First-principles insights on the adsorption properties of NO_2 gas on In_2O_3 nanostructures

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ABSTRACT

The electronic properties, structural stability and NO_2 adsorption properties of pristine In_2O_3 nano structures are studied using density functional theory method employing B3LYP/LanL2DZ basis set. The stability of In_2O_3 nanostructures is confirmed and the energy gap of 3.34 eV is calculated for pristine In_2O_3 nanostructures. The adsorption properties of NO_2 gas on pristine In_2O_3 nanostructures are explored in terms of energy gap, adsorption energy, average energy gap variation and Mulliken charge transfer. Moreover, the interaction of NO_2 gas on In_2O_3 nanostructures are explored in atomistic level and favorable adsorption site is found to be when nitrogen atom in NO_2 gets adsorbed on indium or oxygen atom on In_2O_3 base material. Furthermore, the density of states spectrum confirms the transfer of electrons between NO_2 gas and In_2O_3 base material. The findings show that pristine In_2O_3 nanostructures can be efficiently used as NO_2 sensor, which can detect NO_2 in part per million level in the environment.

KEY WORDS: In_2O_3, Adsorption, NO_2, Nanostructure, Adsorption energy, Energy gap.

1. INTRODUCTION

The recent advancement in chemical sensors is to provide a means to manipulate materials on atom-by-atom basis and to study the adsorption of target gas/vapour in nanoscales. In the past two decades, there has been a considerable development in the synthesis of nanoscale materials and its application as gas/vapour sensor (Huang, 2009; Ramgir, 2013). The metal oxide semiconductor (MOS) is the most attractive class of materials for functional nanodevice and chemical sensors. Various methods have been used for the synthesis of MOS nanostructures (Comini, 2013; Zappa, 2014; Phanichphant, 2014; Wetchakun, 2011; Harraz, 2014; Gwizdz, 2014; Barsan, 2007). Moreover, the nanodevice functionality depends on the dimension of MOS namely one-dimension, two-dimension nanomaterials (Zhao, 2016; Murguia, 2013). Among the various MOS, a unique material is indium oxide (In_2O_3). In_2O_3 has been widely used in the microelectronic field as flat panel display materials, memory devices, solar cells, window heaters and most importantly gas detectors (Gu, 2015; Park, 2016). The application of In_2O_3 thin films and nanoparticles depends upon the controlled synthesis of the materials with specific morphology. Different morphologies such as nanowire, nanobelts, nanocubes, nanoflowers, nanotubes, nanorods and hollow spheres have been prepared by variety of methods namely chemical vapor deposition (CVD), pulsed laser deposition (PLD), alumina or mesoporus silica template method and wet chemical methods (Qurashi, 2010). The reported experimental band gap for In_2O_3 thin films is found to be around 3.5 to 3.7eV respectively (Beena, 2011). Recently, numerous work has been published in the field of sensing hazard gases namely NH_3 (Dai, 2016), HCHO (Wang, 2016), O_3 (Klaus, 2015), CO (Nagarajan, 2015), H_2S (Wang, 2016) and C_2H_5OH (Kim, 2011) using In_2O_3 nanostructures. Among various transition metal oxides, In_2O_3 is a preferred MOS, owing to its marvelous sensitivity and selectivity towards volatile organic compounds and hazard gases for instance CO, NO_2, NH_3 and HCHO. In gas sensing semiconductor materials, high sensitivity can be achieved by increasing surface-to-volume ratio of the material. Moreover, the gas sensing mechanism is much complex, since the selectivity for a particular target gas should be achieved. The sensitivity of metal oxide semiconductor can be improved by incorporating the suitable impurities in the respective base material and by varying the operating temperatures (Xie, 2015). A perfect and efficient metal oxide semiconductor gas sensor should have high sensitivity and selectivity under the low operating temperatures. Cao (2014), synthesized In_2O_3 micro/nanotubes with different diameters and HCHO sensing properties are reported. (Golovanov, 2005) have proposed the theoretical and experimental investigation of In_2O_3 gas sensors synthesized by optimized spray pyrolysis method. Neri (Neri, 2008) explained about chemi resistive carbon monoxide gas sensors based In SnO_x and In_2O_3 nano powders synthesized using starch-aided sol–gel process. (Korotcenkov, 2007) have investigated the impact of additives on structural and gas sensing properties of In_2O_3 nanostructure based ceramics. (Koh, 2006) reported the growth control and material properties of tin-doped and pristine indium oxide thin films synthesized by ion beam method. Wang (2009) proposed phase and shape controlled synthesis of indium oxide with different morphologies and enhance their gas-sensing properties. Based on the above facts, literature survey was performed by SCOPUS database and Cross Ref metadata search. To our knowledge, not much work has been reported to investigate the electronic and NO_2 adsorption properties in In_2O_3 nanostructures. The inspiration behind the present work is to investigate the adsorption of nitrogen dioxide in pristine In_2O_3 nanostructures in the atomistic level. We have reported the adsorption studies of various gases on to metal oxide nanostructures using DFT method

