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Adsorption Properties of Oxygen on *H*-Capped (5, 5) Boron Nitride Nanotube (BNNT)- A Density Functional Theory

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Abstract: The density functional theory (DFT) has been used to simultaneously investigate physic/chemi-sorption properties of oxygen on the (5, 5) boron nitride nanotube (BNNT). Geometry optimizations were carried out at B3LYP/6-31G* level of theory using gaussian 98 suites of program. physisorption of O_2 outside the BNNT with a vertical orientation to the tube axis above a boron atom is the most stable state of physisorption and its binding energy is -0.775 kcal/mol. In the chemisorption of O_2 molecule, the most stable state is above two adjacent B and N atoms of a hexagon with a B-N bond length of 2.503 Å and the binding energy of adsorbed oxygen atoms -14.389 kcal/mol. Based on these results, We also provide the effects of O_2 adsorption on the electronic properties of BNNTs.

Keywords: Boron nitride nanotube (BNNT), Adsorption**,** DFT

Introduction

Since the discovery of carbon nanotube (CNT)[1], numerous attempts have been made to study the properties and applications of this fascinating novel material[2,3]. Recently boron nitride nanotubes (BNNTs), of which BN unit is isoelectronic to C_2 unit in CNT, have attracted increasing attention. The stability of BNNTs were predicted primarily on the basis of semi-experiential tight binding (TB)[4] and local density approximated (LDA) density functional theory[5] calculations in 1994 and their syntheses were realized in 1995 with

arc-charging method using the BN electrode packed into a metal casing[6]. At the same time, further theoretical investigations for the structures and electronic properties of BNNTs have been reported[7-8]. The group III nitrides and especially boron nitride nanotube (BNNT), which always exhibit semi conducting behavior, are considered as especial alternates of CNTs[9,10]. This behavior and also the equality of total B and N atomic number, which are the first neighbors of C in the periodic table to that of two C atoms, made BNNT as interesting subject of many studies[11-13]. Modification of the electronic properties of nanotubes by doping is an important subject for designing nano-devices based on nanotubes. The doped nanotubes can exhibit dramatic changes with respect to the undoped materials. Hence, theoretical calculations may be very useful to understand the nature of absorption and storage processes. First of all, it is most important to investigate the adsorption mechanism of oxygen on the BNNTs for its practical use. In general, adsorption of the oxygen gas on BNNTs surface first occurs as a physisorption state in which the oxygen molecule bonds with the medium surface *via* weak Vander Waals interaction. Then it is followed by the chemisorption step in which the molecule is dissociated and two oxygen atoms are chemically bonded with atoms of the BNNTs surface. Some studies have demonstrated the influence of impurities and doped atoms on the properties of the electronic structure of the BNNTs[14,15]. Adsorption of oxygen on the (5, 5) and (4, 4) CNTs were studied by Froudakis *et al.*[16]. Too Jordan and Soreseu studied[17] the adsorption of singlet and triplet states of oxygen atom and O_2 molecule on the (8, 0) CNT and Hadipour *et al* studied[18] the adsorption of O, O_2 and O_3 on the (5, 0) CNT. However, to our knowledge, the adsorption properties of oxygen on boron nitride nanotube (BNNT) have rarely been studied. Some of studies reported that the BNNTs with well-crystallized structures may be more chemical stable to oxygen than CNTs[19,20]. The high oxidation resistance in BNNTs, combined with its relative uniformity of electronic properties, may be the key advantage for the nanomaterial applications. Jun-Qian Li *et al.*[21] investigated the adsorption and reactivity on single-walled boron nitride nanotubes (10, 0), they found that O_2 prefers to physically adsorb on perfect BNNT and the electronic properties analysis indicates that chemisorbed O_2 can reduce the energy-gap of BN tubes. The present researchers, however, studied simultaneously physisorption and chemisorption properties of oxygen on the (5, 5) boron nitride nanotube (BNNT). First, the most favorable site of physisorption and chemisorptions was investigated. We also provide the effects of O_2 adsorption on the electronic properties of BNNTs.

Computational details

All calculations have been carried out by using the Gaussian 98 suite of programs[22]. The density functional theoretical method with the B_3LYP functional and the 6-31G* basis set were used for all the calculations. In the first step, boron nitride nanotube (BNNT) with chiralitie (5, 5) and length 5 Å were selected. Due to the absence of periodic boundary conditions in molecular calculations, it is necessary to saturate the B and N dangling bonds with hydrogen atoms. The hydrogenated (5, 5) boron nitride nanotube (BNNT) has 70 atoms ($B_{25}H_{20}N_{25}$). The optimized (5, 5) boron nitride nanotube (BNNT) structure has the diameter ~7.16 Å. Adsorptions energies, HOMO, LUMO and density of state (DOS) were carried out with the $B_3LYP/631G^*$.

