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Original Article

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Hydroquinone detection by BN nanotube: DFT studies

Maziar Noei[1]*, Fereshteh Zolfaghari[2], Ali Akbar Salari[2]

[1] *Department of Chemistry, College of Chemical engineering , Mahshahr Branch, Islamic Azad University, Mahshahr, Iran*

[2]Department of Chemistry, College of chemistry, Shahr-E-Rey Branch, Islamic Azad University, Tehran, Iran

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Abstract:

Electrical sensitivity of a boron nitride nanotube (BNNT) was examined toward hydroquinone (C6H4(OH)2) molecule by using density functional theory (DFT) calculations at the B3LYP/6-31G(d) level, and it was found that the adsorption energy (Ead) of hydroquinone on the pristine nanotube is a bout -7.77kcal/mol. But when nanotubes have been doped with Si and Al atomes, the adsorption energy of hydroquinone molecule was increased. Calculation showed that when the nanotube is doping by Al, the adsorption energy is about -19.70kcal/mol and also the amount of HOMO/LUMO energy gap (Eg) will reduce significantly. Boron nitride nanotube is a suitable adsorbent for hydroquinone and can be use in separation processes hydroquinone. It is seem that nanotube (BNNT) is a suitable semiconductor after doping, and the doped BNNT in the presence of hydroquinone an electrical signal is generating directly and therefore can potentially be used for hydroquinone sensors.

Keywords, Sensor, Nanotube, DFT, Hydroquinone

(*) Corresponding Author: e-mail: **Maziar.Noei@hotmail.com**

1. Introduction:

The toxicity of hydroquinone is of interest because of its widespread occurrence in nature, its use in skin lightening preparations and hair dyes, and its industrial uses as reducing agent in photographic developers, and an intermediate in the production of other chemicals. In nature, hydroquinone commonly occurs in plants, most frequently as a glucoside, arbutin [1]. Consumption of coffee or plant products may be the source of hydroquinone metabolites that have been identified in the urine of normal, non-smoking people [2]. Since the discovery of carbon nanotube (CNT) by Iijima [3] the properties and applications of this novel material have been investigated extensively [4-6]. 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 [7-8]. 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 [9-11]. An interesting case for studying about these BNNTs is investigating their composite type [12]. BNNTs unique properties including tensile strength, stiffness and deformation are the features of this nanotube [13-15]. Previously adsorption of different molecules toward nanostructures has been studied [16-19]. In this study, the adsorption of hydroquinone on the pristine case BNNT while Si and Al atoms are in its structure has been investigated.

2. Computational methods:

Computation procedures are include the following:

We have optimized the hydroquinone 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).

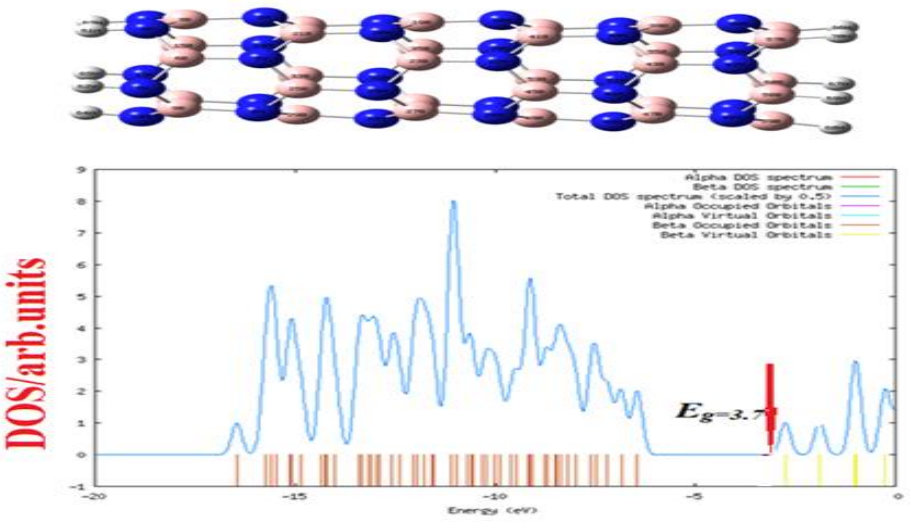

Figure1: BNNT and DOS diagram for E_g of nanotube.

