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Density functional analysis of adsorption of NO_2 on ZnSe nano structures

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ABSTRACT

The pristine nanosheet, nano cone and nanotube structures with equal number of Zn and Se atoms were constructed in order to study the effect of adsorption of NO_2 at Zn and Se sites of the nano structures. The pristine ZnSe and NO_2 adsorbed ZnSe nanostructures were optimized using density functional theory implemented in Gaussian09 pacakage. The B3LYP hybrid exchange correlation with LANL2DZ as basis set was used in this study to exploit the nano structures. Structural and electronic properties of such as HOMO-LUMO, band gap and mulliken population of ZnSe nano structures were studied and reported. Density of States(DOS) spectra of pristine and NO_2 adsorbed ZnSe Nano sheet, cone and tube structures show that nano cone and nanotube structures have a higher number of quasi bound states on both valance and conduction band sides compared to the nano sheet structures. To study the adsorption effect of NO_2 on Zn and Se sites of various ZnSe nanostructures, the adsorption energy was calculated and discussed.The ionization potential and electron affinity and the reactivity descriptors of ZnSe nanostructures such as chemical hardness(□), chemical potential (μ), softness(S) and electronegativity(χ) were calculated for pristine, NO_2 adsorption at Zn site and NO_2 adsorption at Se site for ZnSe nano structures and reported.

Keywords : ZnSe nano structures; adsorption energy; Mulliken population; IP;EA; reactivity descriptors.

INTRODUCTION

ZnSe is a direct band gap semiconductor with bulk band gap of 2.7 eV at room temperature[1]. It is a potentially good material for short-wavelength (blue to the ultra violet range) lasers and other photo-electronic devices and it exhibits tunable-ultraviolet (UV) luminescence via quantum confinement effects[2]. It is one of the encouraging materials for construction of LED[3,4], tunable mid-IR laser sources[5] , blue-green laser diodes[6,7]and for remote sensing applications. The size dependent properties are still under study for small size selinide nanoclusters. One of the main important application of ZnSe is in the field of gas sensing[8] and in particular the sensitivity towards NO_2 is very appreciable. In order to tailor the properties of sensing, of ZnSe towards NO_2, it is necessary to study the various structural and positional possibilities of NO_2 on the ZnSe structure. Density functional theory (DFT)[9-11] is a kind of computational tool which is capable to produce various combinational outputs of the possible nanoclusters based on the electron density of the material. This present work is aimed to study some realistic structures of ZnSe such as nano sheet, none cone and nanotube with the adsorption of NO_2 at Zn and Se sites to elucidate the best adsorption site on the corresponding structures using density functional theory.

MATERIALS AND METHODS

Computational Details

Realistic structures of ZnSe such as nano sheet, nano cone and nanotube were constructed primarily. Then NO_2 adsorption on the Zn and Se sites were also constructed in order to study the effect of adsorption of NO_2 on the ZnSe with respect to the site of attachment. The ZnSe and NO_2 adsorbed nanostructures were optimized using density functional theory implemented using Gaussian09 [12] package. The B3LYP[13,14]hybrid exchange correlation with

LANL2DZ as basis set is used in this study to exploit the nano structures. The LANL2DZ [15,16] basis set is selected since it has the full potential to optimize almost all the atoms in the periodic table. The energy convergence is set to 10^{-5}eV for optimizing all the structures. In order to study the stability, minimum energy obtained from the optimization and the binding energies were calculated and related. The density of states and HOMO-LUMO calculations were carried out using Gaussum 3.0[17]package.

RESULTS AND DISCUSSION

Structural and Electronic properties of ZnSe

Structures of ZnSe such as nano sheet, nano cone and nanotube are shown in the Figure 1(a),1(b) and 1(c) respectively. The average bond length between Zn and Se were obtained by the optimization process is 2.0 Å. To find the structural stability of the structure, it is necessary to analyze its minimum energy. Calculated minimum energy and dipole moment for three different pristine ZnSe nanostructures were shown in Table 1.

