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Methyl acetylene detection by BN nanotube: DFT studies

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Abstract:

Electrical sensitivity of a boron nitride nanotube (BNNT) was examined toward (C_3H_4) molecule by using density functional theory (DFT) calculations at the B_3LYP/6-31G (d) level, and it was found that the adsorption energy (E_{ad}) of methylacetylene (C_3H_4) the pristine nanotubes is a bout -1.78kcal/mol. But when nanotube have been doped with Si and Al atomes, the adsorption energy of methylacetylene molecule was increased. Calculation showed that when the nanotube is doping by Al, the adsorption energy is about -22.73kcal/mol and also the amount of HOMO/LUMO energy gap (E_g) will reduce significantly. Boron nitride nanotube is a suitable adsorbent for methylacetylene and can be use in separation processes methylacetylene. It is seem that nanotube (BNNT) is a suitable semiconductor after doping, and the doped BNNT in the presence of methylacetylene an electrical signal is generating directly and therefore can potentially be used for methylacetylene sensors.

Keywords, Nanotube, DFT, Methylacetylene,Sensor

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1. Introduction:

Methylacetylene is a toxic gas that is a lateral product in dustry and has been detected in the atmosphere [1,2], in the northern auroral region of Jupiter [3], and at the south pole of Saturn [4] and also has been found to be abundant in several interstellar molecular clouds. Methylacetylene is very dangerous for nature and human thus methylacetylene detection and separation is very important. Since the discovery of carbon nanotube (CNT) by Iijima [5] the properties and applications of this novel material have been investigated extensively [6-8]. CNTs have recently emerged as a promising substitute for materials of different properties and various applications in hydrogen storage, gas sensors, textiles and many more [9-10] Boron nitride nanotube (BNNT) has unique properties of a semiconductor behavior. The reason for such behavior is the total atomic number of B and N [11-13]. An interesting case for studying about these BNNTs is investigating their composite type [14]. BNNTs unique properties including tensile strength, stiffness and deformation are the features of this nanotube [15-17]. Previously adsorption of different molecules toward nanostructures has been studied [18-21]. In this study, the adsorption of methylacetylene on the pristine case BNNT while Si and Al atoms are in its structure has been investigated.

2. Computational methods:

2.1. Computation procedures are including the following:

We have optimized the methylacetylene molecule and BNNT at the $B_3LYP/6\text{-}31G$ (d) level of theory. BNNT is made up of 30N, 30B atoms were saturated by 10 hydrogen atoms which are in initial and end part of nanotube. The reason for this act had been done to decrease the boundary effects and totally nanotube is involving 70 (Fig.1).

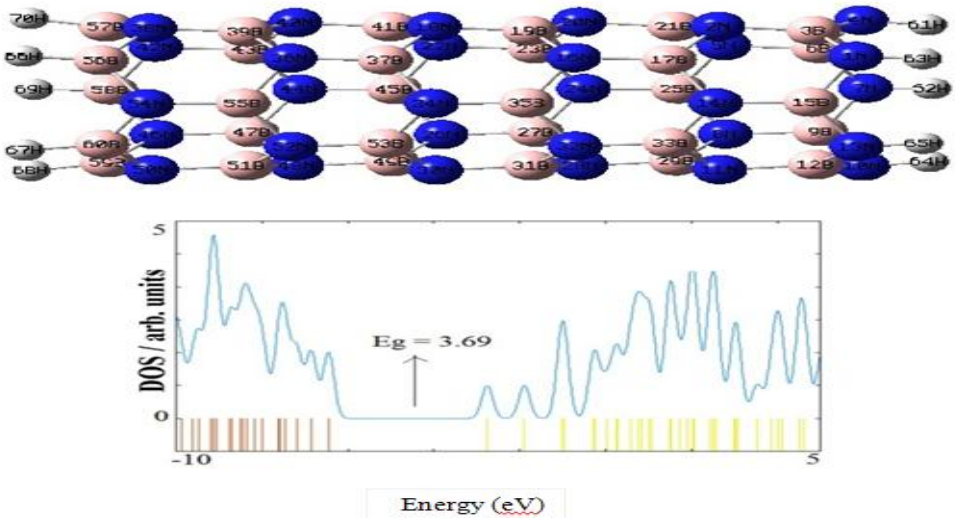

Fig.1: BNNT and DOS diagram for E_g of nanotube.