The BNNT that has been selected is zigzag (5,0) type and GAMESS software[20] is used to perform these calculations . The B3LYP is demonstrated to be a reliable and commonly used functional in the study of different nanostructures[21-23].We made hydroquinone molecule from different positions of the site to be close to the nanotube (Fig.2)and (Fig.3) and it's adsorption has been calculated by using the Eq.(1).

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

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

3. Results and discussion:

Fig.1,shows the structure of boron nitride nanotube (BNNT), in order to obtain the most stable adsorption mode of hydroquinone molecule on different position of BNNT, the most stable configuration is shown in Fig.2a, that oxygen atom of hydroquinone is 4.26Å far from boron atom of the nanotube E_{ad}= -7.77 kcal/mol and the other configuration has shown in Figure 2b, that oxygen atom of hydroquinone is 3.18 Å far from nitrogen atom of the nanotube E_{ad}= -5.88 kcal/mol. 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 (Fig.2b) of hydroquinone and nanotube is about -7.77kcal/mol and then we calculated the HOMO/LUMO energy gap(E_g) for pristine nanotube since the hydroquinone molecule is adsorbed on the nanotubes E_g=3.84ev (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.

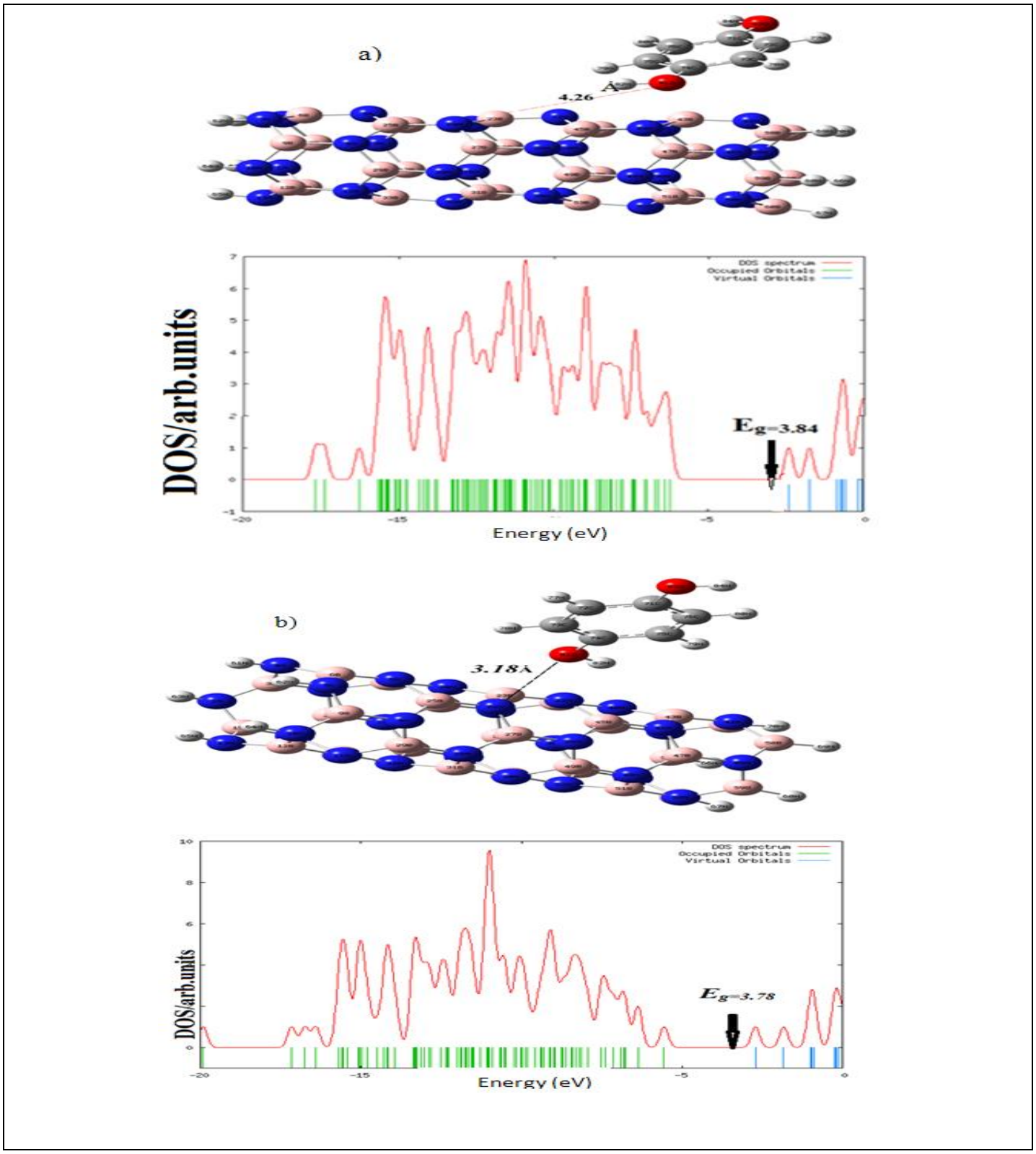

Figure 2: Hydroquinone adsorption on the BNNT and DOS diagram for observing E_g of nanotube. Distance is in Å

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

System	E_{ad}	E_{HOMO}	E_{LUMO}	E_g
BNNT	**-**	**-6.45**	**-2.76**	**3.69**
B-Hyd	**-7.77**	**-6.24**	**-2.47**	**3.84**