Table 1 Minimum energy and Dipole moment of ZnSe nano structures

Structure	Minimum Energy (Hartrees)	Dipole Moment(Debye)
Nano Sheet	-1010.6202	22.6888
Nano Cone	-1041.4042	9.2247
Nano Tube	-1039.7444	11.4871

From the table it is seen that Nano cone structure has minimum energy compared to other two structures. The dipole moment value indicates the charge distribution among the particular structure. Among the three different pristine ZnSe nano structures, Nano cone has minimum dipole moment which indicates the charges are almost equally distributed in comparing with other two structures.

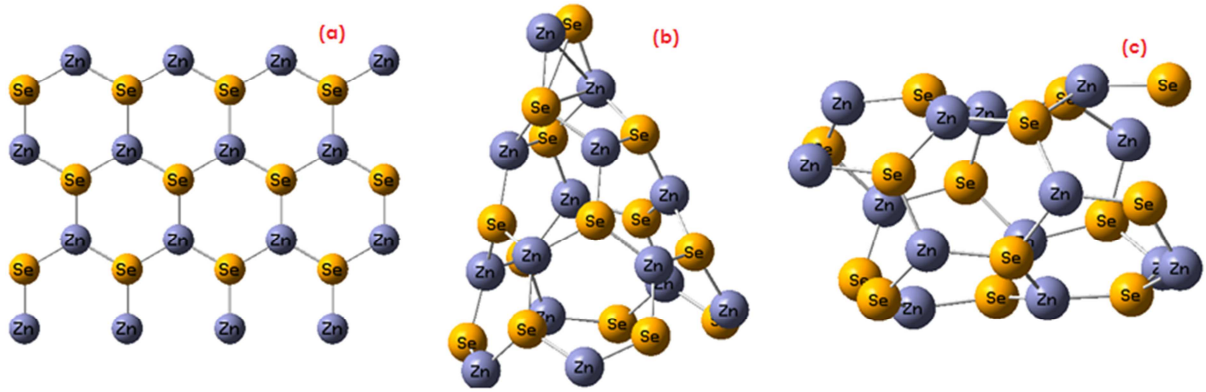

Fig. 1: Pristine ZnSe nano sheet, nano cone and nano tube structures

In order to analyze the sensitivity of the ZnSe structures towards the target molecule(NO_2), it is necessary to study the electrical characteristics of the corresponding structures. The electronic properties of the structures can be explained in terms of its HOMO(highest occupied molecular orbital) and LUMO(lowest unoccupied molecular orbital) energies and the charge transfer between the structure and the gas molecule. The change in charge variation in the structure after the target gas is adsorbed can be calculated using the following equation

$$\Delta Q = Q_{NS+gas} - Q_{NS} \qquad \text{----(1)}$$

where Q_{NS+gas} is the total charge of the nanostructure with the target gas adsorbed and Q_{NS} is the total charge of the nanostructure. The charge of a nanostructure can be calculated from the Mulliken population analysis . This is a very useful tool to analyze the transfer of charge either from gas to base material or base material to gas. From this, negative sign of the charge indicates the transfer from base material to the gas molecule and positive sign indicates the charge transfer from gas molecule to base material. The calculated values of the Mulliken population charges for the NO_2 adsorption are shown in the table 2 for the ZnSe structures. From the table values it is seen that for nanocone, and nanotube structure charge transfer is taking place from the base ZnSe nanostructures to NO_2 gas irrespective of the site of adsorption

Table 2. HOMO,LUMO, Band gap and Mulliken population of ZnSe Nano structures

Structure	Adsorption Site	HOMO (eV)	LUMO (eV)	Energy Gap (eV)	Mulliken Charge (e)	Band Gap variation with respect to its pristine structure (eV)
NanoSheet Pristine	-	-4.5	-1.79	2.71		-
	Zn	-6.2	-0.36	5.85	0.677	3.14
	Se	-5.3	-0.45	4.85	0.151	2.14
NanoCone Pristine	-	-4.65	-2.7	1.95	-	-
	Zn	-5.44	-3.03	2.41	-0.469	0.46
	Se	-4.69	-3.18	1.51	-0.657	0.44
NanoTube Pristine	-	-4.45	-3.88	0.57	-	-
	Zn	-5.02	-4.14	0.88	-0.507	0.31
	Se	-4.63	-3.5	1.13	-0.671	0.56

For all the structures, except Nanosheet , Se adsorption site has a higher population value since the Se atom has Se^{2-} state. Beside this, the Nanosheet structure is not a closed structure with higher edge effects and hence it has a higher population at the adsorbing sites.

