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DFT study of carbon monoxide adsorption on zinc oxide nanocone

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The adsorption of CO molecules on ZnO-NC is investigated using density functional theory in terms of structural, energetic and electronic properties. The results showed that when carbon monoxide approaches with its carbon atom, the adsorption energy is higher than approaching with its oxygen atom. When CO approached with its carbon atom the apex of ZnO-NC, the peak amplitude increases more than by the other adsorption modes, which clearly indicates contingency of the electron transfer from ZnO-NC to CO.

Keywords: carbon monoxide; zinc oxide; nanocones; adsorption.

INTRODUCTION

Carbon monoxide is one of the most abundant gaseous pollutants in the air that occurs primarily from emissions produced by fossil fuel powered engines and has a direct impact on human health. Therefore, many researchers have focused on the adsorption of carbon monoxide specially using DFT calculations to reduce it to a minimum [1-5]. Metal oxides at the nanoscale have high potential for a large number of processes that are important in pollution control [6-9]. ZnO is a semi-conductive metal oxide with a wide direct band gap (Eg ~3.2–3.4 eV at 300 K) and high exciton binding energy (~60 meV) [10]. Currently, numerous articles are reported to detect CO gas by various forms of ZnO such as nanowires, nanodisks, graphene-like nanorods and nanotubes [11-15]. Carbon nanocones (CNC) have attracted increasing scientific and technological interest due to their special electronic and mechanical features. These materials are useful for many research fields including gas sensor and adsorption processes [16-18]. From the literature survey it is found that no work has been reported on ZnO nanocone (ZnO-NC) as a CO sensor. Herein, we have studied the adsorption position of CO on the exterior surface of ZnO-NC using density functional theory (DFT) along with CO adsorption effects on the electronic properties of ZnO-NC.

COMPUTATIONAL DETAILS

The adsorption of CO on ZnO-NC is successfully optimized at different situations using GAMMES suite of programs [19] utilizing density functional theory (DFT) with the Beck's three parameter hybrid functional (B3) with the Lee-Yang-Parr correlation functional (LYP) called B3LYP [20]. Since the atomic numbers of zinc, oxygen, and carbon are 30, 8, and 6, respectively, LanL2DZ basis set is chosen to optimize ZnO-NC structure; furthermore Gauss sum 3.0 package is used to plot the density of states spectrum and HOMO-LUMO gap of ZnO-NC. We have determined the adsorption energy (E_{ad}) of CO gas on ZnO–NC as follows:

$$E_{ad} = E_{(ZnO/CO)} - E_{(ZnO)} - E_{(CO)}$$

where $E_{(ZnO/CO)}$, $E_{(ZnO)}$ and $E_{(CO)}$ are the total energy of CO adsorption on the ZnO-NC surface, the energy of isolated ZnO-NC and CO molecule, respectively. The negative and positive E_{ad} values indicate exothermic and endothermic specificity of adsorption.

RESULTS AND DISCUSSION

CO adsorption on the ZnO-NC

In this work a ZnO-NC consisting of eight zinc atoms and eight oxygen atoms is considered. Full geometry optimization and property calculations is performed on it in the presence of a CO molecule. In order to find the minimum energy, the CO molecule is placed at various situations on the ZnO-NC. Fig. 1a shows ZnO nanocone structure; Figs. 1b and 1c show the adsorption of carbon and oxygen atoms of the CO molecule on the oxygen and zinc atoms in the apex of ZnO-NC, respectively. Similarly, Figs. 1d and 1e show the adsorption of carbon and oxygen atoms on the oxygen and zinc atoms in the neck of ZnO-NC.

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When the carbon monoxide molecule approaches the apex of ZnO-NC with its oxygen atom, the adsorption energy is -9.54 kcal/mol, whereas it increases to -39.53 kcal/mol when the carbon atom approaches the apex of ZnO-NC. Similarly, when the monoxide molecule approaches the neck of ZnO with its oxygen and carbon atom, the adsorption energy is -6.84 kcal/mol and -29.50 kcal/mol, respectively. As shown in Table 1, when carbon monoxide approaches with its carbon atom, the absorption energy is higher than approaching with the oxygen atom. According to the achieved adsorption energies, it is clearly evident that the CO is more likely adsorbed on the apex of ZnO-NC, Table 1.

Electronic properties of ZnO-NC

In order to evaluate the effect of CO adsorption on the electronic properties of ZnO-NC, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are considered. Herein, as can be seen (Table 1), HOMO and LUMO levels for ZnO-NC are at -6.48 and -3.31 eV, respectively, with a Fermi energy level of about -4.90 eV. On the other hand, when CO approaches the apex of ZnO-NC with its carbon atom, the energy gap is 2.93. The interesting thing is that the carbon monoxide approaching the apex of ZnO-NC with its oxygen atom and that approaching the neck of ZnO-NC with its carbon atom lead to the same variation of average energy gap equal to 11.36%. The energy gap and average energy gap are listed in Table 1.

