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C_4H_6 Adsorption on the Surface of a BN Nanotube: DFT Studies

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***Abstract*—**Adsorption of a boron nitride nanotube (BNNT) was examined toward ethylacetylene (C_4H_6) molecule by using density functional theory (DFT) calculations at the B3LYP/6-31G (d) level, and it was found that the adsorption energy (E_{ad}) of ethylacetylene the pristine nanotubes is about -1.60kcal/mol. But when nanotube has been doped with Si and Al atoms, the adsorption energy of ethylacetylene molecule was increased. Calculation showed that when the nanotube is doping by Al, the adsorption energy is about -24.19kcal/mol and also the amount of HOMO/LUMO energy gap (E_g) will reduce significantly. Boron nitride nanotube is a suitable adsorbent for ethylacetylene and can be used in separation processes ethylacetylene. It is seem that nanotube (BNNT) is a suitable semiconductor after doping, and the doped BNNT in the presence of ethylacetylene an electrical signal is generating directly and therefore can potentially be used for ethylacetylene sensors.

***Keywords*—**Sensor, Nanotube, DFT, Ethylacetylene.

I. Introduction

THE C_4H_6 is valuable moieties that can be used in the synthesis of more complex organic molecule. Ethylacetylene is a dangerous toxic gas for nature and human thus ethylacetylene detection and separation is very important. Since the discovery of carbon nanotube (CNT) by Iijima [1], the properties and applications of this novel material have been investigated extensively [2]-[4]. 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 [5], [6]. 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 [7]-[9]. An interesting case for studying about these BNNTs is investigating their composite type [10]. BNNTs unique properties including tensile strength, stiffness and deformation are the features of this nanotube [11]-[13]. Previously adsorption of different molecules toward nanostructures has been studied [14]-[17]. In this study, the adsorption of ethylacetylene on the pristine case BNNT while Si and Al atoms are in its structure has been investigated.

II. Computational Methods

We have optimized the ethylacetylene molecule and BNNT at the B3LYP/6-31G (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).

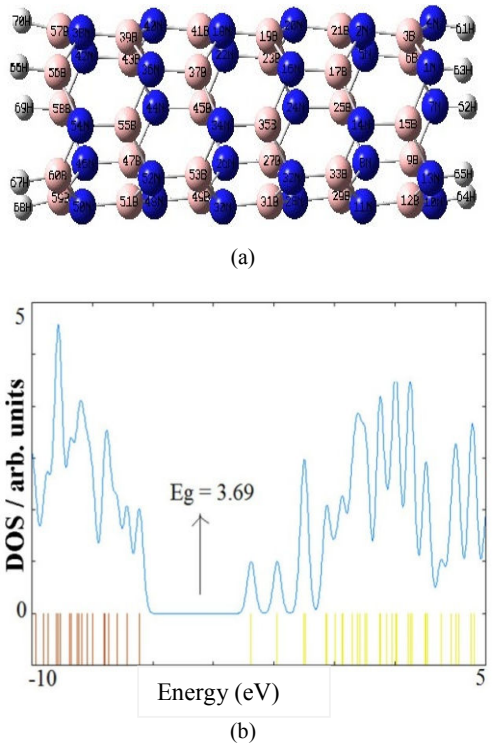

Fig. 1 BNNT, (a) and DOS diagram, (b) for E_g of nanotube

The BNNT that has been selected is zigzag (5, 0) type and GAMESS software [18] is used to perform these calculations. The B3LYP is demonstrated to be a reliable and commonly used functional in the study of different nanostructures [19], [20]. We made ethylacetylene molecule from different positions of the site to be close to the nanotube (Fig. 2) and the adsorption energy has been calculated by using (1):

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

$E_{Ethylacetylene}$ is ethylacetylene molecule's energy, $E_{Nanotube}$ is the nanotube energy and $E_{Nanotube + Ethylacetylene}$ is the nanotube's energy with ethylacetylene. 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 ethylacetylene adsorption on the nanotube and conductivity that which is doping with Si and Al atoms.

