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# Adsorption Study $H_2$and COGases on the Surface of Boron Nitride Nanotube (4, 4) by DFT Calculations

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***Abstract:*** We studied gases molecules $H_2$ and CO on single walled boron nitride nanotube and bundles using Density Functional Theory (DFT). Equilibrium position, adsorption energy and charge transfer are obtained for boron nitride nanotube armchair (4, 4). Both molecules adsorb weakly on nanotube single-walled and can be either charge donors to the nanotube. We find that the CO gas adsorption on the surface of tube is stronger than $H_2$gas. The CO gas adsorption is seen on the all of the sites but the $H_2$ gas adsorption is seen above top N and top B sites.

***Key words:*** DFT, B3LYP, 6-31G, Basis set

## 1. INTRODUCTION

All Density Functional Theory (DFT) quantum calculationsare performed using Gaussian 2009 program package onstructure of (4, 4) single-walled armchair boron-nitridenanotube, 1 nm length consisting 36 B and 36 N atoms as an exemplary ofarmchairnanotubes (Fig. 1). As we mentioned in introduction, close resemblance between boron-nitride nanotubes and carbon nanotubes is that the sum of atomic number of one boron atom and one nitrogen atom is equal to two carbon atomic number sum and hence frequently, the number of boron and nitrogen atom nuclei in boron-nitride nanotube are the same as we presented an example of it in this research. But main difference between boron and nitrogen atoms is presence of nonbonding electron pair in nitrogen valence shell but boron atom has valence shell electron lack. However the binding energy of hydrogen on boron nitride nanotubes is increased by as much as %40 compared to that on carbon nanotubes [1]. This important factor gives boron atom rather acidic property and nitrogen rather basic property and consequently causes the nuclei different behaviors in the boron-nitride nanotube [2]. Hydrogen is attractive as a fuel because its use creates neither air pollution nor greenhouse-gas emissions [3–5]. The use of hydrogen requires an effective, safe, and stable storage medium. However, how to store hydrogen easily and cheaply is still a big and challenging problem [6, 7].

Hydrogen is an ideal material as an alternative energy source. Gas adsorption in boronnitride nanotube and nanotube bundles is an important issue for both fundamental researchand technical application of nanotubes. Considerable experimental andtheoretical efforts have been devoted to hydrogen storagein nanotubebased materials. The effects of gas environment on the electronic properties of boron nitride nanotubes have recently attracted certain attentions [8]. Calculated isotropic chemical shielding for different boron and nitrogen nuclei shows that nanotube various positions do not represent similar structures and there is not a totally homogenous electrostatic environment in nanotube albeit there is thoroughly similar properties in totally symmetrical positions [2].

## 2. COMPUTATIONAL METHODS

The self-consistentfield (SCF) electronic structure calculation isperformed based on density functional theory (DFT). Basedupon the structure first optimized withBecke3, Lee-Yang-Parr (B3LYP) method and6-

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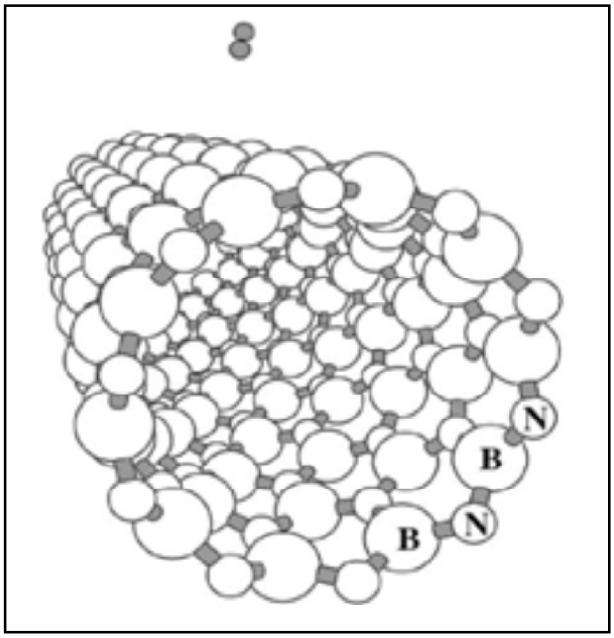


**Figure 1: BN nanotube and $H_2$ molecule above BN**

31G basisset. The equilibrium geometry, adsorption energy and charge transfer are calculated by using the B3LYP method and 6-31G basis set. We find that both the equilibrium distance and the adsorption energy are well reproduced byour present DFT scheme. In order to investigate the binding of hydrogen or carbon mono oxide on BN nanotube we perform a series of total energy calculations using density functional methods.

