



## Ethyl acetylene adsorption on the surface of a BN nanotube: A Computational study

Maziar Noei<sup>1\*</sup>, Ali Moalla<sup>2</sup>, Fatemeh Meshkinnezhad<sup>2</sup>

<sup>1</sup> Department of Chemistry, College of Chemical engineering , Mahshahr Branch, Islamic Azad University, Mahshahr, Iran

<sup>2</sup> Department of Chemistry, College of chemistry, Omidiyeh Branch, Islamic Azad University, Omidiyeh, Iran

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### Abstract:

Electrical sensitivity of a boron nitride nanotube (BNNT) was examined toward ethyl acetylene (C<sub>4</sub>H<sub>6</sub>) molecule by using density functional theory (DFT) calculations at the B3LYP/6-31G (d) level, and it was found that the adsorption energy (E<sub>ad</sub>) of ethyl acetylene 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<sub>g</sub>) 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 as ethylacetylene sensors.

**Keywords:** Sensor, Nanotube, DFT, Ethyl acetylene

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(\*) Corresponding Author: e-mail: [Maziar.Noei@hotmail.com](mailto:Maziar.Noei@hotmail.com)

## 1. Introduction:

Ethyl acetylene is valuable moieties that can be used in the synthesis of more complex organic molecule. Ethyl acetylene is very dangerous for nature and human thus methyl acetylene 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 ethyl acetylene on the pristine case BNNT while Si and Al atoms are in its structure has been investigated.

## 2. Computational methods:

Computation procedures are included the following: We have optimized the ethylacetylene molecule and BNNT at the B3LYP/6-31G (d) level of theory. BNNT is made up of 30Nitrogen, 30BorN 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 atoms (Fig.1). The BNNT that has been selected in this study is zigzag (5,0) type.