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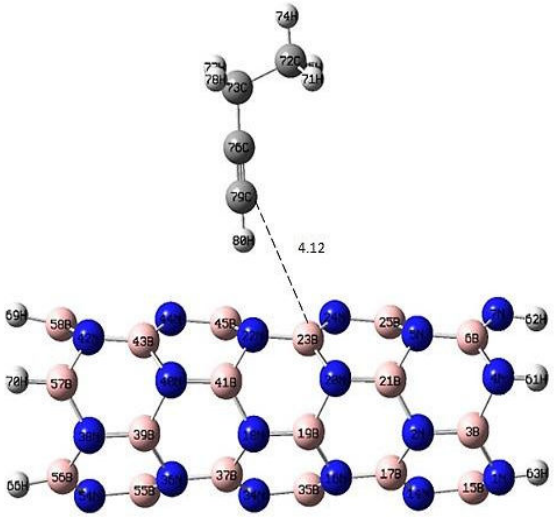

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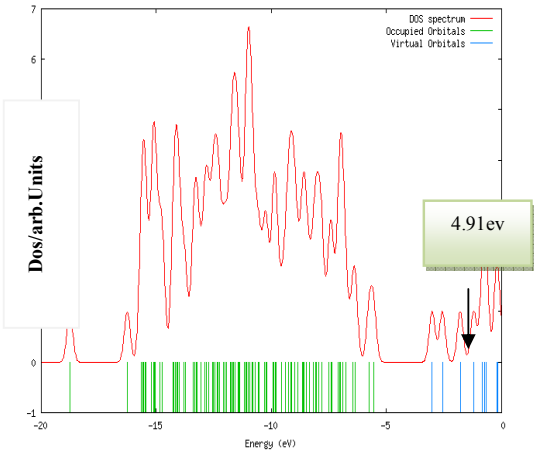


(b)

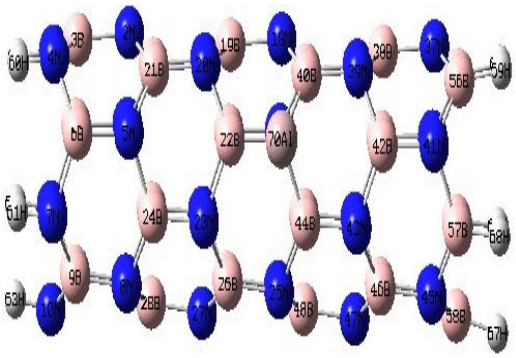
Fig. 2 Etylacetylene adsorption on the BNNT, (a) and DOS diagram, (b) for observing E_g of nanotube, Distance is in Å

III. Results and Discussion

Fig. 1 shows the structure of boron nitride nanotube (BNNT), in order to obtain the most stable adsorption mode of ethylacetylene molecule on different positions of BNNT, the most stable configuration is shown in Fig. 2, that boron atom of ethylacetylene is 4.12 Å 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 I in which adsorption energy (E_{ad}) for mentioned configuration of ethylacetylene and nanotube is about -1.60kcal/mol and then we calculated the HOMO/LUMO energy gap (E_g) for pristine nanotube since the ethylacetylene molecule is adsorbed on the nanotubes (Table I). 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.