N-Hyd	**-5.88**	**-5.56**	**-2.71**	**2.55**
Si_N	**-**	**-6.06**	**-2.7**	**3.36**
Si_N-Hyd	**-6.05**	**-5.26**	**-2.75**	**2.51**
Si_B	**-**	**-5.75**	**-2.68**	**3.07**
Si_B-Hyd	**-3.55**	**-5.5**	**-2.64**	**2.86**
Al_N	**-**	**-5.54**	**-3.00**	**2.54**
Al_N-Hyd	**-19.70**	**-5.01**	**-2.42**	**2.59**
Al_B	**-**	**-6.42**	**-2.67**	**3.75**
Al_B-Hyd	**-33.21**	**-6.12**	**-2.36**	**3.76**

As shown in Table 1, the E_{ad} values corresponding to various adsorption configurations (Fig.2a and Fig.2b) are in the range of −5.88 to −7.77 kcal/mol. In configuration (Fig.2b) with E_{ad} of −5.88 kcal/mol, we have a weak interaction between the tube and O atom of hydroquinone (distance of 3.18 Å).

3.1 Adsorption of C6H4 (OH)2 on Al doped BNNT:

To examine the sensitivity of the adsorption of BNNT of $C_6H_4(OH)_2$ as an adsorbent for $C_6H_4(OH)_2$ 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=2.54eV) is less than the pristine nanotube with E_g=3.69eV (Fig.3), therefore a substantial increase will occur in conductivity and this phenomenon can be explain as Eq.(2),[21]

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

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 is doping on BNNT in the presence of hydroquinone an electrical signal is generation directly and therefore can potentially be used for hydroquinone sensors .The best adsorption energy (E_{ad}=-19.70kcal/mol) is when Al sitting instead of N and hydroquinone 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 hydroquinone 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)

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

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.