## 3. THEORY

The adsorption of carbon mono oxide (CO) gas on $SWNT_{BN\ (4,\ 4)}$ at room temperature is investigated by DFT calculations. In this investigation we report first principles calculations on individual SWNT and tube bundles with adsorption of variety of gas molecules including CO and $H_2$. These observations indicate that hydrogen adsorption on BN nanotubes can be significantly different from that on carbon nanotubes. Boron nitride nanotubes have the same nanostructure as carbon nanotubes but are found to exhibit significant resistance to oxidation at high temperatures. Our systematic study has revealed that BN nanotubes are stable at 700 °C in air and that some thin nanotubes diameter less than 20 nm with perfect multiwall cylindrical structure can survive up to 900 °C. Thermo gravimetric analysis reveals an onset temperature for oxidation of BN nanotubes of 800 °C compared with only 400 °C for carbon nanotubes under the same conditions. This more pronounced resistance of BN nanotubes to oxidation is inherited from the hexagonal BN and also depends on the nanocrystalline structure. This high level of resistance to oxidation allows promising BN nanotube applications at high temperatures [9].

## 4. RESULTS AND DISCUSSION

We have shown through computational simulations thatBN (4, 4) can be good hydrogen storage medium. Our studyalsoshows that a deviation from $sp^2$ bonding tends to increase thebinding energy of hydrogen in BN (4, 4). Thisstudy suggests that asystematic increase of binding energy of hydrogen can beachieved for $sp^2$-like bonding nanostructure materials bymodifying the $sp^2$ bonding. Similar effects are also observedfor carbon nanotubes [1]. Weobtained the gas molecule ondifferent sites of nanotube (Hc: hexagoncenter, Br: bridge bundle BN, TB: on top of the boron atom and TN: on top of the nitrogen atom)**.**Q (e)is charge transfer from molecule to the tube and Table 3 aresummarizes our results on theequilibrium tube-molecule

distance, adsorption energyandcharge transfer for $H_2$ (table 1) and CO molecules (table 2) on $SWNT_{BN\,(4,\,4)}$. In general these gas molecules are weakly banded to the nanotube and the tube-molecule interaction can be identified as physisorption. $H_2$ molecule is charge donor or acceptor with small charge transfer (+0.0015~-0.002 electron per molecule) and weak binding (<0.24eV). For CO which is charge donor the charge transfer isnot negligible. This is also reflected intheir largeradsorption energies.Both the gasses have larger adsorption energies in the state vertical on the top of the boron atom (TB). But no substantial electron density overlap is found in the region between the gas molecule and nanotube, indicating that no chemical bond is formed. The binding curve for CO and $H_2$ molecules adsorbed on $SWNT_{BN\,(4,\,4)}$are shown in figures 2 and 3.

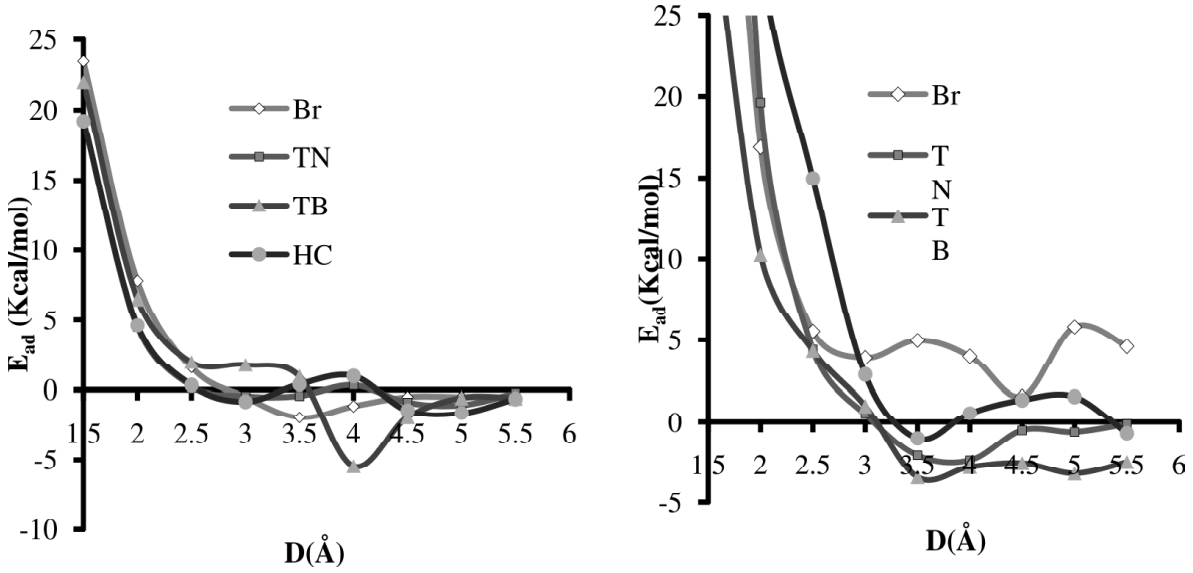


**Figure 2: Adsorption energy (Kcal/mol) as function of tube-molecule distance (Å) for $H_2$ gas (left vertical state andright horizontal state) on the BN (4, 4)**