(Nagarajan, 2015). The novel aspect of this work is to study the adsorption properties of NO_2 gases in In_2O_3 nanostructures and the results are reported.

2. MATERIAL AND METHODS

Computational Methods: The pristine indium oxide nanostructures optimized first and simulated successfully, which is facilitated using Gaussian 09 package. The adsorption properties of NO_2 gas on to In_2O_3nanostructures are studied with the help of Gaussian 09 package. In the present work, Becke's three parameter hybrid functional in combination with Lee-Yang-Parr correlation functional (B3LYP) and LanL2DZ basis set is used to optimize In_2O_3 nanostructures. The most important criterion for simulating In_2O_3 nanostructure is choosing the appropriate basis set. The LanL2DZ basis set also applicable to H, Li-La and Hf–Bi elements. Thus, LanL2DZ is a good choice among other basis sets, which provides the perfect output with pseudo potential approximation (Becke, 1988; Hay, 1985). Xu Mao-Jie have investigated the geometric, vibrational and electronic properties of In_mO_n ($1 \leq m, n \leq 4$) (Xu, 2011) Mukhopadhyay (2010), have investigated the same electronic, structural and vibrational properties of small clusters of indium oxide using B3LYP/LanL2DZ basis set. Furthermore, the reported works strengthen the selection of suitable basis set for the present work.The highest occupied molecular orbital (HOMO), density of states (DOS) spectrum and lowest unoccupied molecular orbital (LUMO) gap of In_2O_3 nanostructures are calculated using the Gauss Sum 3.0 package(Boyle, 2007).The energy convergence is obtained in the range of 10^{-5}eV, while optimizing In_2O_3 nanostructures.

3. RESULTS AND DISCUSSION

The key objective of the present work is to confirm the structural stability of In_2O_3base material and to study the adsorption and electronic properties of NO_2 gas molecules on pristine In_2O_3 nanostructures. The adsorption of NO_2 on In_2O_3 infers the use of In_2O_3 nanomaterials as NO_2 sensor. Figure.1, illustrates the nanostructure of pristine In_2O_3. The nanostructure of In_2O_3 is built from International Centre for diffraction data (ICDD) card no. 88-2160. The pristine In_2O_3 nanostructure has forty eight oxygen atoms and thirty two indium atoms.

