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Research Article

ADSORPTION OF PYRIDINE BY USING BN NANOTUBE: A DFT STUDY

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ABSTRACT
Electrical sensitivity of a boron nitride nanotube (BNNT) was examined toward C_5H_5N molecules by using Density Functional Theory (DFT) calculations at the B3LYP/6-31G(d) level, and it was founding that the adsorption energy(E_{ad}) of pyridine on the pristine nanotube is about 17.0 kcal/mol, but when nanotube has been doped with Si and Al atoms, the adsorption energy(E_{ad}) and recovery time changed and the sensitivity of the nanotube as adsorbent of C_5H_5N molecule was increased. Calculations showed that when the nanotube is doping by Si, the adsorption energy is about -10.6kcal/mol and also the amount of HOMO/LUMO energy gap (E_g) will reduce significantly. Therefore when C_5H_5N molecule adsorption toward to BNNT, the nanotube has produced electrical signals and it seems the BNNT can be used as adsorbents for the sensors which are sensitive about C_5H_5N molecule.

Keywords: *Sensor, Nanotube, DFT*

INTRODUCTION
Pyridine or C_5H_5N is a suitable material to applying for fuel, medicine and dyes (Henry, 2004; Lataye *et al.*, 2006). Pyridine is a toxic liquid and its vapor has undesirable effect on the skin and eyes and also especially is an intense irritant for eyes that the exposure of it causes depression and can have serious health consequences for people (Mohan *et al.*, 2004). Boron nitride nanotubes (BNNTs) have particular and unique properties and also have a semiconductor behavior. This behavior reason is the total atomic number of B and N (Hou *et al.*, 2004; Zhang *et al.*, 2005; Erkoc, 2001). That an interesting case for studying about these BNNTs is investigating, they composite types (Chopra, 1995; Golberg *et al.*, 1999; Tang *et al.*, 2002). Recently carbon nanotubes (CNTs) have emerged as promising alternative for hydrogen storage, gas sensors and others (Fam *et al.*, 2011; Cabria *et al.*, 2006). BNNT has different electronic properties by comparing with the CNT [17], BNNT has a much wider energy, small band gap and finally it is a semiconductor which is a very interesting material for applicative in nanoscale devices (Dresselhaus *et al.*, 1996). Modifying electronic properties of nanotube is an important issue for designing nanao base in nano instruments. BNNT has composed by a single layer rotation of sp^2. BNNT's unique properties including tensile strength, stiffness and deformation are the feature of this nanotube (Rubio *et al.*, 1994; Ouyang *et al.*, 2002; Kane and Mele, 1997). Spiral structure around the pipe can cause the superconducting, conductors, semiconductors or insulators properties. In this study, the adsorption of pyridine on the pristine case BNNT while Al and Si atoms are in its structure has been investigated. Previous time Dr.Baei had studied pyridine adsorption on $B_{12}N_{12}$ nano-cage (Baei, 2013), but by comparing the results it has proved that BNNT is better to be as an adsorbent for pyridine.

MATERIALS AND METHODS
Computation procedures include the following:
We've optimized the pyridine molecule and BNNT at the B3LYP/ 6-31G (d) level of theory. Boron nitride nanotube (BNNT) which is made up of 30 N and 30 B atoms was saturated by 10 hydrogen atoms which are in initial and end part of annotate. The reason for this act had been done to decrease the

boundary effects and totally nanotube is involving 70 atoms (Figure 1). The BNNT that has been selected is zigzag (5, 0) type and GAMESS software is used to perform these calculations. B3LYP has been shown to be safe and reliable command line that usually used and studied for various nanostructures. We made pyridine molecule from different positions of the site to be close to the nanotube and it's adsorption has been calculated by using the equation [1].