Results and Discussion

DFT calculations on physisorption of an O_2 molecule on (5, 5) BNNT

The interaction of the O_2 molecule with the exterior and interior wall of the (5, 5) BNNT was studied by performing a single point energy (SPE) calculation for several orientations of the axis of the molecule. Three possible configurations (*i.e.,* A, B and C) were selected for the perpendicular approach of the molecule to the wall: (A) upon one boron atom, (B) upon

one nitrogen atom and (C) upon the center of a hexagon of boron nitride atoms (upon the exterior wall of the BNNT) and inside the center of a hexagon of boron nitride atoms (the interior wall of the BNNT). The three configurations are given in Figure 1.

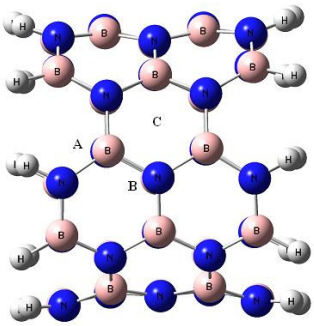


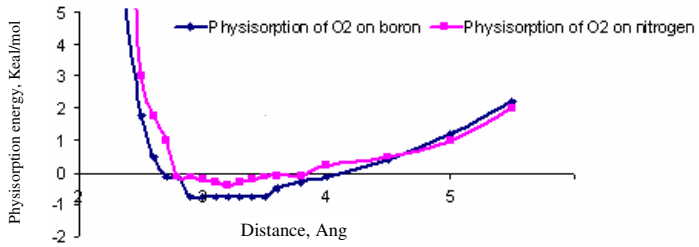
Figure 1. Atomistic configurations of physisorption with the axis of an O_2 molecule perpendicular above a boron atom on the (5, 5) BNNT (A), above a nitrogen atom (B) and exterior / interior a hexagon with a molecular axis perpendicular (C)

The physisorption energy ($E_{physisorption}$) of one O_2 molecule on the BNNT wall can be calculated as follows:

$$E_{physisorption} = E_{BNNT\text{-}O2} - (E_{BNNT} + E_{O2}) \quad (1)$$

Where, $E_{BNNT\text{-}O2}$ is the SPE of the (5, 5) BNNT-O_2 molecule structure, E_{BNNT} is the energy of the optimized BNNT structure and E_{O2} is the energy of an optimized O_2 molecule.

The physisorption energies in the three cases are plotted in Figure 2 and the physisorption energy with the equilibrium distance in each case is summarized in Table 1. From these calculations, to obtaining the physisorption energies is slightly dependent on orientations and locations of an O_2 molecule and the interaction becomes rapidly repulsive as the molecule approaches the BNNT wall. The calculated E_{ads} indicates that O_2 may be absorbed on boron and nitrogen sites with very small differences in total energy (<0.3 kcal/mol) and the calculated E_{ads} of O_2 on boron is more than those of O_2 on nitrogen. Therefore the most stable configuration of O_2 is the case A: the perpendicular approach of O_2 molecule to the (5, 5) BNNT wall on the upon one boron atom with the binding energy of -0.775 kcal/mol and an equilibrium B-O_2 bond length of 3.10 Å. The results of the present study are in complete agreement with the results of Jun-Qian Li[21]. Despite their larger calculated binding energy values, they found that for perpendicular O_2 the most favorable sites that oxygen interacts with a BNNT are on the upon one boron atom with the binding energy of -0.694 kcal/mol and an equilibrium B-O_2 bond length of 3.25 Å. The calculated adsorption energies of O_2 on the perfect BNNTs are obviously lower than those on CNTs[23], being consisted with the experiment result of that BNNTs may be more chemical stable to oxygen than CNTs[24].



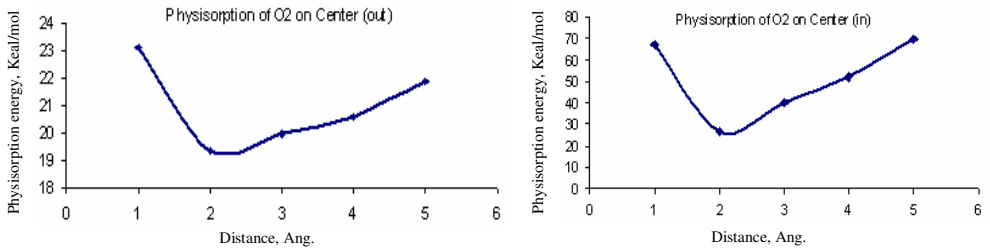


Figure 2. Interaction energy curves of an O_2 molecule physisorbed on the (5, 5) BNNT, obtained by the SPE calculation in which the O=O and all the B-N bond lengths are kept frozen and only the distance between the molecule and the nanotube axis is varied.