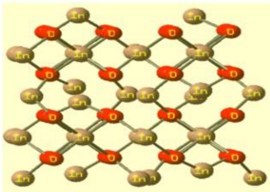

Figure.1. Pristine In_2O_3 nanostructure

Structural stability and electronic properties of In_2O_3 nanostructures: The structural stability of pristine In_2O_3 nanomaterial is depicted in the terms of formation energy, $E_{form} = 1/n\ [E\ (In_2O_3\ nanostructure) - pE(In) - q\ E(O)]$ where E (In_2O_3 nanostructures) refers to the total energy of In_2O_3 nanostructures, E(In), E(O) represent the corresponding energies of isolated indium, oxygen atoms and p, q and n represents the number of indium, oxygen atoms and total number of atoms in the nanostructures respectively. The point group, HOMO-LUMO gap, formation energy and dipole moment of pristine In_2O are tabulated in Table.1. The formation energy of pristine In_2O_3 is observed to be -2.50eV. Before studying the adsorption properties, the stability of In_2O_3nanostructures should be confirmed. The formation energy of In_2O_3 base material ensures the stable structure of In_2O_3. The dipole moment for the pristine In_2O_3 is found to be 4.61 Debye, which indicates that the charges are not evenly distributed in the nanostructure. In_2O_3 nanostructure exhibits C_1 point group, which exhibits only identity operation, E.

Table.1. Formation energy, dipole moment and point group of In_2O_3 nanostructure

Nanostructure	DM (Debye)	PG	HOMO	LUMO	E_g(eV)	Formation energy (eV)
pristine In_2O_3	4.61	C_1	-6.4	-3.06	3.34	-2.50

The electronic properties of pristine indium oxide nanostructures are illustrated in the terms of HOMO and LUMO levels. The HOMO-LUMO gap for pristine In_2O_3 is found to be 3.34 eV. The reported experimental band gap is 3.5eV, which is higher than the calculated value of 3.34 eV (Beena, 2011). Density functional theory is mainly applicable to the ground state. Therefore, the exchange correlation leads to underestimation of band gap for the outermost electronic state. In the present work, the adsorption properties of NO_2 gases on In_2O_3 base material is investigated and compared with its isolated counterpart, hence there will not be any inconsistency in the results. The density of states (DOS) spectrum gives the insights on the localization of charges in different energy intervals for In_2O_3 nanostructures. In the present work, localization of charges is observed to be more in the virtual orbital of In_2O_3 nanostructures, which is observed from more peak maxima. These peak maxima in In_2O_3 nanostructure arises due to the orbital overlapping of indium atom and oxygen atom in In_2O_3 base material. The peak maxima in virtual orbital of In_2O_3 base material is one of the favorable condition for chemical sensors, where the transition of electrons takes places easily between base material and NO_2target gas. The visualization of HOMO-LUMO gap and DOS spectrum of isolated In_2O_3 nanostructure is shown in Figure.2.

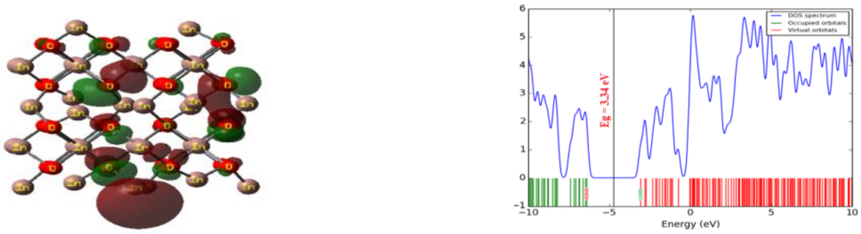

Figure.2. Visualization of DOS and HOMO-LUMO gap of pristine In_2O_3 nanostructure

NO_2 adsorption properties of In_2O_3 nanostructures: The adsorption energy of NO_2 gas molecules on In_2O_3 nanostructures can be expressed as E_{ad}= [E(In_2O_3/NO_2)-E(In_2O_3)-E(NO_2)];

Where E(In_2O_3/NO_2) denotes the energy of In_2O_3/NO_2 complex and E(In_2O_3) and E(NO_2) are isolated energies of In_2O_3 base material and NO_2gas molecules respectively (Nagarajan, 2015; 2016; 2014). The negative value of adsorption energy indicates the strong adsorption of NO_2 gas molecule on In_2O_3 nanostructure. This implies that the energies are transferred from In_2O_3 base material to NO_2 gas molecule. The adsorption of NO_2 gas molecule on In_2O_3 nanostructures on different sites are named as positions A, B and C, which is illustrated in Fig.3a-c respectively. The adsorption energy values of In_2O_3 base material for positions A-C are observed to be -1.28, -1.1, -0.9 eV respectively.

