NO_2-MoS_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_2 considering self-consistent field imposed by the adsorbate molecules is calculated using Launder's Equation.

$$I = \frac{2q^2}{h}\int_{\infty}^{\infty} dET(E)\left(f_L^+ - f_R^+\right), \quad (1.5)$$

where, q = charge of the electrons and h = Plank's constant, f_L^+ 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_2) and the binding energy between MoS_2 and NO_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_2 and NH_3 molecule on MoS_2 surface suggesting weak adsorption energy [12]. However, the adsorption of paramagnetic molecules such as NO_2 and NO shows high adsorption energy, indicating a strong binding between MoS_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_2 and graphene since graphene has been demonstrated to hold excellent sensing properties. For NO, the E_{ad} values on MoS_2 is determined to be 35.8 meV which appears to be larger than that on graphene with 11-29 meV while E_{ad} values for NO_2 on MoS_2 is smaller than that on graphene (55-67 meV) [13]. But, in our observation, we see that in case of adsorbed NO_2 on Fe doped MoS_2 (Fe-MoS2) and Si doped MoS_2 (Si-MoS_2) exhibit high adsorption energy than graphene. Moreover, adsorption of NO_2 on Fe-MoS_2 and Si-MoS_2 show higher sensitivity rather than pristine-, defect MoS_2 as the strong binding energy between NO_2 molecules and doped – MoS_2. However, this strong binding energy may lead the distortion of NO_2, and the device may suffer from longer recovery time [14].

The total charge density illustrates that a weak physisorption takes place between NO_2 molecule and pristine MoS_2, where a strong chemisorptions occurs between NO_2 adsorbed Fe-, Si- and defect- MoS_2. However, in case of the adsorption of NO_2 molecule on Fe-MoS_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_2 is the most suitable for sensing NO_2 compared to defect-pristine- and Si-MoS_2.

It was found that the charge density from total SCF density of NO_2-MoS_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_2/Fe/defect-MoS_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_2/Fe-MoS_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_2/Si-MoS_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_2 molecule acts as the electron donor. In NO_2/Fe-MoS_2, high adsorption energy and large electron density overlap have been observed as a result of the coordination bond placed between NO_2 molecule and Fe atom.

To get the physical insight about the changes in electronic structure rises by the adsorption of NO_2 molecule, the density of states (DOS) are calculated for the system of pristine-,defect-, Fe-and Si-MoS_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_2 molecule, suggesting the weak interaction between MoS_2 and NO_2.

Compared to the pristine-MoS_2, the DOS of defect-MoS_2 shows the dramatically changes after the adsorption of NO_2 molecule, revealing a strong interaction between defect-MoS_2 and NO_2 molecule. In contrast to the pristine-MoS_2, the defect-MoS_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_2 molecule on defect-MoS_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_2 molecule on defect-MoS_2. Furthermore, such strong interaction of NO_2 and defect-MoS_2 can leads the rearrangement of the sheet structure [15, 17]. In case of NO_2/Si-MoS_2, there is a peak before Fermi levels indicating the adsorption sites of NO_2 molecule, and this indicates that the system can exhibits semiconductive behavior. Fe-MoS_2 is more suitable than Si, defect-, MoS_2 is shown by the result of electron density which is discussed before but in case of DOS Si-MoS_2