$E_{ad}= E_{Nanotube + pyridine} - [E_{pyridine} + E_{Nanotube}] +\delta_{BSSE}$ [1]

According to the mentioned equation $E_{pyridine}$ is pyridine molecule's energy, $E_{nanotub}$ is the nanotube energy and $E_{Nanotube + pyridine}$ is the nanotybe's energy with pyridine. In addition, δ_{BSSE} is representing the basis set super position error. In the following steps Si and Al atoms in the nanotube structure have been doped to examine the pyridine adsorption on the nanotube which is doping with Si and Al atoms.

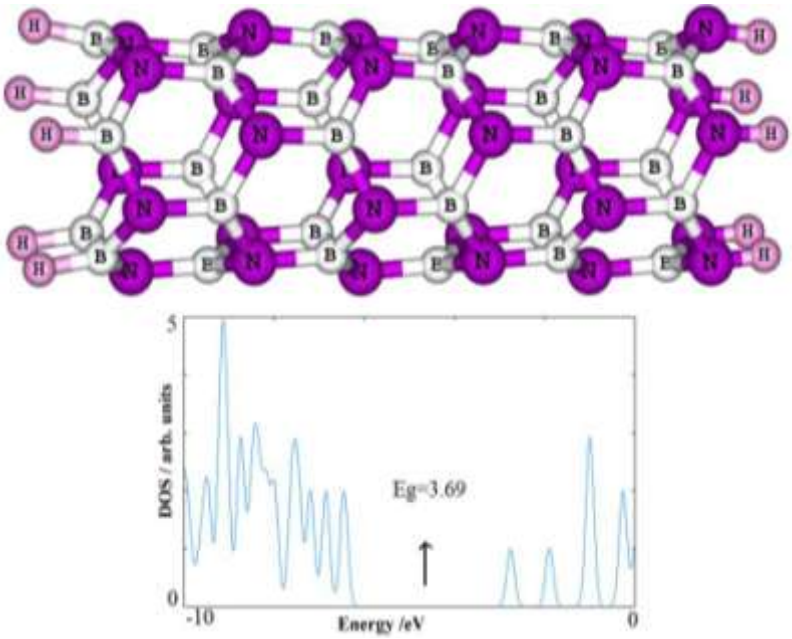

Figure 1: Pyridine adsorption on the BNNT and DOS diagram for observing E_g of Nanotube

RESULTS AND DISCUSSION

Figure 1 is showing the structure of boron nitride nanotube (BNNT), in order to obtain the most stable adsorption mode of C_5H_5N molecule on different positions of BNNT, the most stable configuration has shown in Figure 2, that nitrogen atoms of pyridine is 1.68A° far from boron atom of the nanotube. Detailed information of the structure and electronic properties of BNNT including E_{ad} has been shown in Table 1. That the adsorption energy for mentioned configuration of pyridine and nanaotube is -17.0 kcal/mol. The HOMO/LUMO energy gap (E_g) has been calculated (Table 1). and the diagram which shows E_g has been obtained by using DOS(density of state) software.

Table 1: E_{ad} (kcal/mol), eV for the others

System	E_{ad}	E_{HOMO}	E_{LUMO}	E_g	$^*\Delta E_g$(%)
BNNT	-	-6.45	-2.76	3.69	-
Pyr-BNNT	-17.0	-6.00	-2.33	3.67	+0.01
Si_N	-	-6.06	-3.51	2.55	-
Si_N-p	-10.6	-3.23	-2.61	0.62	-75.6
Si_B	-	-5.73	-2.95	2.78	-
Si_B-p	-25.7	-3.21	-2.66	0.55	-80.2
Al_N	-	-5.54	-3.00	2.54	-
Al_N-p	-40.0	-5.38	-2.56	2.82	+11.0
Al_B	-	-6.41	-2.67	3.74	-
Al_B-p	-43.8	-5.97	-2.64	3.33	-10.9