The BNNT that has been selected is zigzag (5, 0) type and GAMESS software [22] is used to perform these calculations. The B_3LYP is demonstrated to be a reliable and commonly used functional in the study of different nanostructures [23-25]. We made methylacetylene molecule from different positions of the site to be close to the nanotube (Fig.2) and it's adsorption has been calculated by using the Eq.(1).

$$E_{ad}=E_{Nanotube + Methylacetylene} - [E_{Methylacetylene} + E_{Nanotube}] + \delta_{BSSE}(1)$$

According to the mentioned equation $E_{Methylacetylene}$ is methylacetylene molecule's energy, $E_{Nanotube}$ is the nanotube energy and $E_{Nanotube + Methylacetylene}$ is the nanotube's energy with methylacetylene. 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 methylacetylene adsorption on the nanotube and conductivity that which is doping with Si and Al atoms.

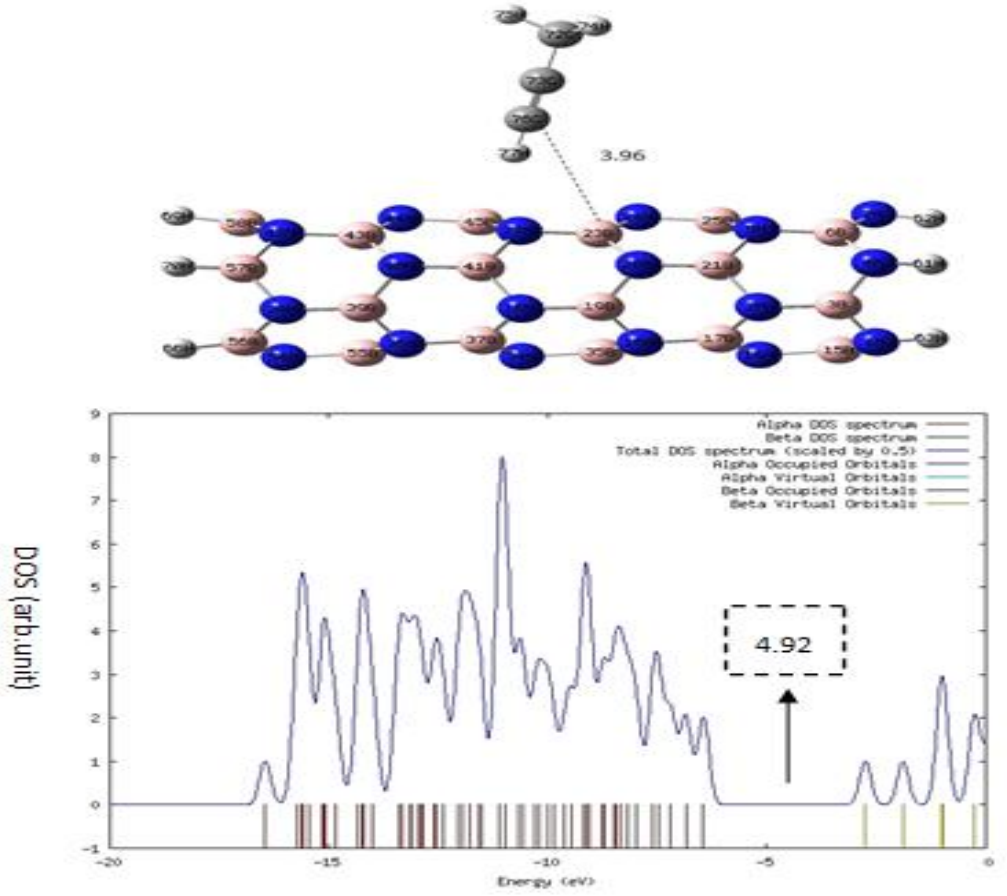

Fig.2: Metylacetylene adsorption (distance unit is angstrom)on the BNNT and DOS diagram for observing E_g of nanotube. Distance is in Å.

