International Journal of New Chemistry, 2014, 1 (2), 68 -76

Published online 2014 in http://www.ijnc.ir/.

Original Article

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Pyrrole adsorption on the surface of a BN nanotube: A Computational study

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Received: 15 August 2014; Accepted: 1 September 2014

Abstract:

Electrical sensitivity of a boron nitride nanotube (BNNT) was examined toward pyrrole (C_5H_6N) 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 pyrrole on the pristine nanotubes is a bout -16.37kcal/mol. But when nanotube have been doped with Si and Al atomes, the adsorption energy of pyrrole molecule was increased. Calculation showed that when the nanotube is doping by Si, the adsorption energy is about -24.29kcal/mol and also the amount of HOMO/LUMO energy gap (E_g) will reduce significantly. It seems that nanotube (BNNT) is a suitable semiconductor after doping, and the doped BNNT in the presence of pyrrole an electrical signal is generating directly and therefore can potentially be used for pyrrole sensors, and BNNT is a suitable adsorbent for pyrrole molecules.

Keywords: Sensor, Nanotube, DFT, Pyrrole

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1. Introduction:

It is well known that substituted pyrroles are an important class of heterocyclic compounds due to their remarkable biological and physical properties [1]. Pyrrole cross-links have been identified in long-lived proteins such as lens crystallins and skin collagen and implicated in the stiffening of arteries and joints associated with aging [2-3]. Since the discovery of carbon nanotube (CNT) by Iijima [4] the properties and applications of this novel material have been investigated extensively [5-7]. 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 [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 [12-14]. BNNT has a smaller band gap of a material that is interesting for applications in nanoscale devices [15]. BNNTs unique properties including tensile strength, stiffness and deformation are the features of this nanotube [16-18]. Previously adsorption of different molecules toward nanostructures has been studied [19-22]. In this study, the adsorption of Pyrrole 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 pyrrole 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 atoms (Fig.1).

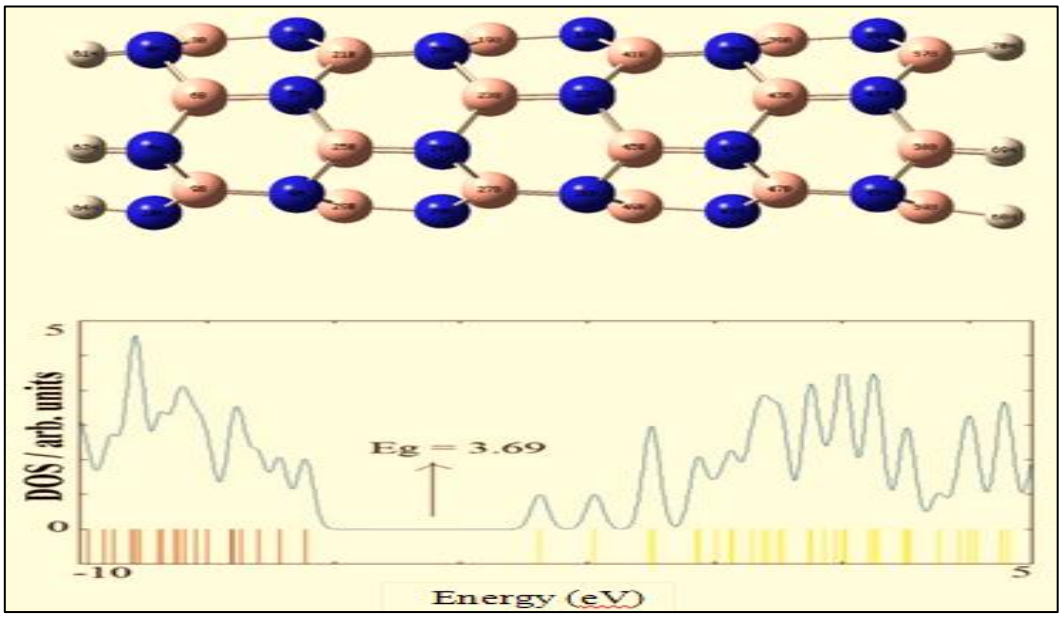

Figure1: BNNT and DOS diagram for E_g of nanotube

The BNNT that has been selected is zigzag (5,0) type and GAMESS software [23] is used to perform these calculations . The B3LYP is demonstrated to be a reliable and commonly used functional in the study of different nanostructures[24-26].We made pyrrole 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).

$$Ead=ENanotube + Pyrrole – [EPyrrole + ENanotube] + \delta BSSE \quad (1)$$

According to the mentioned equation EPyrrole is pyrrole molecule's energy, ENanotube is the nanotube energy and E Nanotube + Pyrrole is the nanotube's energy with pyrrole. In addition, δBSSE 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 pyrrole adsorption on the nanotube and conductivity that which is doping with Si and Al atoms.