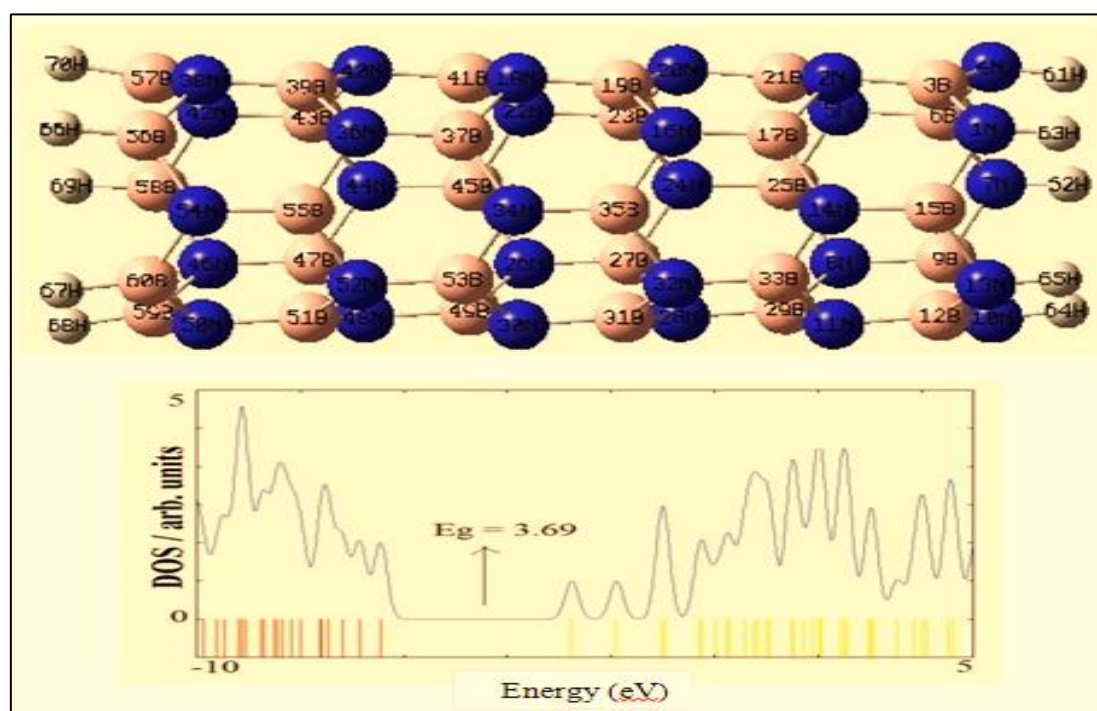
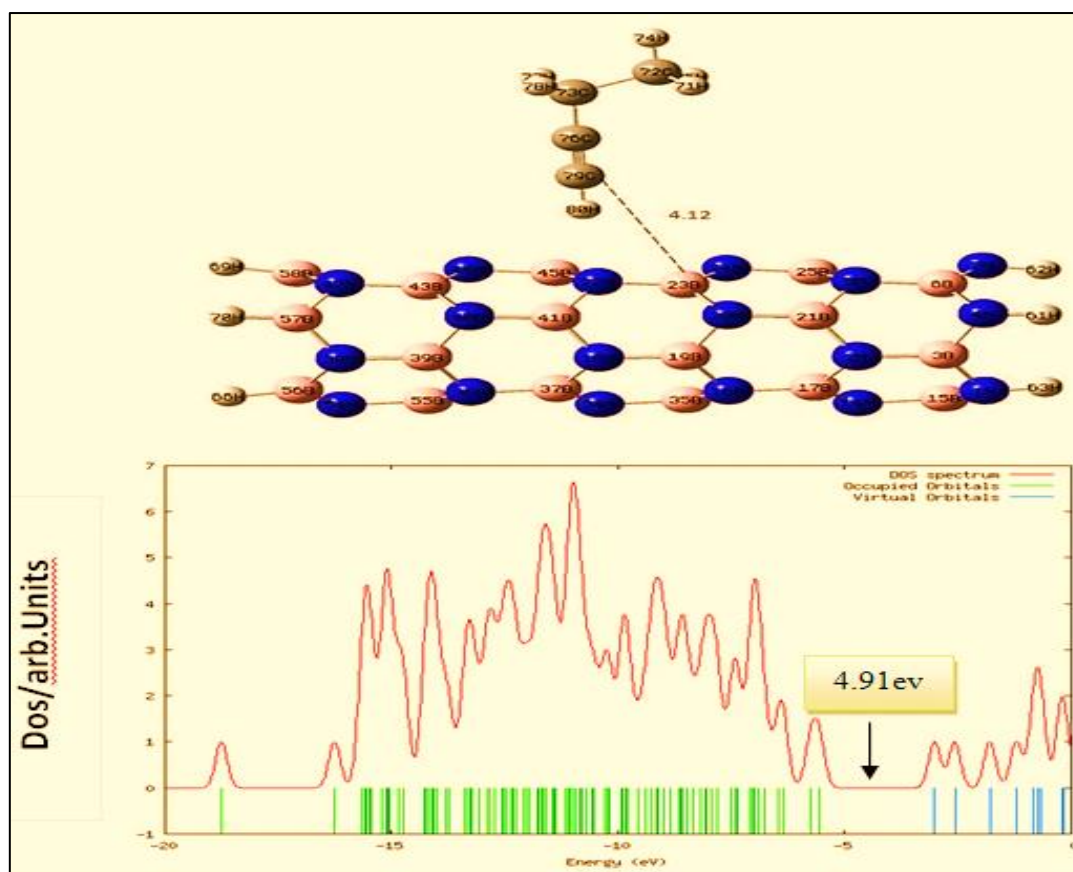


Figure1: BNNT and DOS diagram for  $E_g$  of nanotube

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 its adsorption has been calculated by using the Eq. (1).

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

According to the mentioned equation  $E_{\text{Ethylacetylene}}$  is ethylacetylene molecule's energy,  $E_{\text{Nanotube}}$  is the nanotube energy and  $E_{\text{Nanotube} + \text{Ethylacetylene}}$  is the energy of nanotube with ethylacetylene complex.. In addition,  $\delta_{\text{BSSE}}$  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.



**Figure 2:** Ethylacetylene adsorption on the BNNT and DOS diagram for observing  $E_g$  of nanotube. Distance is in Å

### 3. 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, . In this study 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 1 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 (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.

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

System	$E_{ad}$	$E_{HOMO}$	$E_{LUMO}$	$E_g$
BNNT	-	-6.45	-2.76	<b>3.69</b>
C <sub>4</sub> H <sub>6</sub> /BNNT	-1.60	-6.42	-2.75	<b>4.91</b>
Si <sub>N</sub>	-	-6.06	-2.7	<b>3.36</b>
Si <sub>N</sub> -C <sub>4</sub> H <sub>6</sub>	-2.74	-5.96	-2.66	<b>3.30</b>
Si <sub>B</sub>	-	-5.75	-2.68	<b>3.07</b>
Si <sub>B</sub> -C <sub>4</sub> H <sub>6</sub>	-1.96	-8.95	-1.28	<b>7.67</b>
Al <sub>N</sub>	-	-5.54	-3.00	<b>2.55</b>
Al <sub>N</sub> -C <sub>4</sub> H <sub>6</sub>	-24.19	-6.17	-2.41	<b>3.76</b>
Al <sub>B</sub>	-	-6.42	-2.67	<b>3.75</b>
Al <sub>B</sub> -C <sub>4</sub> H <sub>6</sub>	-1.64	-5.80	-1.85	<b>3.95</b>