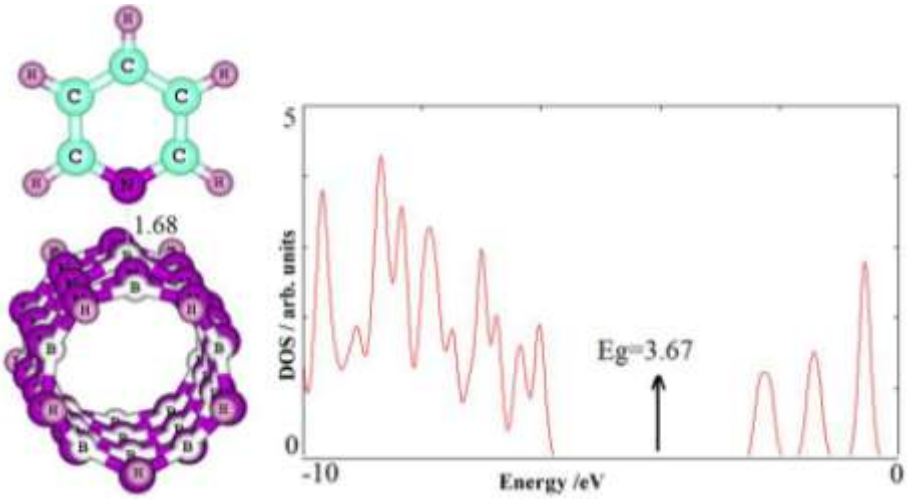

Figure 2: pyridine adsorption on the BNNT and DOS diagram for observing E_g of Nanotube

Adsorption of C_5H_5N on Al-doped BNNT:

To examine the sensitivity of the adsorption of boron nitride nanotube of pyridine as an adsorbent for pyridine it examining has done tow times, once B atom doped by Al atom and other time N atoms by Al has been doped. Doped calculation of Al on BNNT shows that the value of E_g is less than the pristine nanotube (Figure 3) and the best adsorption energy (E_{ad}) is when Al sitting instead of B and pyridine has been absorbed. DOS diagram clearly shows that when Al is doped on BNNT it will become a semiconductor, Then the investigation of C_5H_5N adsorption for doped Al on boron nitride nanotube from nitrogen side of pyridine has been studied (Figure 4). Optimization of these type of interactions is desirable for gas detection because such strong interactions means that the BNNT is a suitable absorbent for pyridine molecule. If E_{ad} is significantly increased then it expect that recovery time will be so long, meanwhile according to transition state theory and recovery time can be explain as equation 2.

$\tau = \upsilon_0^{-1} \exp(-E_{ad}/kT)$ [2]

That in this equation τ represents the recovery time, T is temperature, k is Boltzman constant and υ_0 is attempt frequency. According to this equation as often as adsorption energy is increasing the recovery time becomes longer and computation in Table show that the recovery time and adsorption energy is in suitable level. After computations we got it that when Al is sitting instead of N on BNNT the HOMO/LUMO energy gap will decrease (Figure 4).