TABLE I
EAD (kcal/mol), eV for the Others

System	E_{ad}	E_{HOMO}	E_{LUMO}	E_g
BNNT	-	-6.45	-2.76	3.69
C_4H_6/BNNT	-1.60	-6.42	-2.75	4.91
Si_N	-	-6.06	-2.7	3.36
Si_N-C_4H_6	-2.74	-5.96	-2.66	3.30
Si_B	-	-5.75	-2.68	3.07
Si_B-C_4H_6	-1.96	-8.95	-1.28	7.67
Al_N	-	-5.54	-3.00	2.55
Al_N-C_4H_6	-24.19	-6.17	-2.41	3.76
Al_B	-	-6.42	-2.67	3.75
Al_B-C_4H_6	-1.64	-5.80	-1.85	3.95



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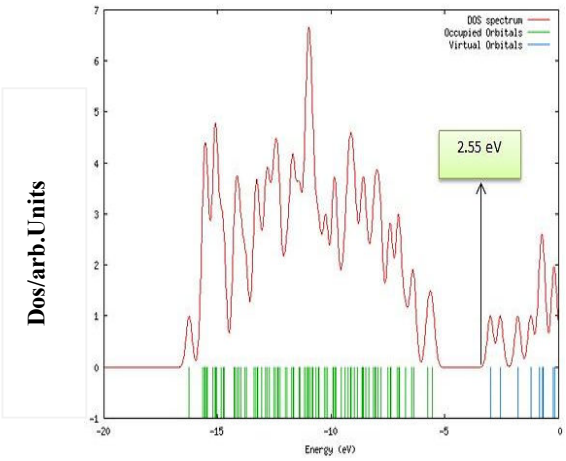


(b)

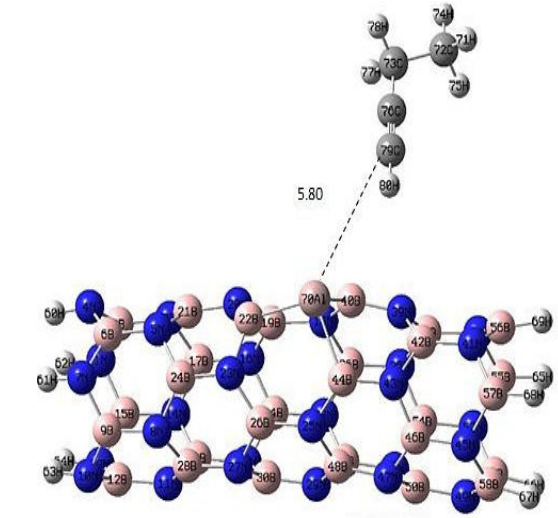
Fig. 3 Doped nanotube by Al_N, (a) and DOS diagram, (b) for E_g of nanotube

To examine the sensitivity of the adsorption of BNNT of C4H6 as an adsorbent for C_4H_6 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) and the best adsorption energy (E_{ad}= -24.19kcal/mol) is when Al sitting instead of N and ethylacethlene 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 mean that the BNNT is a suitable absorbent for ethylacetylene 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 , as (2).

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

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 (Table I).



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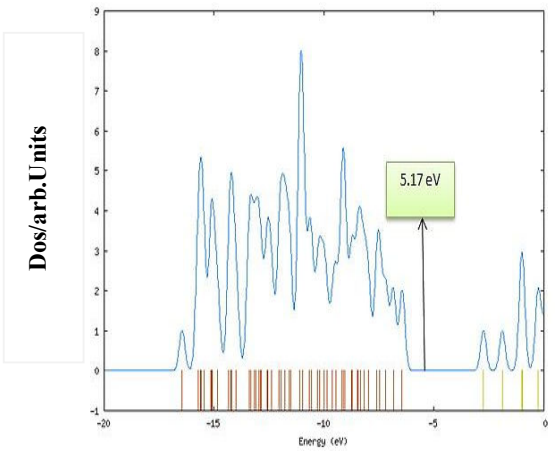


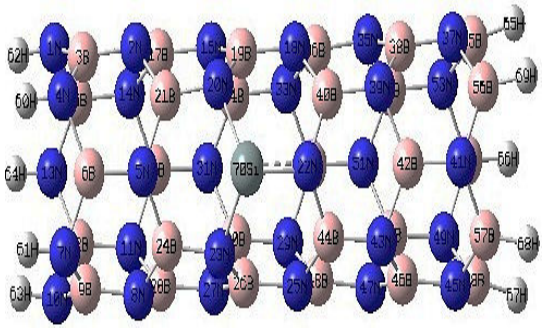
(b)