#### 3.1. Adsorption of C<sub>4</sub>H<sub>6</sub> on Al doped BNNT:

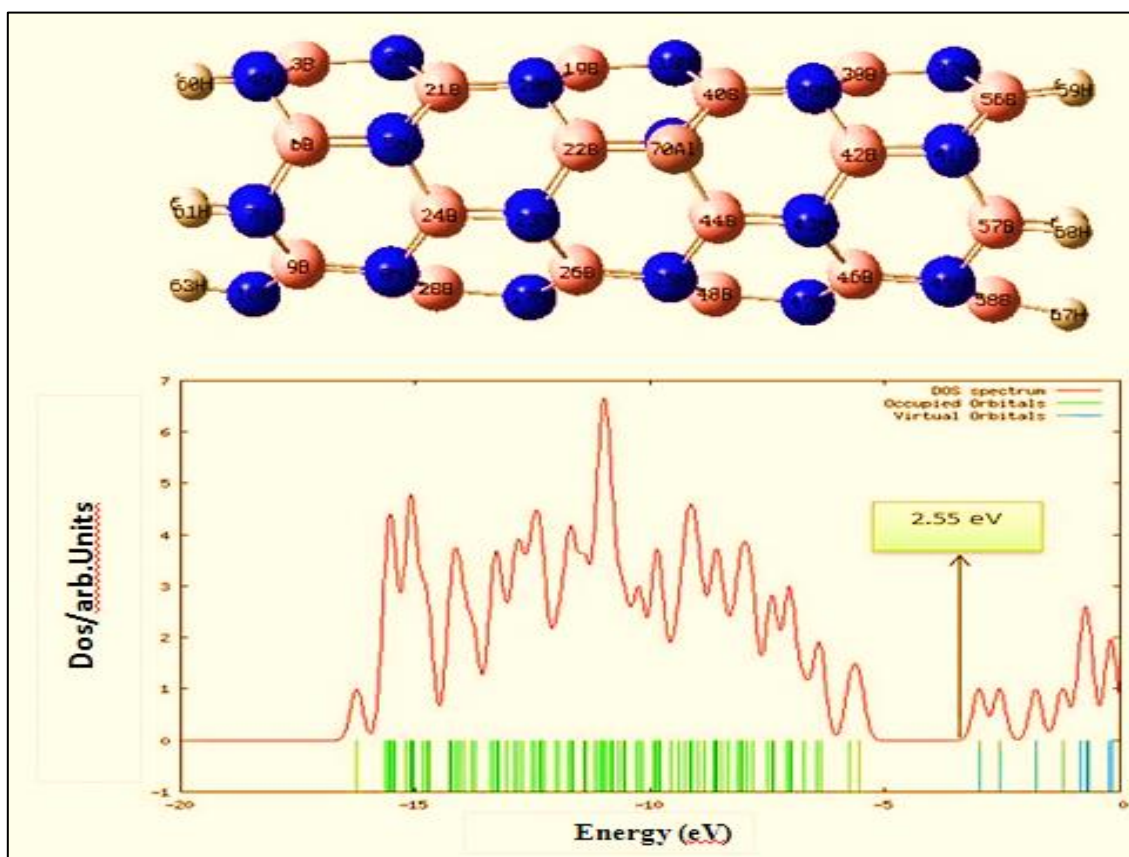
To examine the sensitivity of the adsorption of BNNT of C<sub>4</sub>H<sub>6</sub> as an adsorbent for C<sub>4</sub>H<sub>6</sub> its examining has been done two times, once B atom doped by Al atom and other time N atom by Al atom has been doped. Doped calculation of Al on BNNT shows that the value of HOMO/LUMO energy gap ( $E_g=2.55$ eV) is less

than the pristine nanotube with  $E_g=3.69\text{eV}$  (Fig.3) and the best adsorption energy ( $E_{ad}=-24.19\text{kcal/mol}$ ) is when Al sitting instead of N and ethylacethylene 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 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 can be explain as Eq.(2)