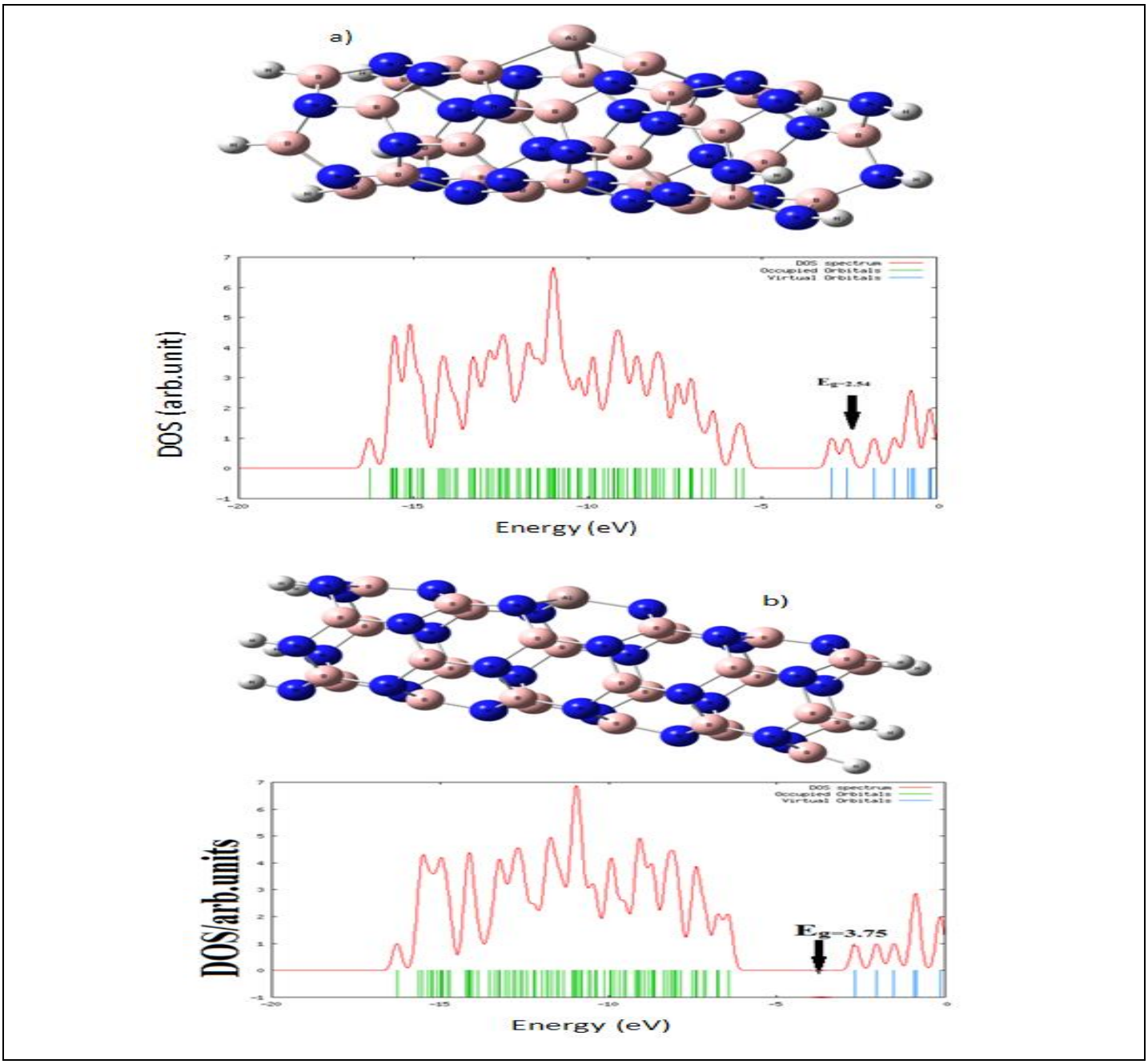

Figure3: a) Doped nanotube by Al_N and DOS diagram for $E_g$of nanotube **b)** Doped nanotube by Al_B and DOS diagram for E_g of nanotube.