In order to examine the sensitivity of NO_2 at the sites of Zn and Se, it is important to examine the DOS spectra of the pristine and NO_2 adsorbed ZnSe nanostructures. Figure 2 shows the DOS spectrum of pristine and NO_2 adsorbed on Zn and Se sites of NanoSheet structures.

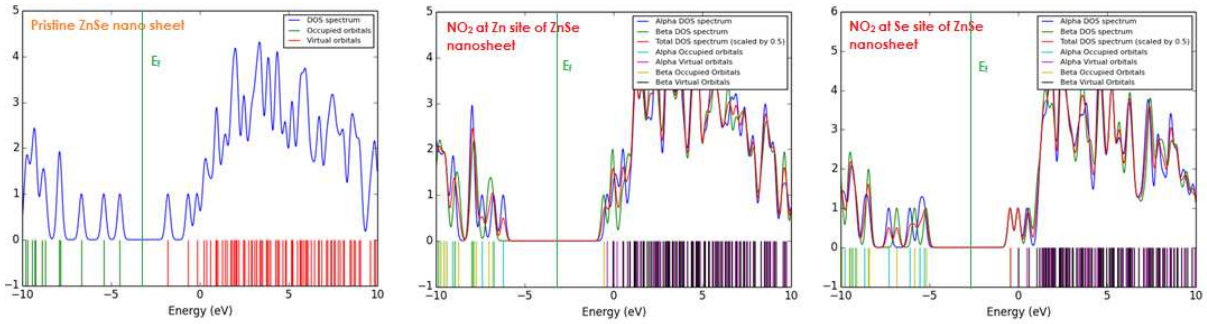

Fig. 2: DOS spectra of pristine and NO_2 adsorbed ZnSe Nano sheet.

DOS of the pristine ZnSe nano sheet shows more number of energy states above the Fermi level. The energy gap is found to be 2.71 eV for this structure. However, when NO_2 is adsorbed on either Zn or Se site, due to the exchange of charges between the ZnSe sheet and the NO_2 gas molecule, spin up and spin down states are formed and this shows the change in the energy gap. The NO_2 gas molecule adsorption on the Zn site alters the band gap of the structure more than twice of the value (5.85 eV). However, NO_2 adsorbed on the Se site, affects the band gap and it is increased (4.85eV) as compared to the pristine structure. The band gap difference is more for the pristine ZnSe nanosheet and NO_2 adsorbed at Zn and Se sites..

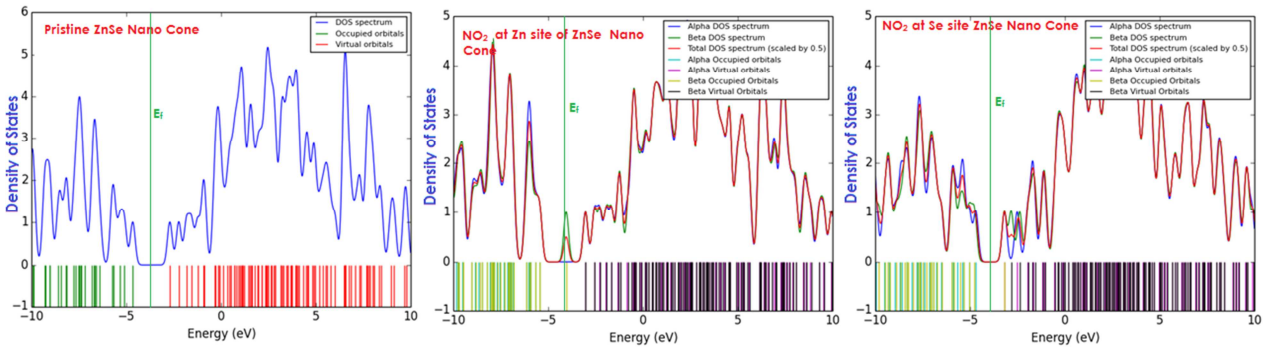

Fig. 3: DOS spectra of pristine and NO_2 adsorbed ZnSe Nano cone

In the case of Nanocone structure, the DOS shows (in Fig. 3) the pristine structure has the band gap as 1.95 eV. As in the Nanosheet, when the NO_2 is adsorbed with the Nano cone structure on both Zn and Se sites, the band gap is changed and also the number of energy states on valance band and conduction bands are increased. When the NO_2 molecule is adsorbed on the Zn site of the Nano cone structure, the valence band get maximum number of states compared to the pristine and the NO_2 adsorption on Se site of the nano cone structure. This indicates more number

of localization of states produced at certain levels, which in turn increases the energy gap. While comparing pristine and NO_2 adsorption at Se site, NO_2 adsorption on Zn site has more number of energy states.