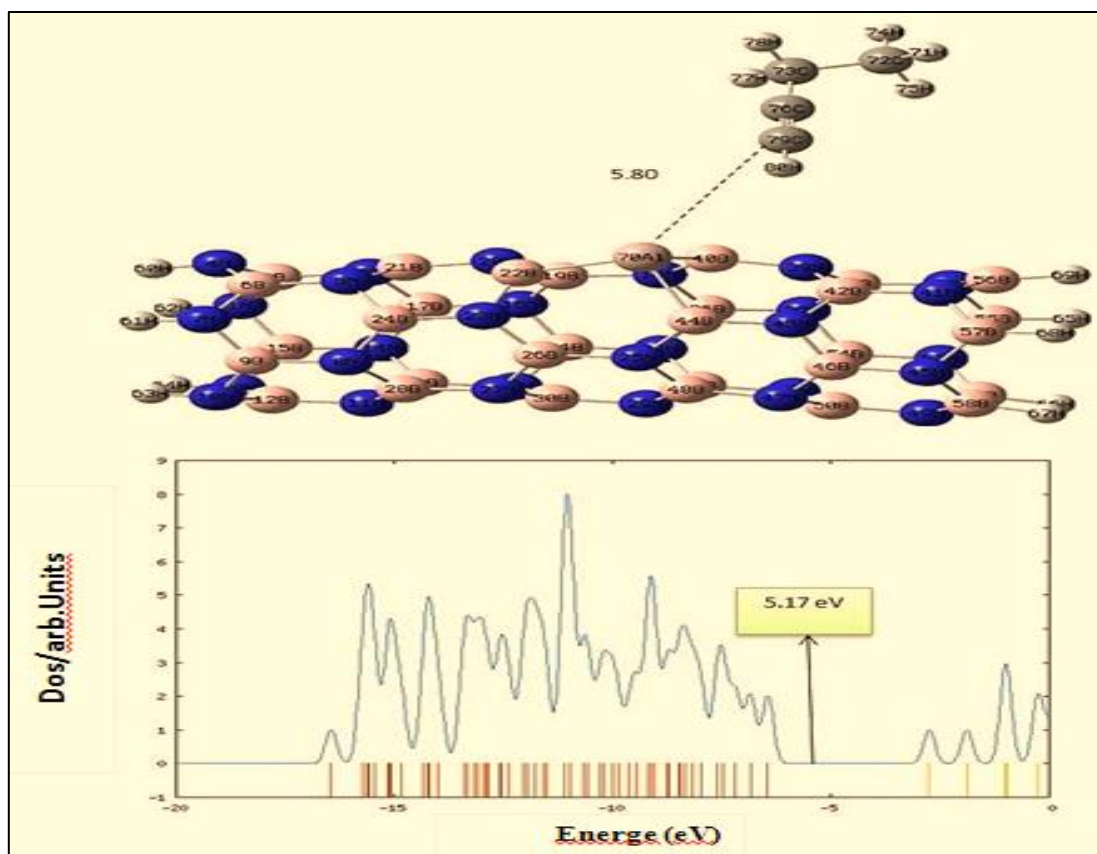
$$\tau = \nu_0^{-1} \exp(-E_{ad}/kT) \quad (2)$$

where T is the temperature, k is the Boltzmann's constant, and  $\nu_0$  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 table 1.



**Figure3:** Doped nanotube by  $\text{Al}_N$  and DOS diagram for  $E_g$  of nanotube



**Figure 4:** E ethylacetylene adsorption on doped nanotube by AlN and DOS diagram for observing  $E_g$  of nanotube.. Distance is in Å.

### 3.2. Adsorption of C<sub>4</sub>H<sub>6</sub> 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 (Fig.6). Computations showed that when B replaced by Si in BNNT the HOMO/LUMO energy gap will become less  $E_g=3.07\text{eV}$ . When Si is sitting of N, and the adsorption energy of ethylacetylene (C<sub>4</sub>H<sub>6</sub>) on nanotube is more ( $E_{ad}=-2.74\text{kcal/mol}$ ) than when we just use the pristine nanotube ( $E_{ad}=-1.60\text{ kcal/mol}$ ). After adsorption of C<sub>4</sub>H<sub>6</sub> on the mentioned nanotube that has been doped by Si the HOMO/LUMO energy gap ( $E_g=3.30 - 7.67\text{eV}$ ) will be increase the pristine of nanotube and therefore a substantial decreasing will occur in conductivity and this phenomenon can be explain as Eq.(3), [ 21]

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

where  $\sigma$  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.