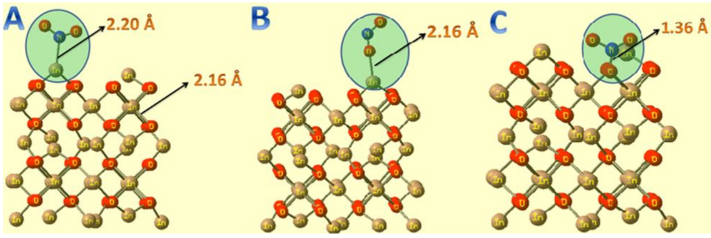

Figure 3 (a) NO_2 adsorbed on position A (b) NO_2 adsorbed on position B(c) NO_2 adsorbed on position C

Table.2 represents adsorption energy, energy gap, Mulliken charge transfer and average energy gap variation of NO_2gas molecule adsorbed on pristine In_2O_3 nanostructure. Moreover the adsorption of nitrogen atom in NO_2 molecule, when gets adsorbed on indium atom in In_2O_3 nanostructure is observed to have more adsorption energy than other positions. The important parameter, which is used to study the transfer of electrons between the adsorbate and the base material, is inferred using Mulliken charge transfer analysis (***Q***) (Mulliken, 1955; Chandiramouli, 2015; Nagarajan, 2014). Usually, the negative value of Mulliken charge represents the transfer of electrons from In_2O_3 base material to NO_2 gas molecule. However, the positive value of Mulliken charge represents the transfer of charge from target gas to the base material. In the present work, for all the cases, negative value of Mulliken charge is observed.

Table.2. Adsorption energy, Mulliken population, HOMO-LUMO gap and average energy gap variation of In_2O_3 nanostructures

Nanostructures	E_{ad} (eV)	Q (e)	E_{HOMO}	E_{FL} (eV)	E_{LUMO}	E_g (eV)	E_g^a %
pristine In_2O_3	-	-	-6.4	-4.73	-3.06	3.34	-
Position A	-1.28	-0.653	-7.45	-5.89	-4.33	3.12	7.05
Position B	-1.1	-0.769	-7.25	-5.585	-3.92	3.33	0.3
Position C	-0.9	-0.004	-5.66	-4.61	-3.56	2.1	59.05

Figure.4 a represents the Mulliken charge in pristine In_2O_3 nanostructure. Figure 4b-d represents the transfer of electrons from In_2O_3 base material to NO_2 gas molecules for different positions A, B and C respectively (arrows in the figure point the transfer of Mulliken charges from In_2O_3 base material to NO_2 target gas).

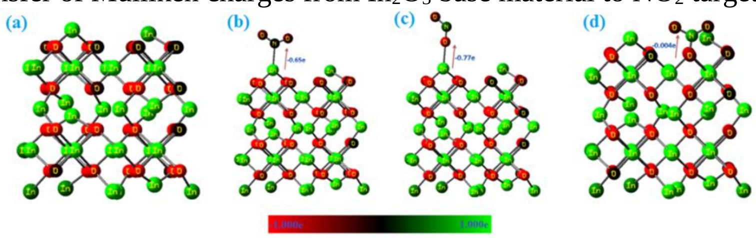

Figure.4. (a) Mulliken charge on pristine In_2O_3 nanostructue, (b) Mulliken charge transfer for position A, (c) Mulliken charge transfer for position B, (d) Mulliken charge transfer for position C

This further confirms the transfer of charges between In_2O_3 base material and NO_2 gas. Moreover, the magnitude of the Mulliken charge transfer is found to be more for positions A and B rather than position C. The transfer of charge is governed due to the charge transfer between indium and nitrogen and oxygen anions. However, there is no significant charge transfer, when nitrogen atom in NO_2 gets adsorbed on oxygen atom in In_2O_3 nanostructure. Furthermore, the conductivity of the In_2O_3 nanostructure increases due to the narrowing of HOMO-