Table 1. Physisorption energy (kcal/mol) and equilibrium distance (Å) (rd) of an O_2 molecule on the (5, 5) BNNT.

	A	B	C exterior	C interior
Physisorption energy, kcal/mol	-0.775	-0.400	19.322	26.419
Distance from the BNNT (Å)	3.10	3.20	2.10	-2.10

DFT calculations on chemisorption of O_2 molecule on (5, 5) BNNT

Like the physisorption of an O_2 molecule, the chemisorption energy of an O_2 molecule on the BNNT wall is defined as follows:

$$E_{chemisorption} = E_{BNNT\text{-}O2} - (E_{BNNT} + E_{O2}) \quad (2)$$

Where $E_{BNNT\text{-}O2}$, E_{BNNT} and E_{O2} are the total energies of the fully optimized BNNT-O_2 structure, nanotube alone and oxygen molecule, respectively. According to this definition, a stable system has a negative binding energy. For the adsorption of individual O_2 on BNNT (5, 5), we considered four possible sites (*i.e.*, the A site above the two adjacent boron and nitrogen atoms, the B site above the two opposite boron and nitrogen atoms, the C site above the two boron atoms, and the D site above the two nitrogen atoms) as described in Figure 3. In this states, parallel bonding geometries of O_2 adsorbed on BNNT surface are considered.

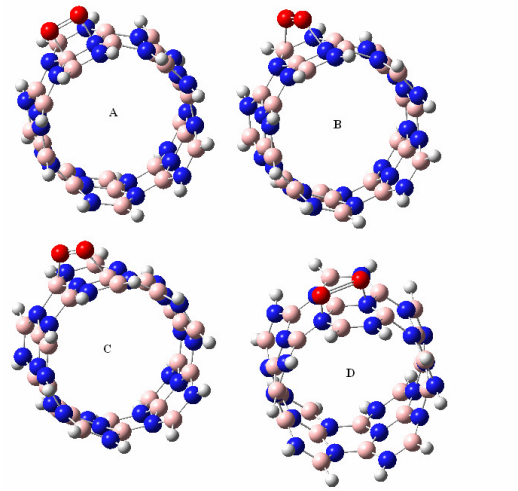


Figure 3. Four chemisorption states of an O_2 molecule on the wall of the (5, 5) BNNT

After structural relaxation, we found the adsorption of O_2 molecule at A site is the most stable with the binding energy of -14.389 kcal/mol. This value is more stable than case B, C and D of (5, 5) BNNT. This isn't probably very surprising, since bonding to adjacent boron and nitrogen atoms would imply a loss of one B-N π bond, while the case (B ,C) or (D) with a gap of one or two boron and nitrogen atom(s) would have greater disruption of the B–N π system. These results show that the energy for binding an O_2 molecule to a BNNT depends on its adsorption site. Too the newly formed B-O and N-O bond lengths are 1.42 and 1.39 Å, respectively. This result is consistent with an observation of Jun-Qian Li[21] in that the B-O bond length is 1.44 Å. The chemisorption of oxygen on the BNNT enables the sp2 hybridization of the B-N bond in the BNNT wall to change into the sp3 hybridization; hence, the B-N bond length increases. The strong chemical interaction elongates the distance of O–O from 1.22 Å to 1.49 Å longer than an adjacent B-N bond length of 1.42 Å to minimize the O=O repulsion.

Electronic properties

Finally, we studied the influence of O_2 molecule adsorptions on the electronic properties of BNNT. The calculated band-gap of the clean perfect (5, 5) BNNT is about 5.42 eV[25] but the calculated band gap of the hydrogenated (5, 5) boron nitride nanotube ($B_{25}H_{20}N_{25}$) is 6.31 eV. The effects of oxygen molecule on adsorptions energies in BNNTs relate to their electronic structure. When oxegen molecule physically is adsorbed on the BNNTs, the interaction of them becomes very weak and the electronic properties of these tubes are not changed obviously. When oxygen molecule chemically adsorb on the BNNTs, the interaction of them is not noticeable; the electronic properties of these tubes are changed obviously. In this study, the presence oxygen molecule slightly reduces the energy gap of pristine (5, 5) BNNT and the band gap is calculated 5.25 eV. For these systems, significant changes in the DOS are not observed near the Fermi level. However, the adsorption of oxygen molecule chemically reduces the band gap and increases the electrical conductance of the (5, 5) BNNT.