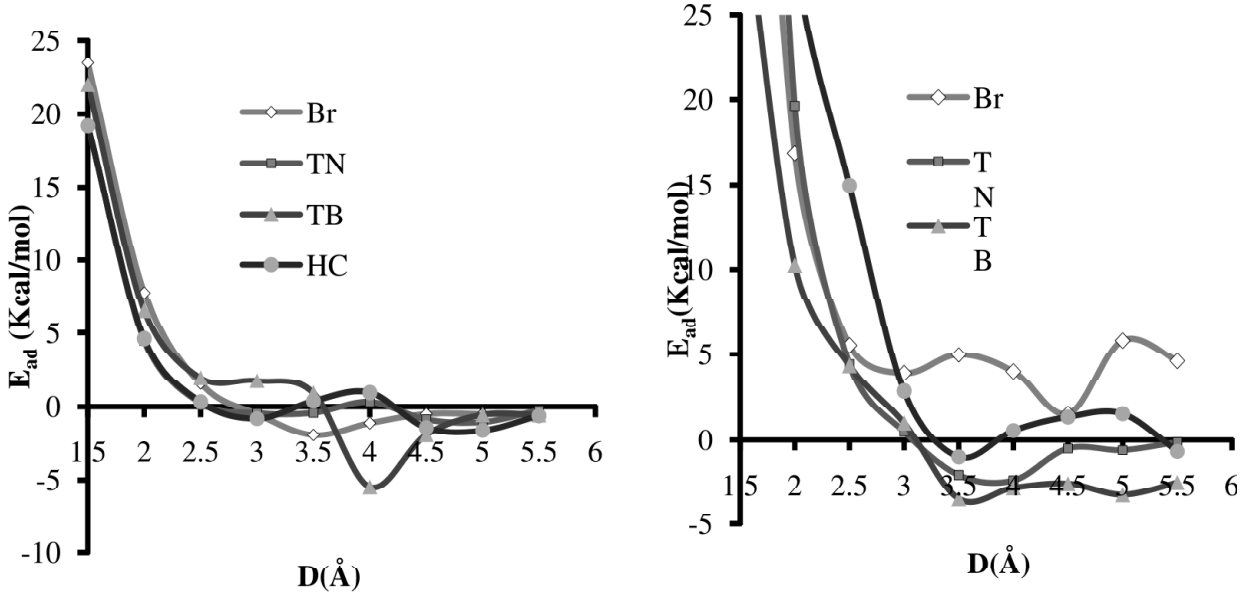


**Figure 3: Adsorption energy (Kcal/mol) as function of tube-molecule distance (Å) for CO gas (left vertical state and right horizontal state) on the BN (4, 4)**

**Table 1**
**Adsorption energy (Kcal/mol) for $H_2$ gas (vertical state andhorizontal state) on the BN (4, 4)**

**$H_2$ - Horizontal**

| | *D(Å)* | *1.5* | *2* | *2.5* | *3* | *3.5* | *4* | *4.5* | *5* | *5.5* | *6* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $E_{ad}$(Kcal/mol) | Br | 61.79 | 16.85 | 5.53 | 3.91 | 4.97 | 4.00 | 1.55 | 5.80 | 4.60 | 1.55 |
| | TN | 84.73 | 19.63 | 4.41 | 0.50 | -2.05 | -2.36 | -0.50 | -0.60 | -0.12 | -0.50 |
| | TB | 33.36 | 10.25 | 4.35 | 1.00 | -3.42 | -2.79 | -2.55 | -3.19 | -2.48 | -2.44 |
| | Hc | 53.49 | 28.14 | 14.97 | 2.85 | -1.00 | 0.56 | 1.36 | 1.55 | -0.68 | -0.68 |

**$H_2$ - Vertical**

| | *D(Å)* | *1.5* | *2* | *2.5* | *3* | *3.5* | *4* | *4.5* | *5* | *5.5* |
|---|---|---|---|---|---|---|---|---|---|---|
| $E_{ad}$(Kcal/mol) | Br | 23.48 | 7.80 | 1.55 | -0.50 | -1.93 | 1.12- | -0.50 | -0.50 | -0.50 |
| | TN | 19.20 | 4.47 | 0.25 | -0.44 | -0.42 | -0.31 | -0.87 | -1.05 | -0.25 |
| | TB | 22.00 | 6.52 | 1.93 | 1.74 | 0.90 | -5.46 | 1.92 | -0.56 | -0.56 |
| | Hc | 19.20 | 4.60 | 0.31 | -0.81 | 0.37 | 0.93 | -1.43 | -1.62 | -0.62 |