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LUMO gap, when NO_2 gets adsorbed on the pristine In_2O_3 nanostructure compared to its isolated counterpart. For all the cases, the decrease in the band gap is observed. However, the decrease in the band gap is not significant for positions A and B. In contrast for position C, the band gap decreases drastically, this is due fact that the adsorption of nitrogen atom in NO_2 molecule, when gets adsorbed on oxygen atom in In_2O_3 base material, the orbital overlapping further decreases the band gap of In_2O_3 base material. Thus the conductivity increases upon adsorption of NO_2 gas on In_2O_3 nanostructure. Usually in chemi resistive type of gas/vapour sensor the adsorption of oxygen molecules from air results in the transfer of electrons between In_2O_3 base material and oxygen, thus the oxygen consumes the electrons from the conduction band of In_2O_3, upon interaction of target gas/vapour the adsorbed oxygen releases the electrons back to the base material, thus the variation in resistance is measured in the chemiresistor film (Banica, 2012). In the present work, the adsorption of NO_2 leads to narrowing of band gap, which in turn increases the conductivity of the In_2O_3 nanostructure. Using the two probe method, the variation in the resistance can be recorded, which is in direct proportion to the concentration of the target gas/vapour present in the atmosphere (Chandiramouli, 2015). Figure.5 a- 5c represents the HOMO and LUMO visualization and DOS spectrum of pristine In_2O_3 nanostructures and NO_2gas adsorbed on positions A, B and C respectively. From the DOS spectrum it is observed that for pristine In_2O_3 nanostructures, the energy gap is found to be 3.34 eV. Besides, on adsorption of NO_2 on In_2O_3 nanostructures, alpha and beta orbitals are observed in the DOS spectrum for all the positions A, B and C.