As shown in Table 1, the HOMO/LUMO energy gap (E_g) values corresponding to various adsorption configurations (Fig.3a and Fig.3b) are in the range of 2.54 – 3.75 eV. In configuration (Fig.3a) with E_g of 2.54 eV, the value of HOMO/LUMO energy gap is less than the pristine nanotube.

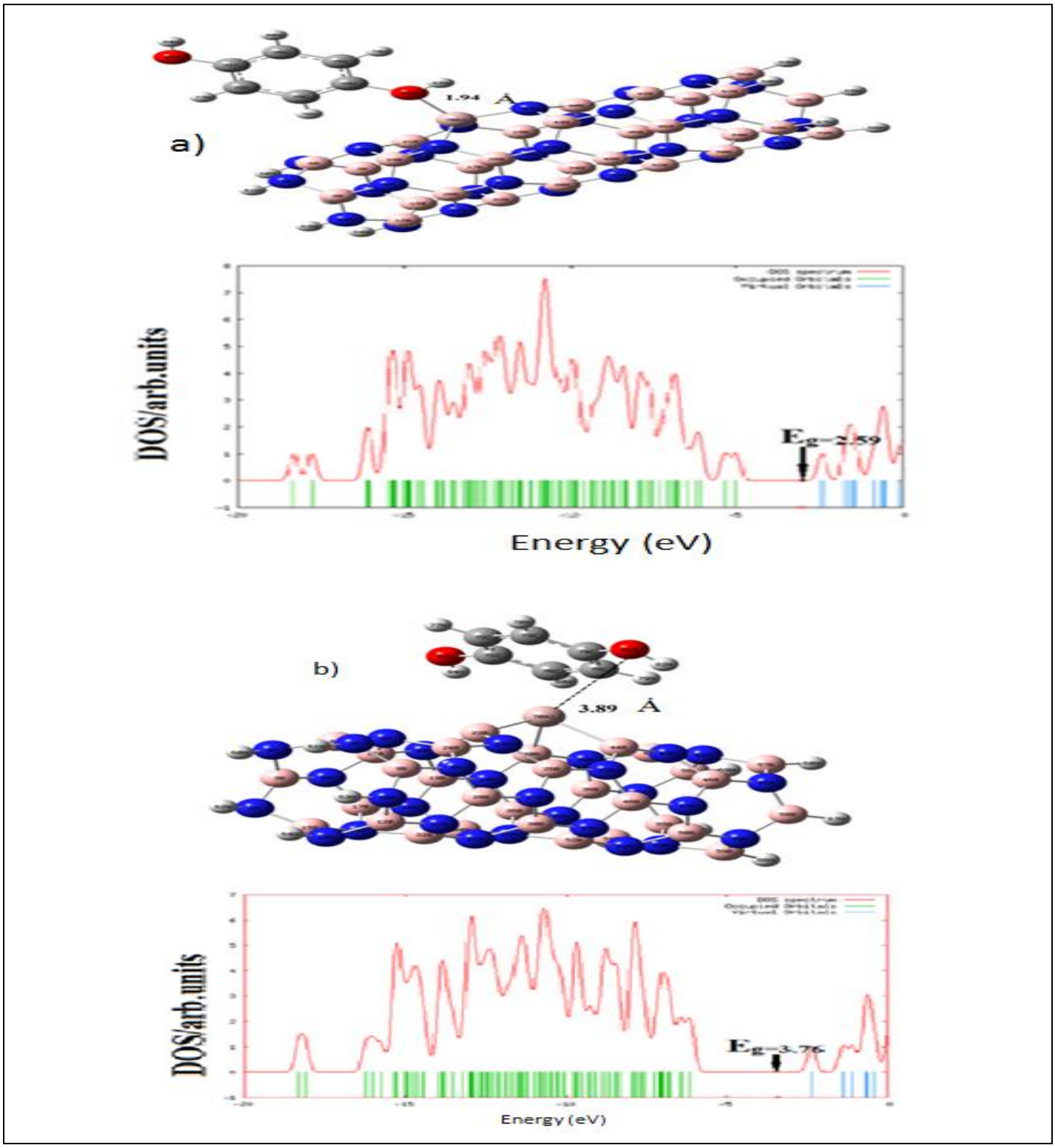

Figure 4: a)Hydroquinone adsorption on doped nanotube by AlN and DOS diagram for observing Eg of nanotube. b) Hydroquinone adsorption on doped nanotube by AlB and DOS diagram for observing Eg of nanotube. Distance are in Å.

According to Table 1, the E_{ad} values corresponding to various adsorption configurations (Fig.4a and Fig.4b) are in the range of −19.70 to −33.21 kcal/mol, we have a suitable interaction between the tube and O atom of hydroquinone .

3.2 Adsorption of C6H4(OH)2 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 be decrease E_g=3.36eV (Fig.6).When Si is sitting of N and B, and the adsorption energy of hydroquinone on nanotube is less (E_{ad}= -6.05kcal/mol) than when we just use the pristine nanotube (E_{ad}= -7.77kcal/mol). After adsorption of $C_4H_6(OH)_2$ on the mentioned nanotube that has doped by Si the HOMO/LUMO energy gap (E_g=2.86eV) will be increase of pristine nanotube (E_g=2.55eV), therefore Si is not suitable element for doping in BNNT when in this study the adsorption of hydroquinone on BNNT.