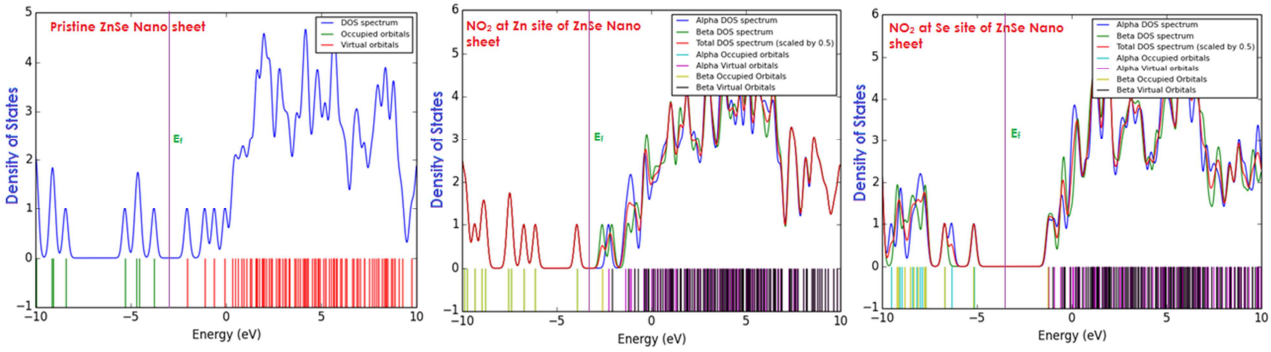

Fig. 4: DOS spectra of pristine and NO_2 adsorbed ZnSe Nano tube

In the case of Nano tube structure(Fig.4), the DOS spectra of the pristine structure shows the less number of valence band states than the conduction band states. The calculated band gap is 0.57 eV When the NO_2 molecule is adsorbed on the Zn site of the Nano tube structure, due to spin up and spin down states of the molecule alpha and beta bands are formed and the band gap is increased slightly compared to the pristine structure. A similar effect is observed in the DOS spectrum of NO_2 adsorption on the Se site of the Nano tube structure. The calculated band gap in this structure is 1.13eV.

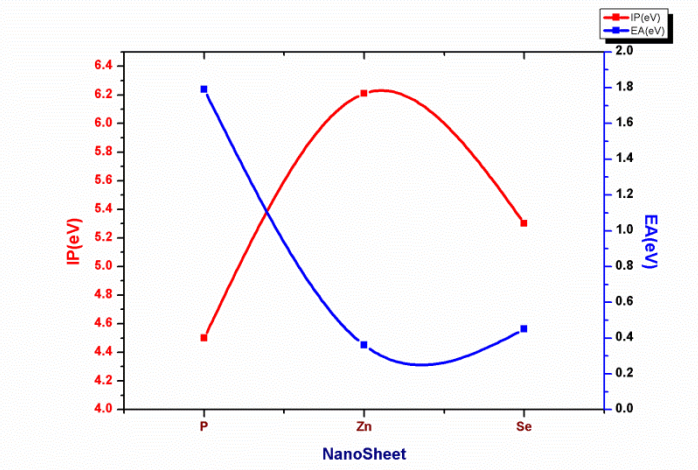

Fig. 5(a): IP and EA curves of pristine, NO_2 adsorption of Zn and Se sites of ZnSe nanosheet