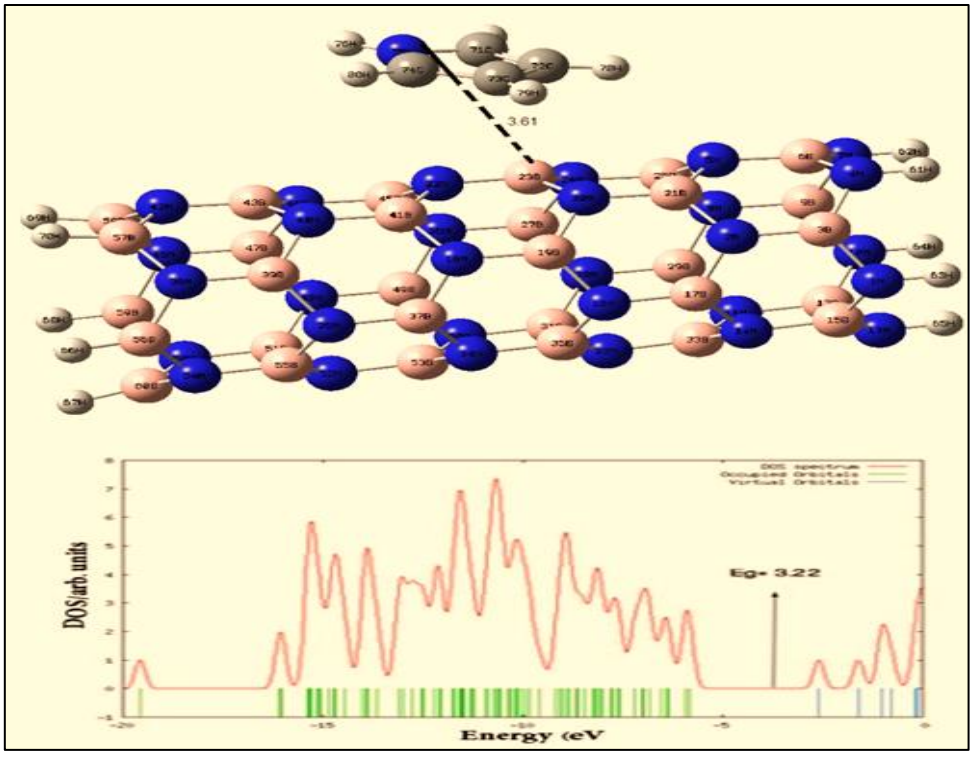

Figure 2: Pyrrole adsorption on the BNNT and DOS diagram for observing Eg of nanotube. Distance is in Å.

3. Results and discussion:

Fig.1, shows the structure of boron nitride nanotube (BNNT), in order to obtain the most stable adsorption mode of C5H6N molecule on different positions of BNNT, the most stable configuration is shown in Fig.2, that boron atom of pyrrole is 3.16Å far from nitrogen atom of the nanotube .

Detailed information of the structure and electronic properties of the BNNT including the HOMO/LUMO energy gap (Eg) are shown in Table 1 in which adsorption energy (Ead) for mentioned configuration of pyrrole and nanotube is about -16.37kcal/mol and then we calculated the HOMO/LUMO energy gap (Eg) for pristine nanotube since the pyrrole molecule is adsorbed on the nanotubes (Table1). Diagram which shows HOMO/LUMO energy gap (Eg) has been calculated, and the diagram which shows Eg has been obtained by using density of state (DOS) software.

<Table 1>

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**
$BNNT_B$-P	-16.37	-5.81	-2.59	**3.22**
Si_N	-	-6.06	-2.7	**3.36**
Si_N-p	-24.29	-4.67	-2.41	**2.26**
Al_B	-	-5.54	-3.00	**2.54**
Al_B-p	-26.66	-6.06	-2.26	**3.8**

3.1. Adsorption of C_5H_6N on Al doped BNNT:

To examine the sensitivity of the adsorption of BNNT of C5H6N as an adsorbent for C5H6N its examining has been done, the B atom doped by Al atom. Doped calculation of Al on BNNT shows that the value of HOMO/LUMO energy gap (Eg=2.54ev) is less than the pristine nanotube with Eg=3.69ev (Fig.3), and the best adsorption energy (Ead=-26.66kcal/mol) is obtained when Al sitting instead of B and pyrrole has been adsorbed. DOS diagram clearly shows that when Al is 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 pyrrole molecule. If Ead 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)

$$\tau = \upsilon 0\text{-}1 \exp(-Ead/kT) \qquad (2)$$

where T is the temperature, k is the Boltzmann's constant, and υ0 is the attempt frequency.

According to this equation as often as adsorption energy (Ead) is increasing the recovery time becomes

longer and calculation in Table 1 show that the recovery time and adsorption energy is suitable level (Fig.4).