When CO approaches the apex of ZnO-NC, the Mulliken charge on the adsorbed CO is negative, which means that the CO molecule may acts as an electron acceptor-like agent, whereas approaching the neck of ZnO-NC leads to a positive charge on the CO. The charge transfer from the Zn-NC to the carbon monoxide confirms this prediction (Fig. 1b).

Table 1. Adsorption energies of CO on the ZnO-NC (Ead, kcal/mol), Mulliken charge on the adsorbed CO (Q, e), and HOMO (EHOMO), LUMO energies (ELUMO), Fermi level energies (EFL), HOMO–LUMO energy gap (Eg) and average energy gap variation in (%) of ZnO-NC in eV.

CO adsorbed on ZnO-NC	*Ead* (kcal/mol)	Q (e)	*E*HOMO	*E*FL (eV)	*E*LUMO	*Eg* (eV)	%
a	-	-	-6.48	-4.90	-3.31	3.17	-
b	-39.53	-0.14	-6.13	-4.66	-3.20	2.93	7.57
c	-9.54	0.10	-6.15	-4.74	-3.34	2.81	11.36
d	-29.50	-0.39	-6.61	-4.84	-3.08	3.53	11.36
f	-6.84	0.09	-6.38	-4.76	-3.14	3.24	2.21

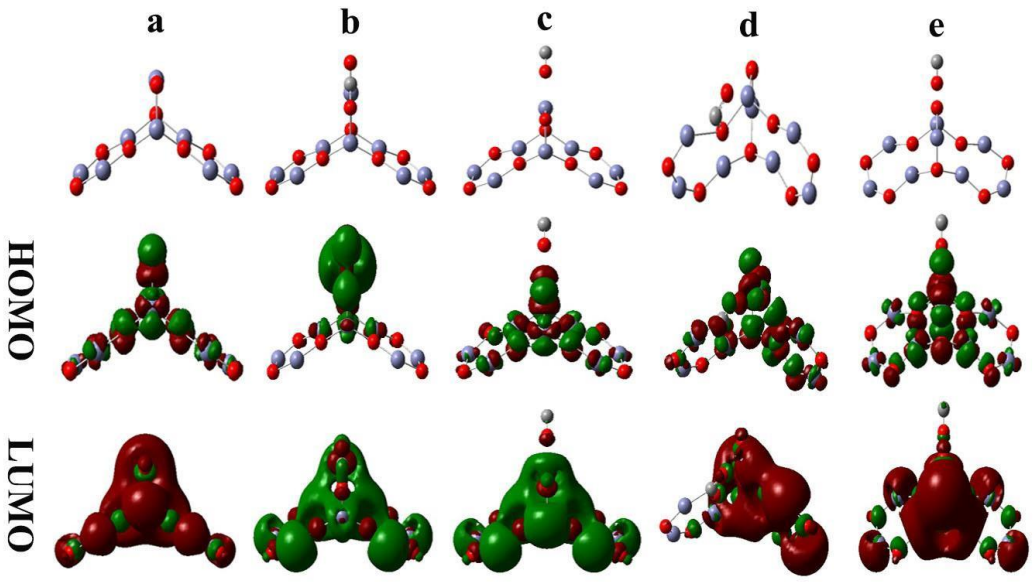

Fig. 1. HOMO–LUMO visualization of adsorbed CO on ZnO-NC: a) pure ZnO-NC b) adsorbed CO with its carbon atom on the apex of ZnO-NC c) adsorbed CO with its oxygen atom on the apex of ZnO-NC d) adsorbed CO with its carbon atom on the neck of ZnO-NC e) adsorbed CO with its oxygen atom on the neck of ZnO-NC.