Fig. 4 Eethylacetylene adsorption on doped nanotube by Al_N, (a) and DOS diagram, (b) for observing Eg of nanotube, Distance is in Å

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 (Fig. 6). Computations showed that when B replaced by Si in BNNT the HOMO/LUMO energy gap will become less E_g=3.07eV. When Si is sitting of N, and the adsorption energy of ethylacetylene (C_4H_6) on nanotube is more (E_{ad}= -2.74kcal/mol) than when we just use the pristine nanotube (E_{ad}= -1.60 kcal/mol). After adsorption of C4H6 on the mentioned nanotube that has been doped by Si the HOMO/LUMO energy gap (E_g=3.30 - 7.67eV) will be increase the pristine of nanotube and therefore a substantial decreasing will occur in conductivity, as (3), [21].

$$\sigma \propto \exp(-E_g/2kT) \quad (3)$$

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 therefore Si is not a suitable for doping in BNNT.



(a)

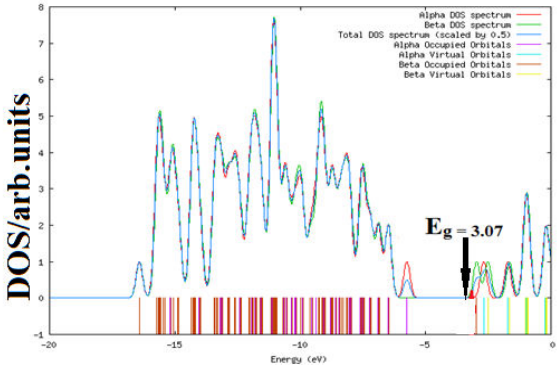


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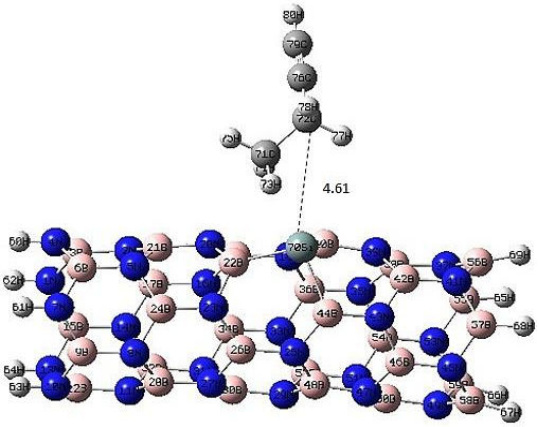
Fig. 5 Doped nanotube by Si_B, (a) and DOS diagram, (b) for E_g of nanotube



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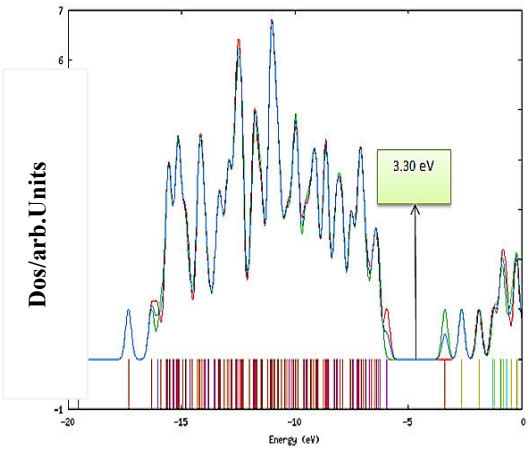

(b)

Fig. 6 Eethylacetylene adsorption on nanotube doped by Si_N, (a) and DOS diagram, (b) for observing of E_g nanotube. Distance is in Å

IV. Conclusion

The adsorption of an ethylacetylene (C_4H_6) 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 ethylacetylene molecule in gas sensors which are sensitive about ethylacetylene. 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.

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