1.3. Results and discussion:

Fig.1 shows the structure of boron nitride nanotube (BNNT), in order to obtain the most stable adsorption mode of methylacetylene molecule on different positions of BNNT, the most stable configuration is shown in Fig.2, that boron atom of methylacetylene is 3.96Å far from carbon atom of the nanotube. Detailed information of the structure and electronic properties of the BNNT including the HOMO/LUMO energy gap (E_g) are shown in Table 1 in which adsorption energy (E_{ad}) for mentioned configuration of methylacetylene and nanotube is about -178kcal/mol and then we calculated the HOMO/LUMO energy gap (E_g) for pristine nanotube since the methylacetylene molecule is adsorbed on the nanotubes (Table1). Diagram which shows HOMO/LUMO energy gap (E_g) has been calculated, and the diagram which shows E_g has been obtained by using density of state (DOS) software.

Table1. E_{ad}(kcal/mol), eV for the others

System	E_{ad}	E_{HOMO}	E_{LUMO}	E_g
BNNT	-	-6.45	-2.76	**3.69**
BNNT-C3H4	-1.78	-6.45	-2.75	**3.71**
SiN	-	-6.06	-2.7	**3.36**
SiN-C3H4	-9.42	-6.37	-1.52	**4.85**
SiB	-	-5.75	-2.68	**3.07**
SiB-C3H4	-11.02	-5.57	-1.43	**4.14**
AlN	-	-5.54	-3.00	**2.55**
AlN-C3H4	-2.37	-5.56	-3.02	**2.60**
AlB	-	-6.42	-2.67	**3.75**
AlB-C3H4	-22.73	-6.17	-2.41	**3.76**

1.3.1. Adsorption of C_3H_4on Al doped BNNT:

To examine the sensitivity of the adsorption of BNNT of C_3H_4 as an adsorbent for C_3H_4 its examining has been done two times, once B atom doped by Al atom and other time N atom by Al atom has been doped. Doped calculation of Al on BNNT shows that the value of HOMO/LUMO energy gap (E_g=2.55eV) is less than the pristine nanotube with E_g=3.69eV (Fig.3), After adsorption of C_3H_4 on the mentioned nanotube that has doped by Al the HOMO/LUMO energy gap (E_g=2.60eV) will decrease and therefore a substantial increase will occur in conductivity and this phenomenon can be explain as Eq. (2), [23]

$$\sigma \propto \exp(-E_g /2kT) \quad (2)$$

where σ is conductance, T is temperature, k is 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 Al doping on BNNT in the presence of methylacetylene electrical signal is generation directly and therefore can potentially be used for methylacetylene sensors and the best adsorption energy (E_{ad}= -22.73kcal/mol) is when Al sitting instead of B and methylacetylene has been adsorbed (Fig.4). DOS diagram clearly shows that when Al doped on the BNNT, it will become a semiconductor. Optimization of these types of interactions is desirable for gas detection because such strong interactions means that the BNNT is a suitable absorbent for methylacetylene molecule. If E_{ad} is significantly increased then it is expected that recovery will be so long, meanwhile according to transition state theory and recovery time can be explain as Eq.(3)

$$\tau = \upsilon_0^{-1} \exp(-E_{ad}/kT) \qquad (3)$$

where T is the temperature, k is the Boltzmann's constant, and υ_0 is the attempt frequency.According to this equation as often as adsorption energy (E_{ad}) is increasing the recovery time becomes longer and calculation in Table1.