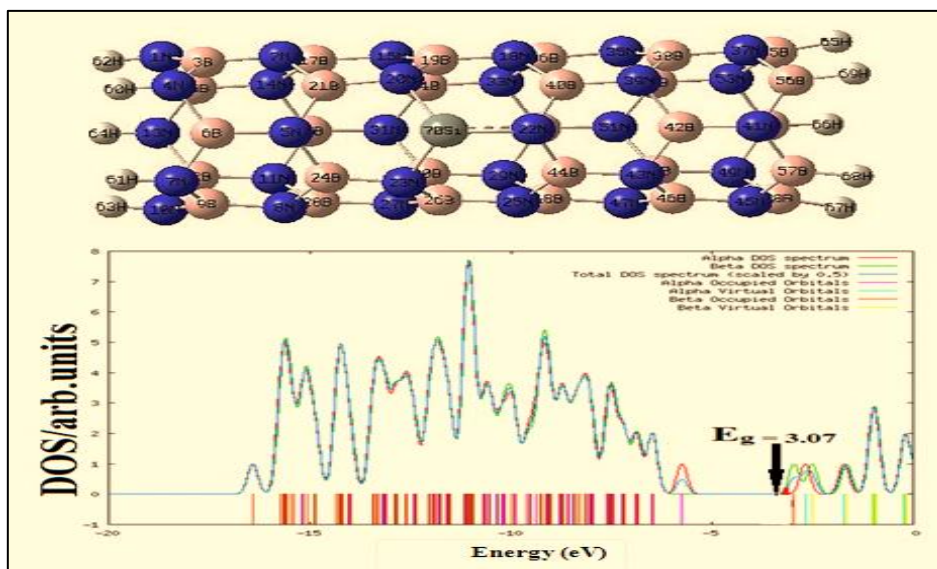


Figure 5: Doped nanotube by  $Si_B$  and DOS diagram for  $E_g$  of nanotube.

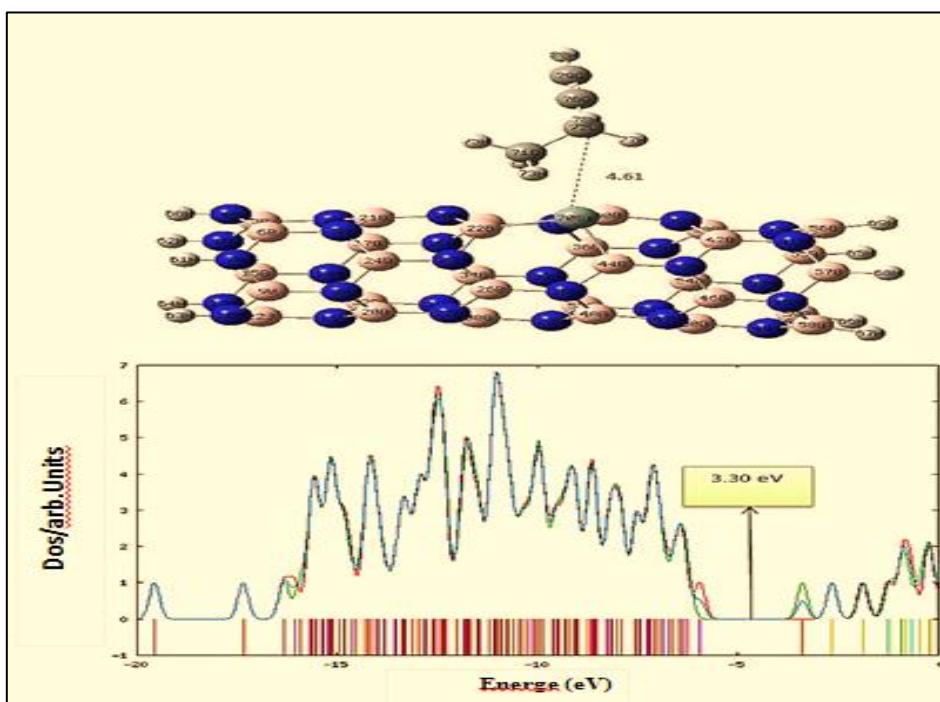


Figure 6: Ethylacetylene adsorption on nanotube doped by  $Si_N$  and DOS diagram for observing of  $E_g$  nanotube. Distance is in Å.

## 4. 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.

## 5. Acknowledgment:

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