Conclusion

We have theoretically studied the adsorptions, both physisorption and chemisorption of oxygen on the (5, 5) BNNT through the DFT calculations. Our results indicate that the interaction of O_2 with the (5, 5) BNNT belongs to weak physisorption. The results confirm the experimental facts that the (5, 5) BNNT structures have strong resistance to oxidation. In this study, the presence of O_2 molecule slightly reduces the energy gap of pristine (5, 5) BNNT and increases the electrical conductance of the (5, 5) BNNT.

References

1 Ijima S, *Nature*, 1991, **354**, 56-58.
2 Zurek E and Autschbach J, *J Am Chem Soc.,* 2004, **126**, 13079-13088.
3 Nojeh A, Lakatos G W, Peng S, Cho K and Pease R F W, *Nano Lett.,* 2003, **3(9)**, 1187-1190.
4 Rubio A, Corkill J L and Cohen M L, *Phys Rev., B*1994, **49** ,5081.
5 Blase X, Rubio A G, Louie S and Cohen M L, *Eruophys Lett.,* 1994, **28**, 335.
6 Chopra N G, Luyken R J, Cherrey K, Crespi V H, Cohen M L, Louie S G and Zettl A, *Sci.,* 1995, **269**, 966.
7 Rubio A, Miyamoto Y, Blase X, Cohen M L and Louie S G, *Phys Rev B.,* 1996**, 53**, 4023.

8 Zhang P and Crespi W H, *Phys Rev B,* 2000, **62**, 11050.
9 Zhang D and Zhang R Q, *Chem Phys Lett.,* 2003, **371**, 426-432.
10 Mirzaei M and Hadipour N L, *Physica E.,* 2008, **40**, 800-804.
11 Hou S, Shen Z, Zhang J, Zhao X and Xue Z, *Chem Phys Lett.,* 2004, **393**, 179.
12 Zhang M, Su Z M, Yan L K, Qiu Y Q, Chen G H and Wang R S, *Chem Phys Lett.,* 2005, **408** 145.
13 Erkoc S, *J Mol Struct (Theochem)*, 2001, **542,** 89.
14 Mirzaei M, *Physica E.,* 2009, **41**, 883-885.
15 Mirzaei M, *Monatsh Chemie.,* 2009, **140**, 1275.
16 Froudakis G E, Schnell M, Muhlhaeser M, Peyerimhoff S D, AndriotisA N, Menon M and Sheetz R M, *Phys Rev B,* 2003, **68,** 115435.
17 Sorescu D C, Jordan K D and Avouris P, *J Phys Chem B,* 2001, **105,** 11227.
18 Rabee Khorrampour M, Esrafili D and Hadipour N L, *Physica E.,* 2009, **41(8),** 1373-1378.
19 Tang C C and Bando Y, *Appl Phys Lett.,* 2003, **83,** 659-661.
20 Ma R, Golberg D, Bando Y and Sasaki T, *Phil Trans Roy Soc A,* 2004, **362**, 2161.
21 Chen Y, Hu C L, Li J Q, Jia G X and Zhang Y F, *Chem Physics Lett.,* 2007, **449,**149.
22 Frisch M J, Trucks G W, Schlegel H B, Scuseria G E, Robb M A, Cheese- man J R, Zakrzewski V G, Montgomery Jr J A, Stratmann R.E, Burant J C, Dapprich S, Millam J M, Daniels A D, Kudin K N, Strain M C, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson G A, Ayala P Y, Cui Q, Morokuma K, Malick D K, Rabuck A D, Raghavachari K, Foresman J B, Cioslowski J, Ortiz J V, Baboul A G, Stefanov B B, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin R L, Fox D J, Keith T, Al-Laham M A., Peng C Y, Nanayakkara A, Gonzalez C, Challacombe M, Gill P M W, Johnson B, Chen W, Wong M W, Andres J L, Gonzalez C, Head-Gordon M, Replogle E S and Pople J.A., GAUSSIAN 98, Gaussian, Inc, Pittsburgh, PA, 1998.
23 Ricca A and Bauschlicher C W, *Phys Rev B,* 2003, **68**, 035433.
24 Wu X J, Yang J L, Hou J G and Zhu Q S, *J Chem Phys.,* 2006, **124**, 054706.
25 Jia J F, Wu H S and Jiao H, *Physica B,* 2006, **381**, 90.