**Table 2**
**Adsorption energy (Kcal/mol) for CO gas (vertical state andhorizontal state) on the BN (4, 4)**

CO - Horizontal

| | *D(Å)* | *1.5* | *2* | *2.5* | *3* | *3.5* | *4* | *4.5* | *5* | *5.5* |
|---|---|---|---|---|---|---|---|---|---|---|
| $E_{ad}$(Kcal/mol) | Br | 316.72 | 88.85 | 19.28 | 2.25 | -2.22 | -1.10 | -0.42 | -0.48 | -0.42 |
| | TN | 258.20 | 91.03 | 3.00 | -1.60 | -1.35 | -1.10 | -0.73 | -0.66 | -0.66 |
| | TB | 156.38 | 40.33 | 8.16 | 1.96 | -0.29 | 0.95 | 0.64 | 0.95 | 0.70 |
| | Hc | 150.32 | 37.35 | 2.56 | -2.53 | -4.08 | -0.79 | -0.29 | 0.45 | 0.57 |

CO - Vertical

| | *D(Å)* | *1.5* | *2* | *2.5* | *3* | *3.5* | *4* | *4.5* | *5* | *5.5* |
|---|---|---|---|---|---|---|---|---|---|---|
| Ead(Kcal/mol) | Br | 112.20 | 28.16 | 3.31 | -1.35 | -0.73 | -4.64 | -0.79 | -0.79 | -0.79 |
| | TN | 175.32 | 35.30 | 4.62 | -0.23 | -1.22 | -1.04 | -0.91 | -0.85 | -0.85 |
| | TB | 52.45 | 11.57 | -6.32 | -1.91 | -1.66 | -1.16 | -0.85 | -0.71 | -0.60 |
| | Hc | 60.32 | 13.75 | 1.32 | -2.84 | -0.19 | -0.20 | 0.44 | 0.36 | 0.42 |

**Table 3**
**Equilibrium tube-molecule distance (D), adsorption energy ($E_{ad}$) and charge transfer (Q) of molecules $H_2$ and CO to the BN (4, 4) individual SWNT. Results are given for the sites: TB (top of the boron atom), TN (top of the nitrogen atom), Br (top of the center BN bond), Hc (top of the center BN hexagon) and state gas molecule: H (horizontal) and V (vertical)**

| *Site* | *TB* | | *TN* | | *Hc* | | *Br* | |
|---|---|---|---|---|---|---|---|---|
| *State* | *H* | *V* | *H* | *V* | *H* | *V* | *H* | *V* |
| CO | | | | | | | | |
| D(Å) | 3.5 | 2.5 | 3 | 3.5 | 3.5 | 3 | 3.5 | 4 |
| $E_{ad}$(meV) | -12.6 | -274.0 | -69.4 | -52.9 | -177.0 | -123.1 | -96.2 | -201.2 |
| Q(e) | -0.009 | -0.019 | -0.008 | -0.004 | -0.008 | -0.014 | -0.01 | -0.002 |
| $H_2$ | | | | | | | | |
| D(Å) | 3.5 | 4 | 4 | 5 | 3.5 | 5 | 4.5 | 3.5 |
| $E_{ad}$(meV) | -148.0 | -236.7 | -102.3 | -45.5 | -43.6 | -70.2 | +67.2 | -83.6 |
| Q(e) | -0.002 | >+0.0001 | -0.0004 | +0.0001> | -0.001 | +0.0001> | -0.002 | +0.0015 |

The given numbers for D is the distance between center of the site (TB,TN,Hc, and Br) and center of the bond gasmolecule in the horizontal form or center of the nearest atom gas molecule to tube in the vertical form. The adsorption energy $E_{ad}$is defined as thetotal energy gained by molecule adsorption at equilibrium distance: $E_{ad}= E_{tot}$ (tube ~ molecule) – E (tube) – E (molecule).

## 5. CONCLUSIONS

Both molecules are weakly adsorbed on $SWNT_{BN\ (4,\ 4)}$with small charge transfer, while they can be either a charge donor to the nanotube.The adsorption of some gas molecules on $SWNT_{BN}$can cause a significant change in electronic and transport properties of the nanotube due to the charge transfer and charge fluctuation. The molecule adsorption on top of the boron atom and surface of the nanotube bundle is stronger that on the other sites. The adsorption Co gas molecule is stronger than $H_2$ molecule and adsorption seen on the all of the sites. But for $H_2$ adsorption on the Br and HC sites is very weakly and charge transfer is from nanotube to the hydrogen molecule.

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