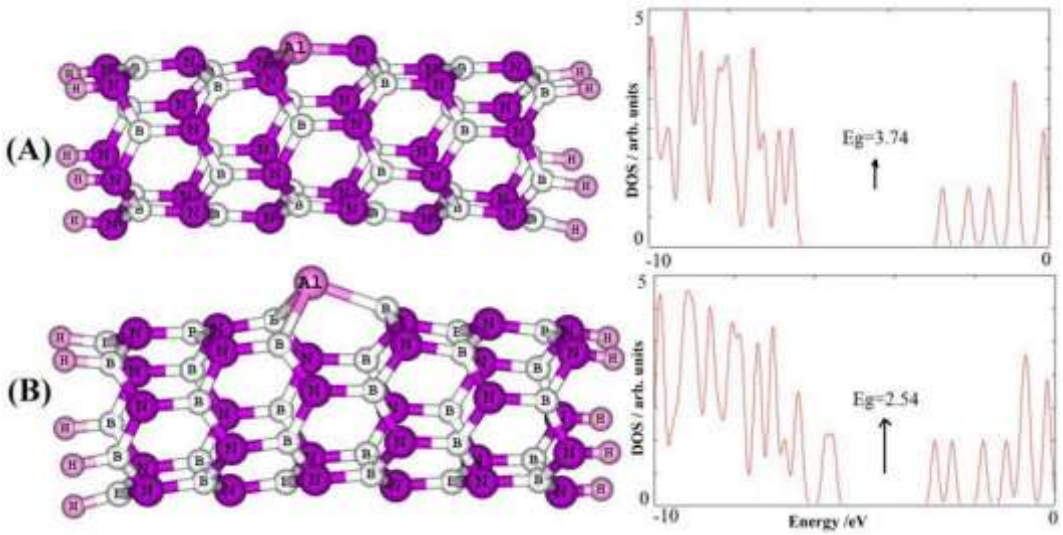

Figure 3: Doped nanotube by Al and DOS diagram for observing E_g nanotube

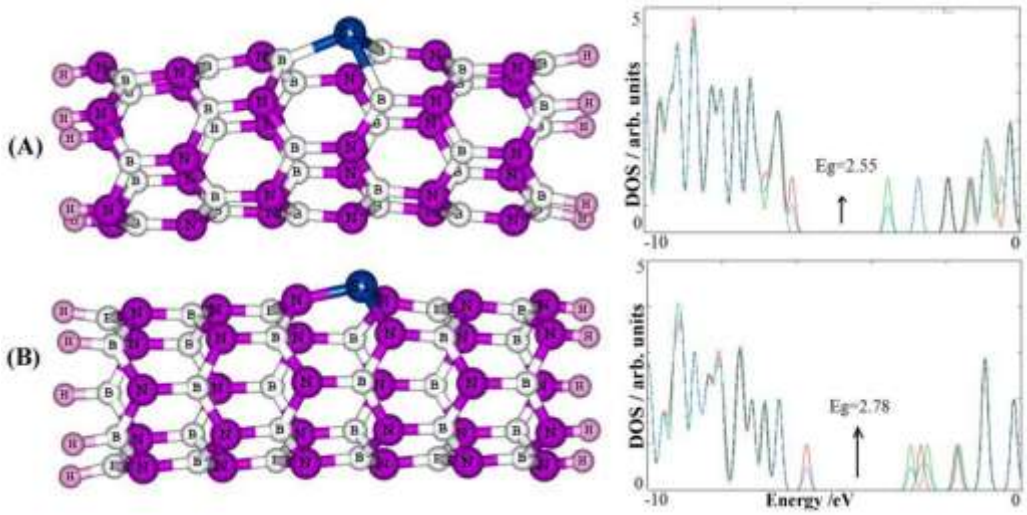

Figure 4: Doped nanotube by Si and DOS diagram for observing E_g nanotube

Adsorption of C_5H_5N on Si-doped BNNT:

At this stage doping of nanotube have been studied with another element. First, instead of B atom in the boron nitride nanotube a Si atom and then instead of N atom a Si atom replaced in a nanotube (Figure 5), and then geometrical structures and electronic properties of BNNT has been doped and its adsorption behavior have been studied. Computations showed that when Si replaced by N in BNNT the E_g will become less (Figure 6).