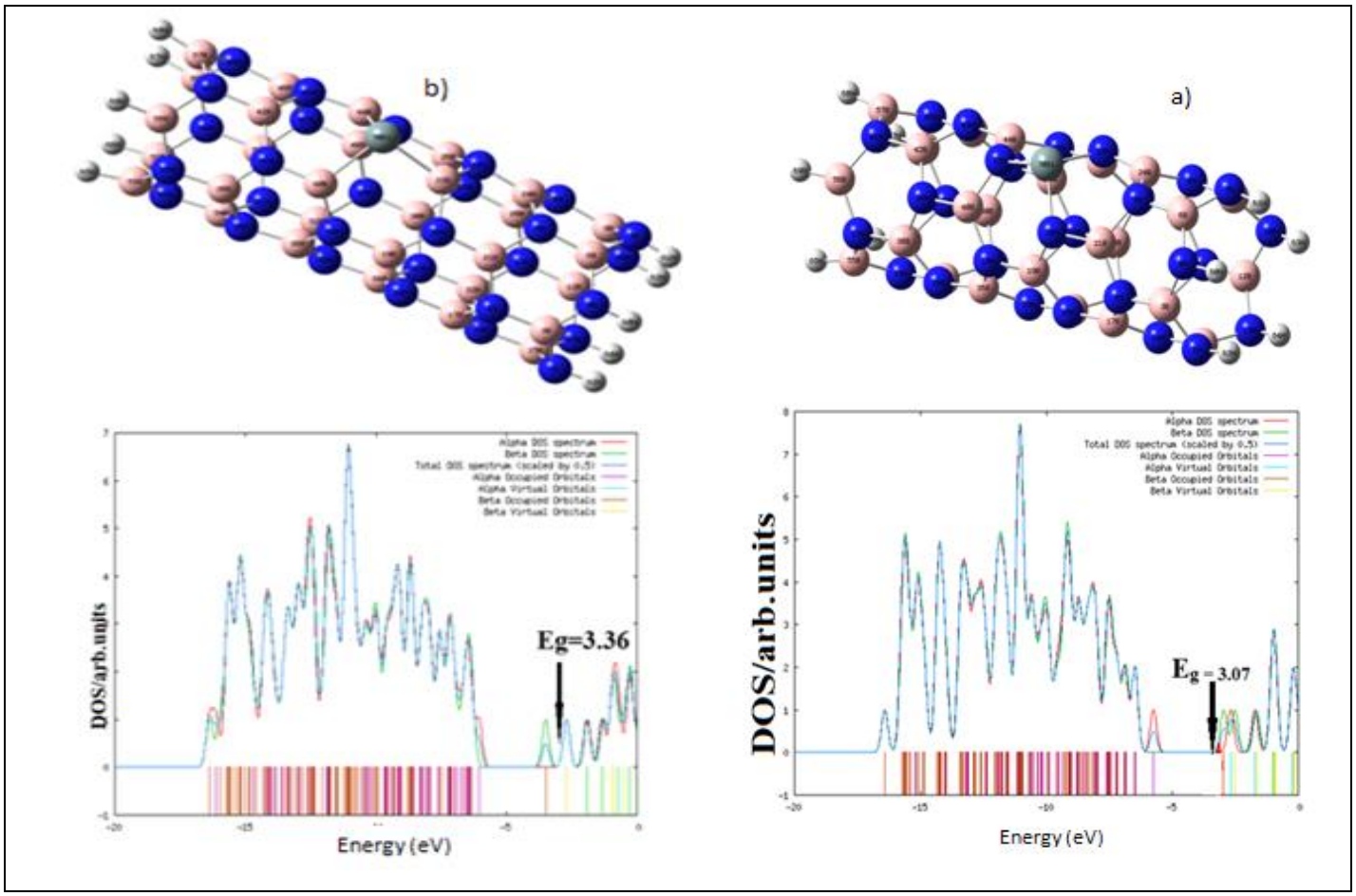

Figure 5: a) Doped nanotube by Si_N and DOS diagram for E_g of nanotube. **b)** Doped nanotube by Si_B and DOS diagram for E_g of nanotube.

As shown in Table 1, the HOMO/LUMO energy gap (E_g) values corresponding to various adsorption configurations (Fig.5a and Fig.5b) are in the range of 3.07 – 3.36 eV and in tow configurations, the value of HOMO/LUMO energy gap is less than the pristine nanotube.