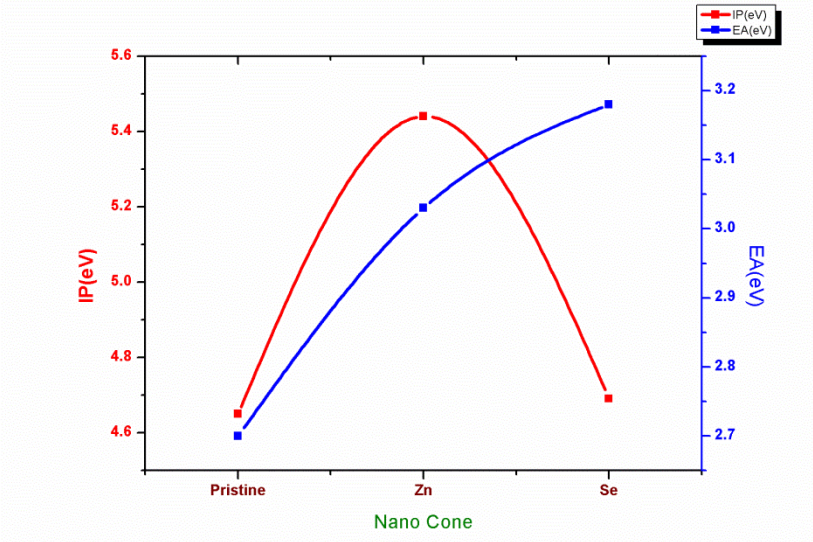

Fig. 5(b): IP and EA curves of pristine, NO_2 adsorption of Zn and Se sites of ZnSe nanocone

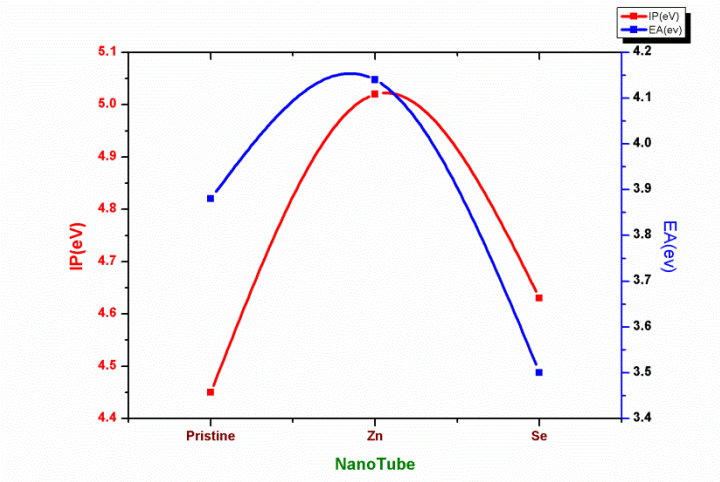

Fig. 5(c): IP and EA curves of pristine, NO_2 adsorption of Zn and Se sites of ZnSe nanotube

Electronic properties of nanostructures can also be studied in terms of ionization potential (IP) and electron affinity(EA). The IP describes how much energy is required to remove an electron from the ZnSe nano structure and EA describes the altered energy of the ZnSe nano structure after an electron is added with it. Fig 5(a),5(b) and 5(c) shows the variation of IP and EA of three different ZnSe nano structures of pristine, NO_2 adsorption on Zn site and NO_2 adsorption of Se site respectively.

The IP value f nano cone and nano tube possess similar trend means that, for all the ZnSe structures pristine and NO_2 adsorbtion on the Se site exhibits low IP value than that of NO_2 adsorption of Zn site structure. This indicates on pristine and NO_2 adsorption at Se sites, there is not a much strong attraction between the electrons and the nucleus.The high value of EA is observed for NO2 adsorbed at Se site of a ZnSe nanocone structure (3.2eV) . This indicates that this (nanocone) structure is good for chemical sensing.

Mulliken population analysis

In the adsorption process, there may be a chance of charge transfer between the base material and the adsorbent. This can be analyzed in terms of Mulliken population analysis. For ZnSe nano sheet structure charge transfer takes place from the gas molecule to the base material when NO2 is adsorbed at Zn and Se site. This is indicated by the positive sign of the Mulliken value. The calculated average Mulliken population charge for the nano sheet structure adsorbed at Zn and Se are 0.677 e and 0.151e.