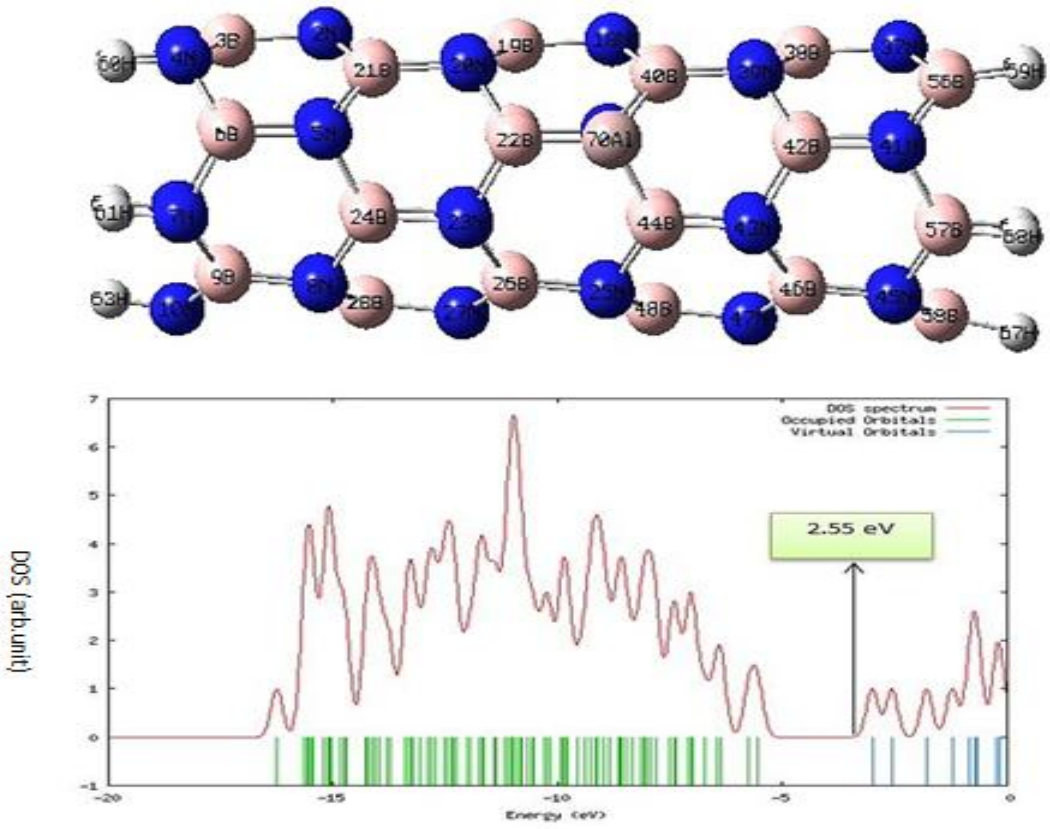

Fig.3: Doped nanotube by Al_N and DOS diagram for E_g of nanotube

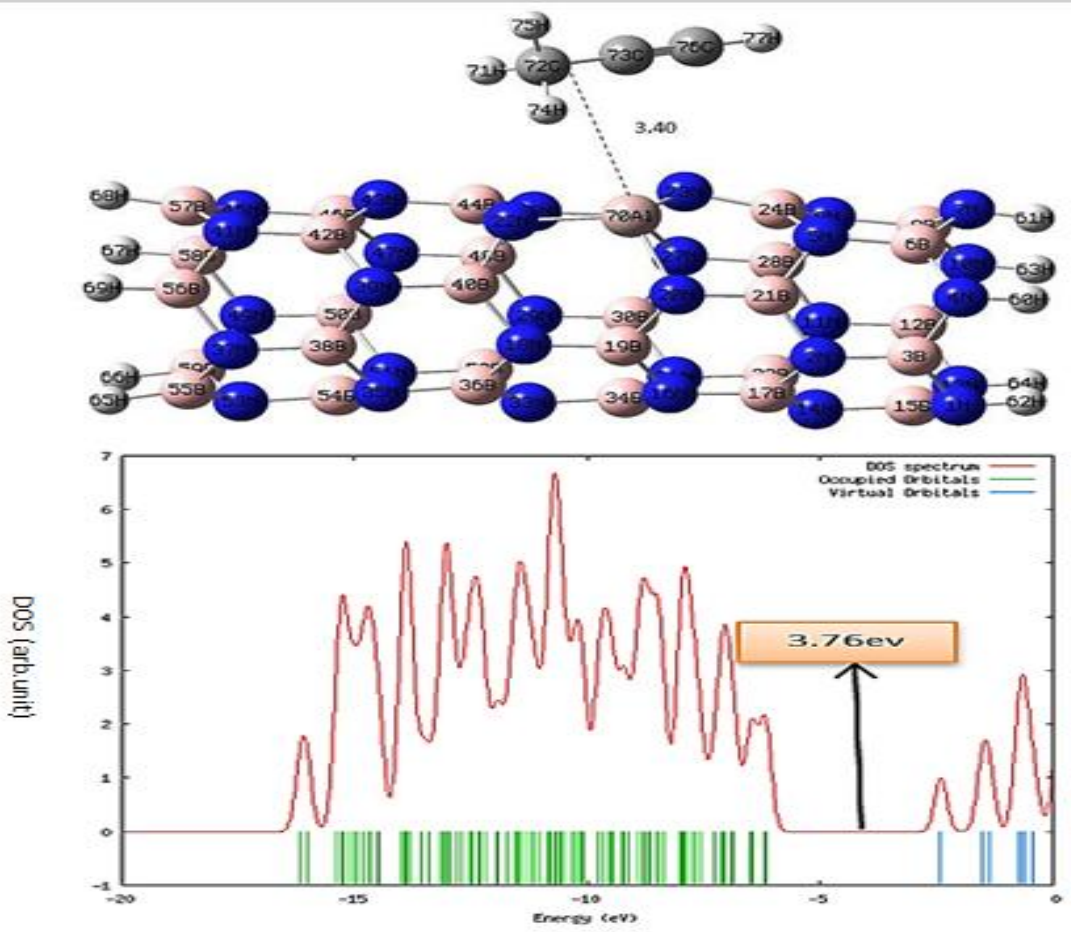

Figure 4: Methylacetylene adsorption (distance unit is angstrom) on doped nanotube by Al_B and DOS diagram for observing E_g of nanotube. Distance is in Å.

1.3.2. Adsorption of C_3H_4 on Si doped BNNT:

At this stage doping has 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 (Fig.5), and then geometrical structures and electronic properties of BNNT are doped and their adsorption behavior are studied. Computations showed that when N replaced by Si in BNNT the HOMO/LUMO energy gap will become less (E_{ad}=3.36 kcal/mol) than the pristine nanotube E_g=3.69eV (Fig.6). When Si is sitting of N and B, and the adsorption energy of methyl acetylene on nanotube (Fig.6) is more (E_{ad}=-11.02kcal/mol) than when we just use the pristine nanotube (E_{ad}= -1.78kcal/mol).