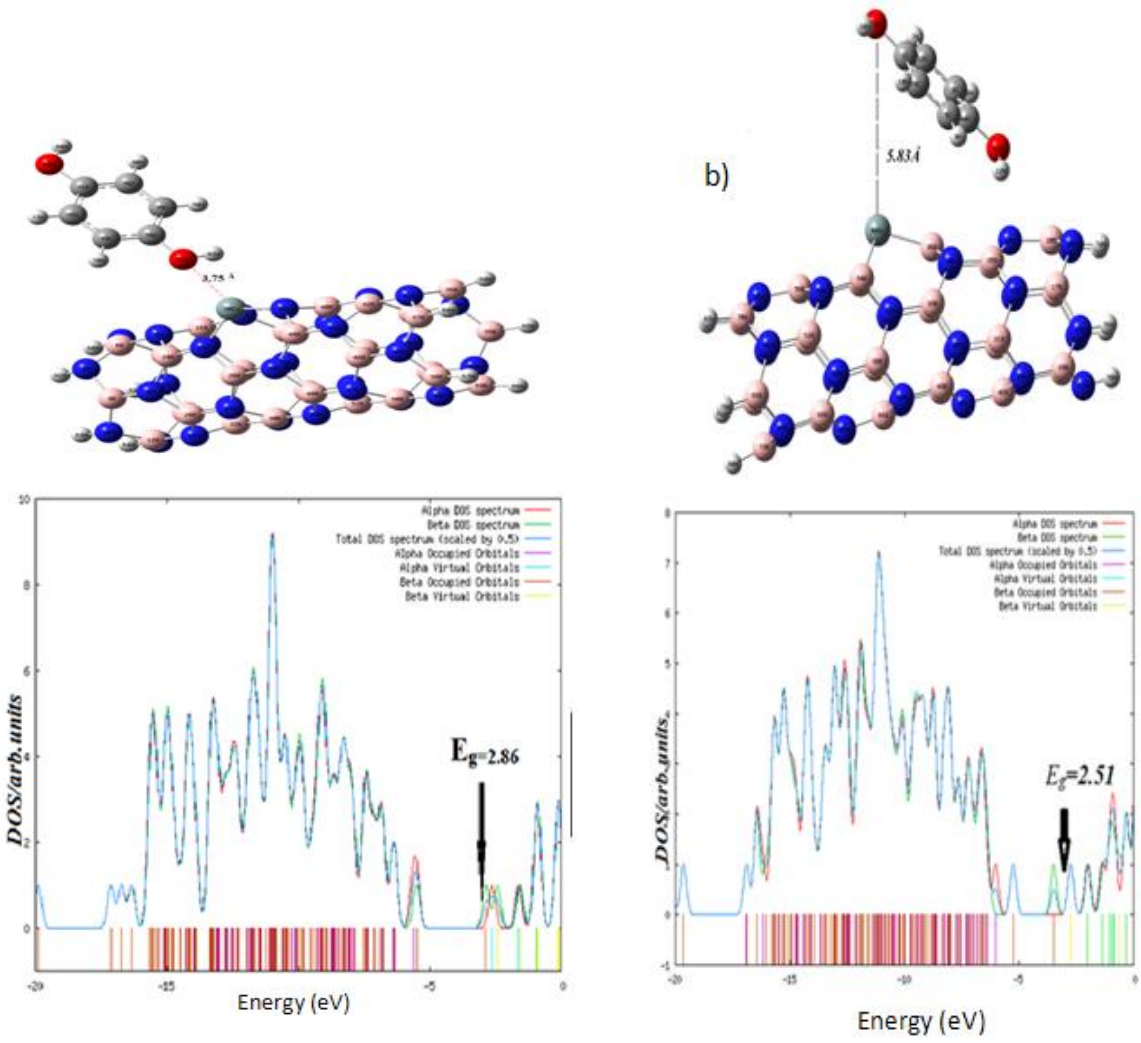

Figure 6:a)Hydroquinone adsorption on doped nanotube by SiN and DOS diagram for observing of Eg nanotube. b) Hydroquinone adsorption on doped by SiB and DOS diagram for observing of Eg nanotube. Distance are in Å

According to Table 1, the E_{ad} values corresponding to various adsorption configurations (Fig.6a and Fig.6b) are in the range of −3.55 to −6.05 kcal/mol, which is smaller than that in the configurations (Fig.4a and Fig.4b) and the pristine nanotube.

4. Conclusion:

The adsorption of an hydroquinone ($C_6H_4(OH)_2$) molecule on the surface of BNNT (boron nitride nanotube) has been studied by using density functional theory (DFT) , adsorption energy values corresponding to the adsorption of ($C_6H_4(OH)_2$) on pristine BNNT was calculated to be in the range of −5.88 to −7.77 kcal/mol,

the HOMO/LUMO energy gap (E_g) values corresponding to that various adsorption configurations were in the range of 2.55 – 3.84 eV and then we doped the Al atom in the structure of the nanotube, the E_{ad} values corresponding to various adsorption configurations were in the range of −19.70 to −33.21 kcal/mol and the HOMO/LUMO energy gap values corresponding to that various adsorption configurations were in the range of 3.07 – 3.36 eV. The results show it is clearly possible to modify the nanotube as an effective adsorbent of hydroquinone molecule in gas sensors which are sensitive about hydroquinone. These results may be open a new gate to chemically modifiing the nanotubes in a way to expand the fields of their applications in industry and technology.

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6. References:

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