In the nanocone and nanotube structures, the sign of the Mulliken value indicates that the base material has given charge to the NO_2 molecule . When the NO_2 molecule is adsorbed on the Zn sites of ZnSe cone and tube structures, more number of charges are transferred from the base material to the NO_2 molecule. The average Mulliken population charge for the Zn sites of the cone and tube structures are -0.469 e and -0.507 e respectively. However, NO_2 adsorption on the Se site of the ZnSe nanostructures will show almost equal amount of charge transfer from the Nano structure to the NO_2 molecule. The calculated average Mulliken population charge for Se sites of the ZnSe cone and tube are -0.657 e and -0.671 e respectively.

Adsorption of NO_2 on Zn and Se sites of ZnSe nanostructures

To find the most favorable adsorbing site for the gas molecule, the NO_2 molecule is placed on the three base structures (nanosheet,nanocone and nanotube) of ZnSe at Zn and Se sites respectively. The corresponding figures are shown in Fig. 6 and Fig. 7 respectively. The structures are optimized with and without the NO_2 gas molecules, to find out the interaction energy between the gas molecule and the adosorbarate.

The adsorption energy can be calculated using the following formula[18]

$$E_{ad}=E_{tot}(ZnSe\text{-}NO_2)-E_{tot}(ZnSe)-E_{tot}(NO_2) \quad \text{----(2)}$$

where $E_{tot}(ZnSe\text{-}NO_2)$ is the total energy with gas molecule on ZnSe structure, $E_{tot}(ZnSe)$ is the total energy of ZnSe structure and $E_{tot}(NO_2)$ is the total energy of the gas molecule. The calculated adsorption energy values are shown in the table 3. If the E_{ad} is less than zero, then the total energy of the system is exothermic and spontaneous. However, if E_{ad} has positive value, then the adsorption process is very difficult since it requires energy for the process(endothermic).

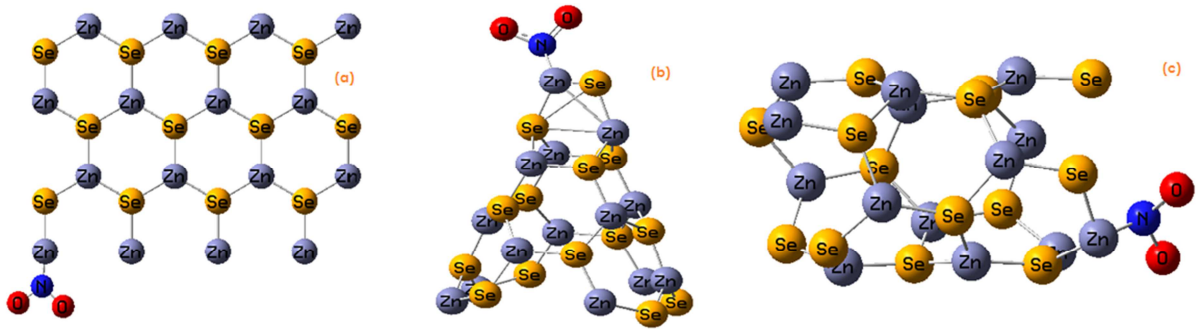

Fig. 6: NO_2 adsorption on Zn sites of ZnSe nanosheet, nano cone and nano tube structures

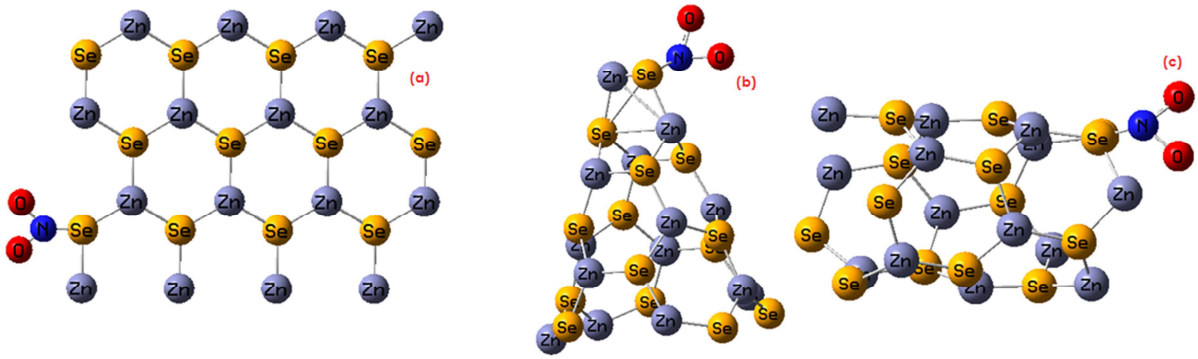

Fig. 7: NO_2 adsorption on Se sites of ZnSe nanosheet, nano cone and nano tube structures