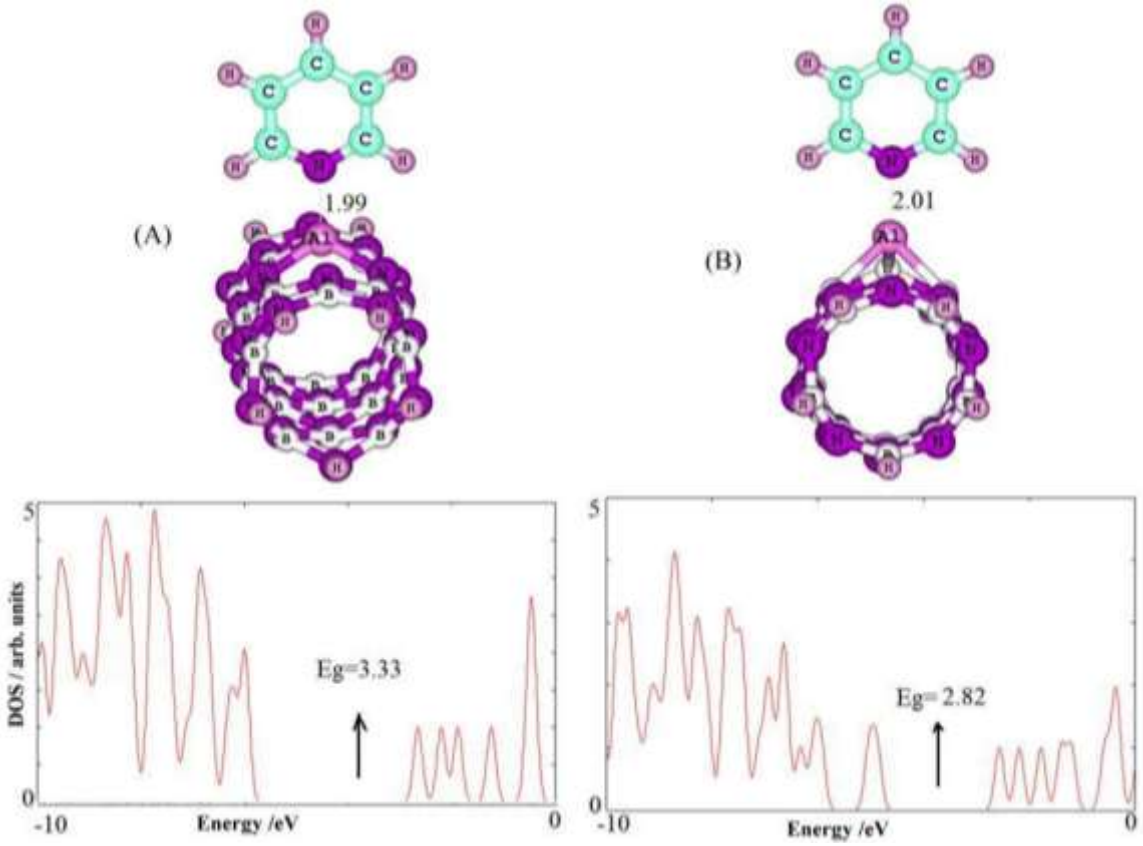

Figure 5: pyridine molecule adsorption by the Al doped nanotube and DOS diagram for observing E_g of nanotube