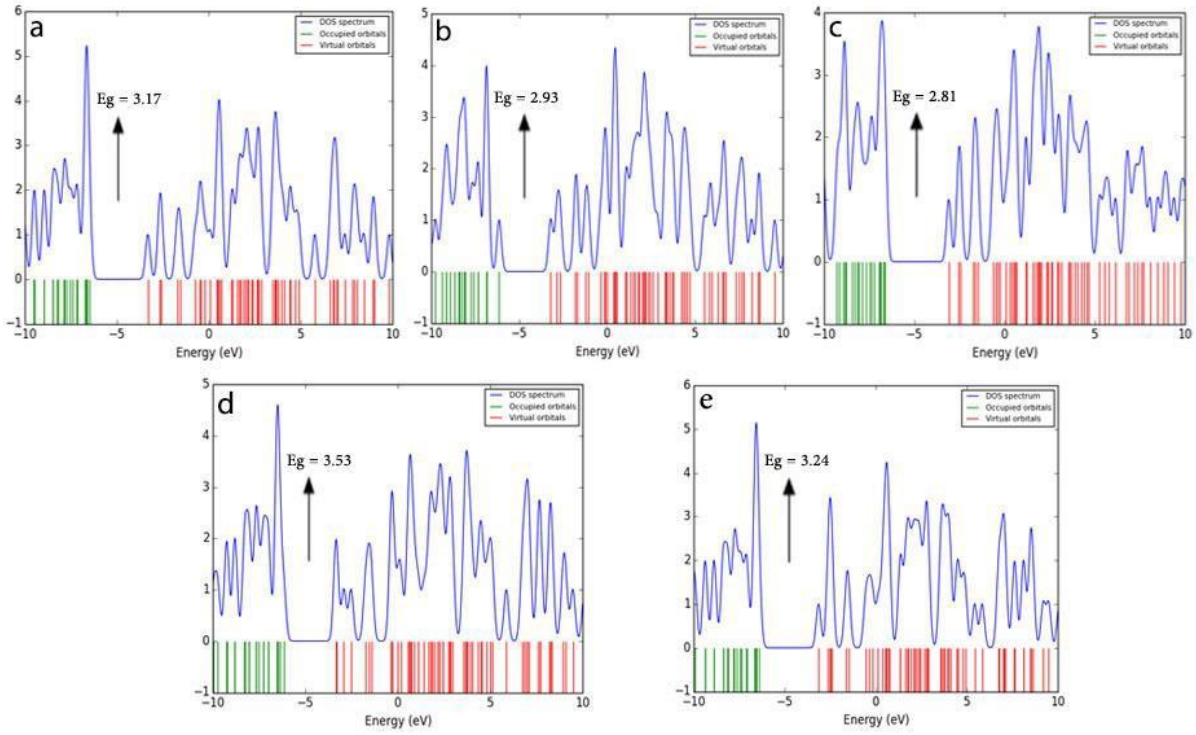

Fig. 2. HOMO–LUMO gap and DOS spectrum: a) pure ZnO-NC b) adsorbed CO with its carbon atom on the apex of ZnO-NC c) adsorbed CO with its oxygen atom on the apex of ZnO-NC d) adsorbed CO with its carbon atom on the neck of ZnO-NC e) adsorbed CO with its oxygen atom on the neck of ZnO-NC.

The density of state (DOS) of the molecule-nanocone was calculated, Fig. 2. Since the electronic configuration of zinc is $3d^{10}$ and oxygen is $2p^4$, for CO-ZnO-NC more peaks are observed in the virtual orbital than for pure ZnO-NC. Further approaching of carbon monoxide with its carbon atom to the apex of ZnO-NC increases peak amplitude more than other adsorption modes. Fig. 1b clearly reveals the fact that there is electron transfer from ZnO-NC to carbon monoxide.

CONCLUSIONS

We have explored the adsorption of a CO molecule on a ZnO nanocone (ZnO-NC) based on the DFT approach. The possible adsorption positions of CO on ZnO-NC were described in terms of HOMO-LUMO, adsorbed energy and energy gap. Mulliken charge on the CO adsorption and density of state spectrum confirmed the probability of CO absorption on the apex of ZnO-NC, it also revealed that the favored adsorption takes place between the carbon atom of CO and the oxygen atom of ZnO. So, in addition to existing structures of ZnO (nanowire, nanodisk, graphene-like, nanorod and nanotube), ZnO-NC can be a favorable structure for CO adsorption because of its excellent gas sensing properties.

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DFT- ИЗСЛЕДВАНЕ НА АДСОРБЦИЯТА НА ВЪГЛЕРОДЕН ОКСИД ВЪРХУ НАНОКОНУС ОТ ЦИНКОВ ОКСИД

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(Резюме)

Изследвана е адсорбцията на молекули от CO върху ZnO-NC с помощта на DFT–теорията. Изучени са структурните, енергетичните и електронните свойства на адсорбцията. Резултатите показаха, че когато CO-молекулата се доближава с въглеродния си атом, адсорбционната енергия е по-голяма. Когато CO-молекулата се доближава с въглеродния си атом към върха на ZnO-NC, амплитудата на пика нараства повече, отколкото при други модели на адсорбция, което говори за предимно електронен пренос от ZnO-NC към CO.