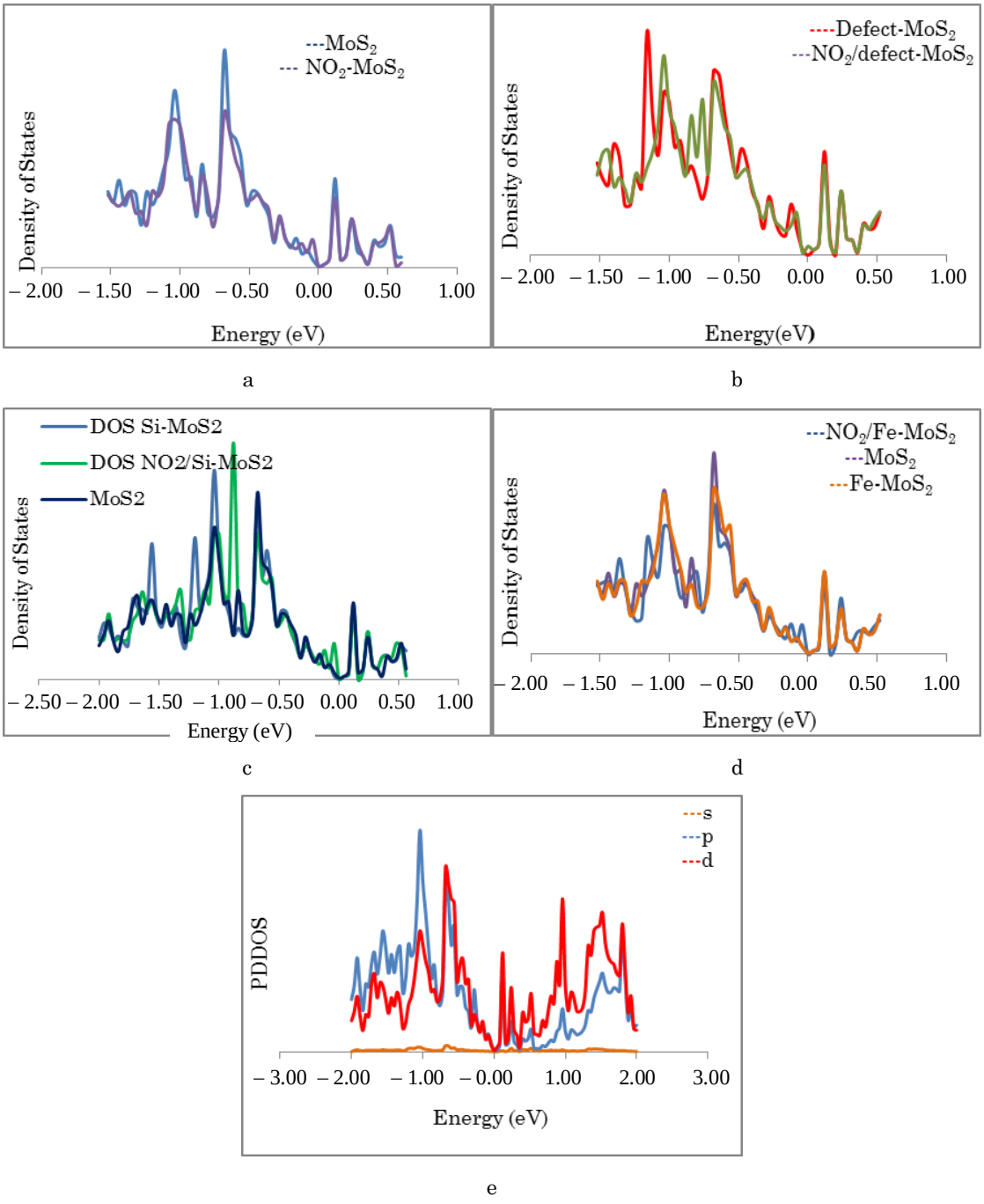
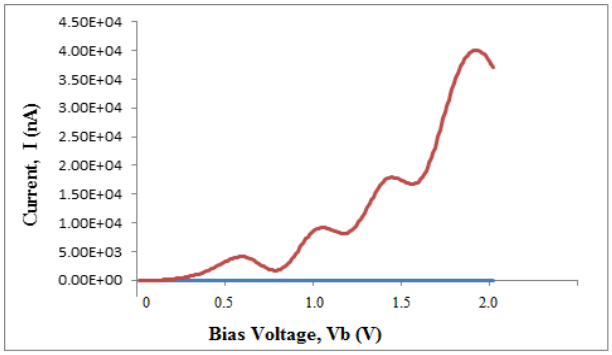


Fig. 1 – DOS of MoS_2 and NO_2 -MoS_2 (a), DOS of defect-MoS_2 and NO_2/defect-MoS_2 (b),The spin-up electronic density of states for pristine,Si-MoS_2 and NO_2/Si-MoS_2(c), The spin-up electronic density of states for pristine, Fe-MoS_2 and NO_2/Fe-MoS_2 (d), The PDDOS of Fe in Fe-MoS_2 (e)

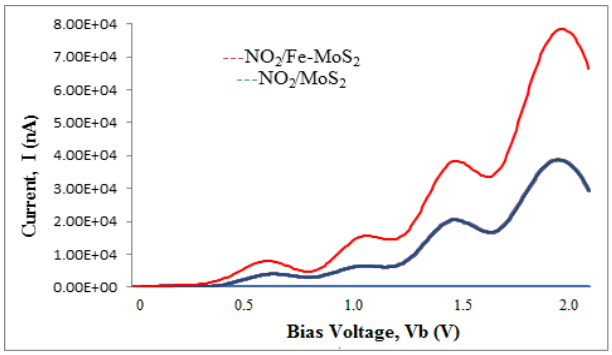
behaves more for sensing property than others are shown in Fig. 1c. If we consider the strong magnetic property of Fe atom, both Fe-MoS_2 and NO_2/Fe-MoS_2 could be also magnetic. Fig. 1d illustrates the spin up channel of the Fe-MoS_2 shows two new states, one near – 1.0 eV in the valence band and the 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



a



b

Fig. 2 – *I-V* curves of the MoS_2 (a), *I-V* curves of the NO_2-MoS_2 and NO_2/Fe-MoS_2 (b)

the PDOSs. The d-orbital splitting of MoS_2 explains the magnetic properties of NO_2/Fe-MoS_2 system that is understood by the classic Ligand Field Theory (LFT) [16].

The *I-V* curve is another parameter to investigate the feasibility of using MOS_2 as sensing medium to detect gas molecule. The effects of NO_2 molecule adsorption on the transport properties of electrical devices based on MoS_2 are further investigated. The *I-V* curve of pristine MoS_2 is 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 NO_2/defect-MoS_2 and have a little bit effect on NO_2-MoS_2.

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