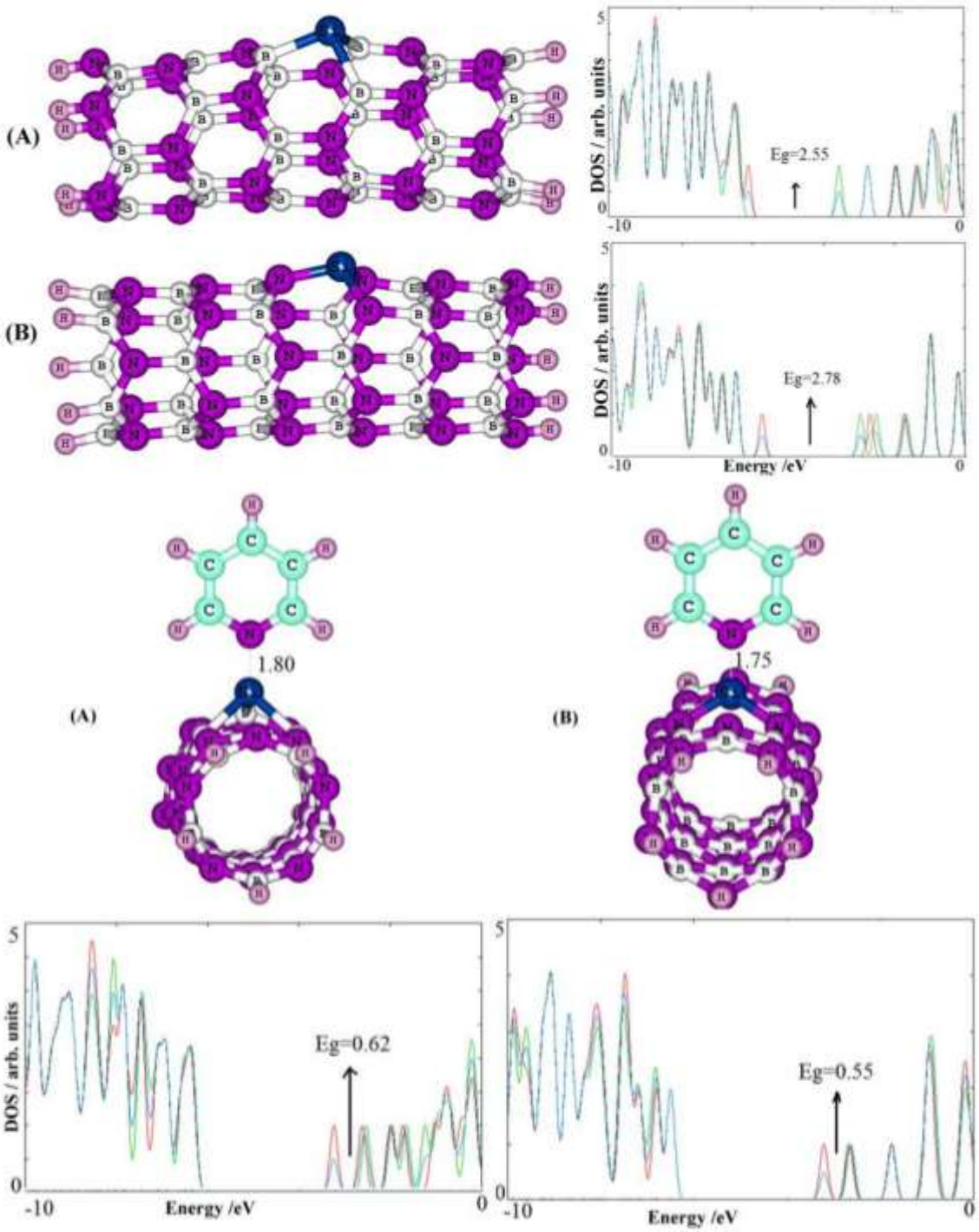

Figure 6: pyridine molecule adsorption by the Si doped nanotube and DOS diagram for observing E_g of nanotube

When Si is sitting instead of N and B adsorption energy of pyridine on nanotube is less than when we just use the pristine nanotube (not doped) and the same when Al is sitting instead of N and B (Table 2) and therefore due to less absorption energy the recovery time is shorter and shows that BNNT that has been doped by Si is a good adsorbent for pyridine gas sensors which are sensitive to this. After adsorption of C_5H_5N on the mentioned nanotube that has doped by Si HOMO/LUMO energy gap (E_g) will decrease

and therefore a substantial increasing will happen in conductivity that this phenomenon can be explain as equation 3, (Li, 2006).

$$\sigma \propto \exp\left(\frac{-E_g}{2kT}\right) \quad [3]$$

Where σ is conductance, T is temperature, k is the Boltzmann constant. According to this equation as often as E_g is smaller it leads the conductivity to be more it can be concluded that when Si is doping on BNNT in the presence of C_5H_5N an electrical signal is generation directly and therefore can potentially be used for C_5H_5N sensors.

Conclusion

The adsorption of an pyridine (C_5H_5N) molecules on the surface of BNNT (boron nitride nanotube) has studied by using density functional theory (DFT) and then we doped the Si and Al atoms in the structure of the nanotube, the results show it is clearly possible to modifying nanotubes as an effective adsorbent of pyridine molecule in gas sensors which are sensitive about pyridine. These results may be open a new gate to chemically modifying the nanotubes in away to expand the fields of its applications in industry and technology.

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