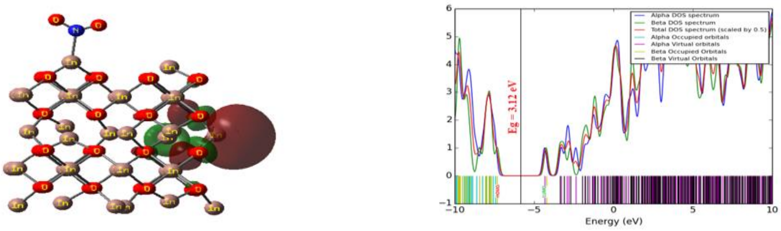

Figure 5 (a). Visualization of DOS and HOMO-LUMO gap of position A

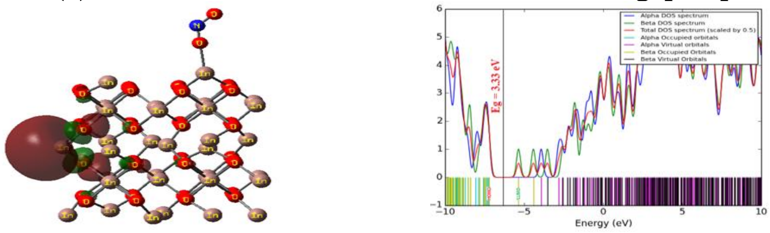

Figure 5 (b). Visualization of DOS and HOMO-LUMO gap of position B

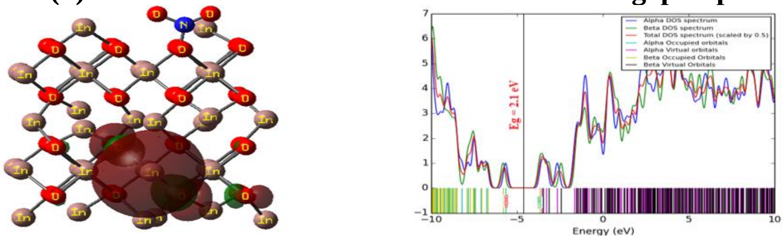

Figure 5 (c). Visualization of DOS and HOMO-LUMO gap of position C

The alpha and beta orbital arises due to spin up electron and spin down electron respectively (Sriram, 2015). Since the electronic configuration of nitrogen and oxygen is $1s^2 2s^2 2p^3$ and $1s^2\ 2s^2 2p^4$ respectively. Upon adsorption of indium and oxygen atom in In_2O_3 base material, the orbital overlapping with indium and oxygen leads to alpha and beta orbitals. The formation of alpha and beta orbitals strongly confirms the adsorption of NO_2 on In_2O_3 nanostructures. Comparing, the average energy gap for all the positions, for positions A and C the average energy gap is found to be prominent. In order to conclude the favorable adsorption site of NO_2 on pristine In_2O_3 nanostructure, the parameters namely adsorption energy, HOMO-LUMO gap, Mulliken charge transfer and average energy gap variation should be taken into consideration before conclusion. Among all the positions, positions A and C is found to be more favorable than position B. For positions A and C, the adsorption energy and average energy gap variation is found to be significant. However, Mulliken charge transfer for position C is not considerable, which is due to the adsorption of nitrogen atom on oxygen atom in In_2O_3 base material. From the observation, it can be concluded that when nitrogen atom in NO_2 gas molecule gets adsorbed on indium or oxygen atom in In_2O_3 base material, it is found to be the favorable site for adsorption. In order to validate the results of present work, the results should be compared with the experimental work. (Ilin, 2016) studied NO_2 sensing properties of nanocrystalline In_2O_3. The conductivity of In_2O_3 film varies upon exposure of NO_2 gas on film surface, which is also influenced with ultraviolet light exposure. Xiaolong Hu (2015) synthesized Cu-doped In_2O_3 hierarchical flower microstructures and studied the response towards NO_2 gas via chemiresistor method. The variation in the resistance is observed upon exposure of NO_2 gas. Sowti Khiabani (2012) fabricated NO_2 gas sensor through AC electrophoretic deposition using electrospun In_2O_3 nanoribbons. They reported that for an operating temperature of 150-300^{o}C, the response towards $NO_2$is in the order of 1-17 parts per million (ppm). Liping Gao (2015), synthesized porous corundum type In_2O_3 nanosheets. The results show that In_2O_3 nanosheets shows maximum response to 10 ppm NO_2 at an operating temperature of 250^{o}C. The reported sensing response of NO_2 gas by chemiresistor method further strengthens the present work, in which the change in resistance can be measured through two probe method. Furthermore, in the present study the adsorption characteristics of NO_2 gas molecules on In_2O_3 nanostructures are studied in atomistic level, which can be suggested that In_2O_3 is one of the important materials to detect the presence of NO_2 gas in the order of ppm level.

4. CONCLUSION

Using DFT method the structural stability, electronic and NO_2 adsorption properties on In_2O_3 nanostructures are explored with B3LYP/LanL2DZ basis set. The structural stability of pristine In_2O_3 is confirmed with formation energy. The HOMO-LUMO gap for isolated In_2O_3nanostructure is found to be around 3.34 eV, which is comparable with experimental results. The adsorption properties of NO_2 on In_2O_3 nanostructures are investigated in terms of Mulliken charge transfer, adsorption energy, energy gap and average energy gap variation. Besides, the DOS spectrum confirms the strong adsorption of NO_2 on In_2O_3 nanostructures, which is inferred with the alpha and beta orbitals found in DOS spectrum. In addition, more peak maxima are observed in the virtual orbital, which is one of the promising conditions for chemical sensors. Moreover, the favorable adsorption site of NO_2 gas molecule on In_2O_3 nanostructure is when nitrogen atom gets adsorbed on indium or oxygen atom on In_2O_3 base material. In addition, the findings of the present work show that In_2O_3 nanostructures can be efficiently used as NO_2 sensor, which can detect the concentration of NO_2 in part per million level in the atmosphere.

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