Table 3 Adsorption energies of NO_2 at Zn and Se sites on the ZnSe nano structures

Structure	Adsorption Site	Adsorption Energy(Hartrees)
NanoSheet	Zn	0.1794
	Se	0.8412
NanoCone	Zn	1.7346
	Se	1.8716
NanoTube	Zn	-0.0437
	Se	0.0981

The adsorption energy values indicate that the ZnSe structures exhibit both endothermic and exothermic adsorption. In the case of Nanosheet, irrespective of the adsorption site either Zn or Se the adsorptions are endothermic adsorption. However, for the nanocone structures both the adsorption sites have positive adsorption energy and it is endothermic adsorption . In contrast to both structures, Nanotube exhibits both endothermic and exothermic adsorption. The NO_2 adsorbed at Zn site shows exothermic value and Se site shows endothermic adsorption. From the results it can be concluded that irrespective of the structure, Zn is the most favourable site compared to Se site since it has lesser adsorption energy value.

Reactivity descriptors

Reactivity descriptors of ZnSe nanostructures such as chemical hardness(η), chemical potential (μ), softness(S) and electronegativity(χ) can be calculated for pristine, NO_2 adsorption at Zn site and at the Se site for ZnSe nano structures by using the following formula[19,20]

$$\eta = (IP - EA) / 2 \quad (3)$$
$$\mu = -(IP + EA) / 2 \quad (4)$$
$$S = 1 / \eta \quad (5)$$
$$\chi = (IP + EA) / 2 \quad (6)$$

where IP and EA are the ionization potential and electron affinity of the corresponding nano structures. The reactivity descriptors for the three different ZnSe nano structures of pristine and NO_2 adsorption on Zn and Se sites are shown in table 4. The electronegativity and hardness are used to make predictions about the chemical behavior of the substance. The chemical hardness is the measure of resisitance of an atom to a charge transfer which is in this case is very high for ZnSe nanosheet structures compared to other ZnSe structures. Similarly, softness is a quantity which describes the capacity of an atom or group of atoms to receive a charge carrier[21]. From the hardness and

softness descriptors of ZnSe nano structures, it is shown that nano sheet has less probability for reacting with other molecules.

Table 4. Reactivity descriptors of ZnSe nano structures

Structure	Adsorption Site of NO_2	Hardness(η)	Chemical Potential(μ)	Softness (S)	Electronegativity(χ)
Nanosheet		1.355	-3.145	0.7380	3.145
	Zn	2.925	-3.285	0.34188	3.285
	Se	2.425	-2.875	0.4123	2.875
NanoCone		0.975	-3.675	1.0256	3.67
	Zn	1.205	-4.235	0.8298	4.23
	Se	0.755	-3.935	1.3245	3.93
NanoTube		0.285	-4.165	3.5087	4.16
	Zn	0.440	-4.580	2.2727	4.58
	Se	0.565	-4.065	1.7699	4.06

CONCLUSION

Three different ZnSe nano structures such as nanosheet, nanocone and nano tube were optimized in order to find the adsorption effect of NO2 moleule on it. From the DOS and HOMO-LUMO analysis, the observed band gap is high for pristine nanosheet (2.71eV), NO2 adosorbed at the Zn site of ZnSe(5.85eV) and NO2 adsorbed at Se site(4.85eV) of nanosheet structures compared to other two structures. When the NO2 molecule is adsorped on the nano sheet structure the band gap is increased which in turn reduces the adsorption probability for nano sheet structure compared to other two structures. This is affirmed by the studies of adsorption energy as well as the reactivity descriptors. Contrasting with nano sheet and nanotube ZnSe structures, nano tube has much sensitivity over the NO2 molecule than the nano cone ZnSe structure irrespective of the site of adsorption. This is affirmed with the investigations of adsorption vitality and also the reactivity descriptors. Contrasting and nano cone and nano tube ZnSe structures, nano tube has much sensitivity over the NO2 molecule than the nano cone ZnSe structure irrespective of the site of adsorption.

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