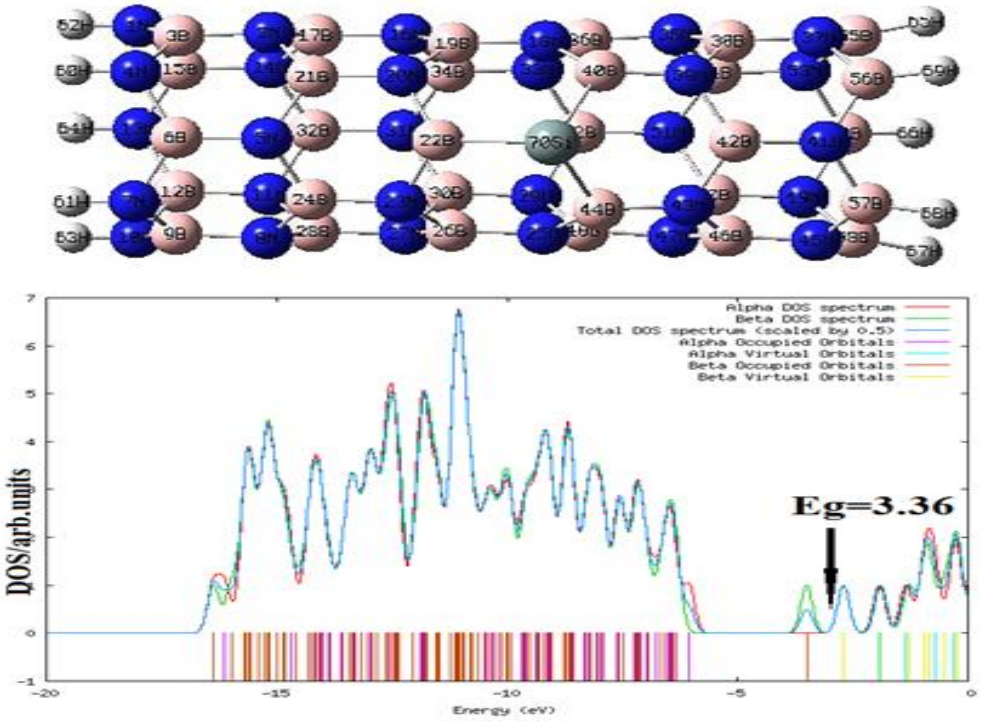

Fig.5: Doped nanotube by Si_N and DOS diagram for E_g of nanotube

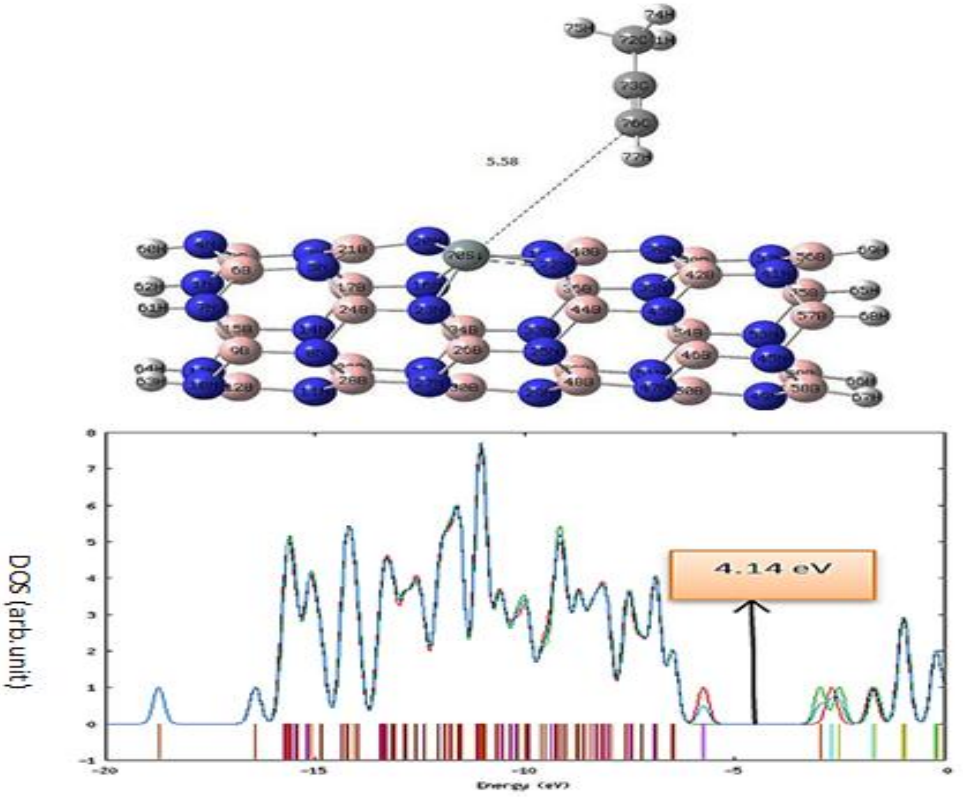

Figure 6: Methylacetylene adsorption (distance unit is angstrom) on doped nanotube by Si_B and DOS diagram for observing of E_g nanotube. Distance is in Å.

1.4. Conclusion:

The adsorption of an Methyl acetylene (C_3H_4) molecules on the surface of BNNT (boron nitride nanotube) has been studied by using density functional theory (DFT) and then we doped the Al atom in the structure of the nanotube, the results show it is clearly possible to modify the nanotube as an effective adsorbent of methyl acetylene molecule in gas sensors which are sensitive about methylacetylene. These results may be open a new gate to chemically modify the nanotubes in a way to expand the fields of their applications in industry and technology.

1.5. Acknowledgment:

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