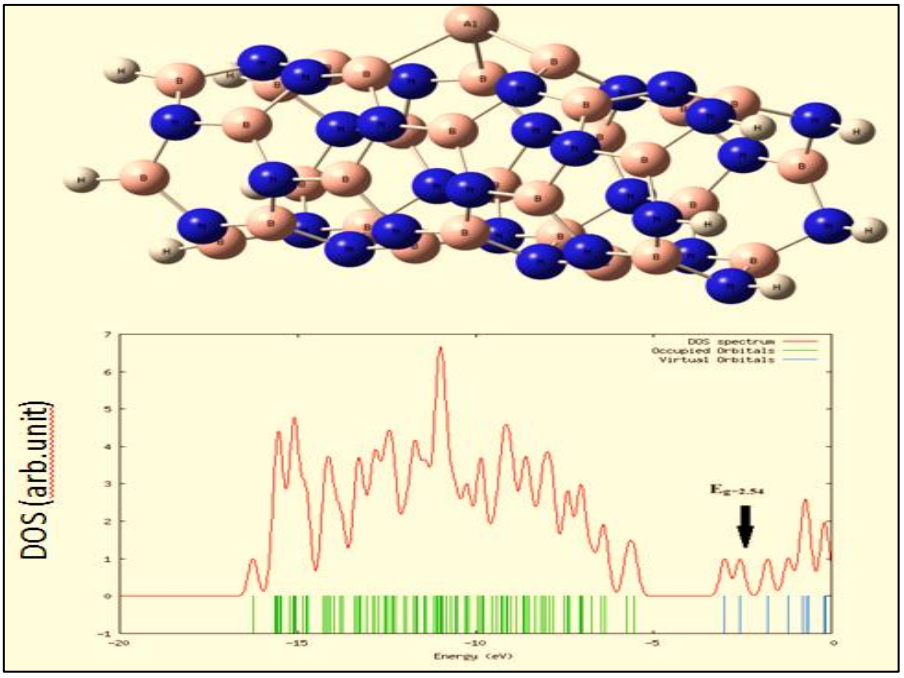

Figure 3: Doped nanotube by Al and DOS diagram for E_g of nanotube.

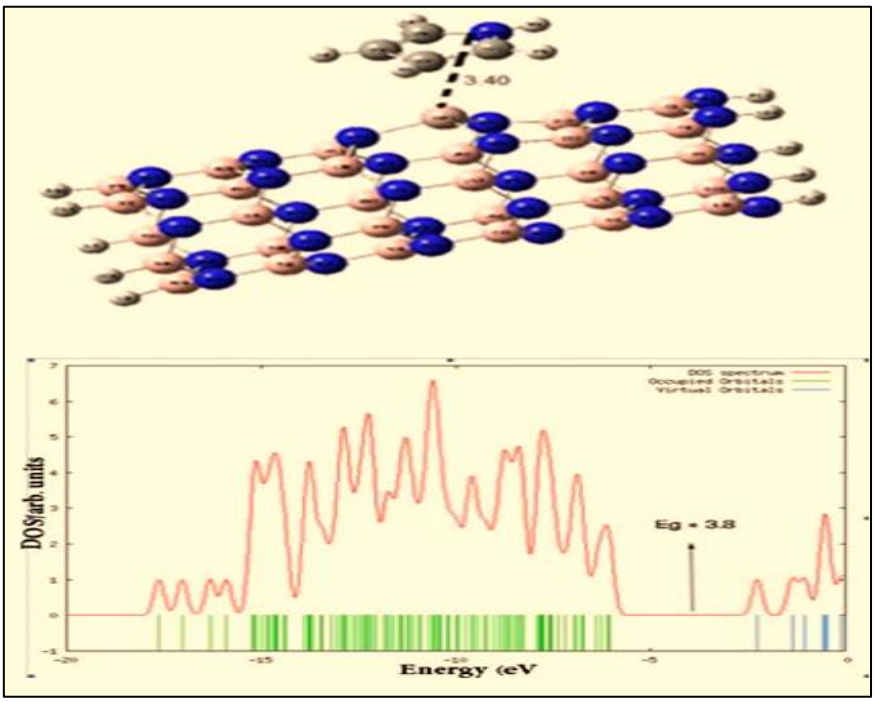

Figure 4: Pyrrole adsorption on doped nanotube by Al and DOS diagram for observing E_g of nanotube. Distance is in Å.

3.2. Adsorption of C_5H_6N on Si doped BNNT:

At this stage doping has been studied with another element. So, instead of N atom in the boron nitride nanotube a Si atom (Fig.5), and then geometrical structures and electronic properties of BNNT are doped and their adsorption behavior are studied. Computations showed that when N is replaced by Si in BNNT the HOMO/LUMO energy gap will become less of Eg =3.36ev(Fig.6). When Si is sitting of N, and the adsorption energy of pyrrole on nanotube is more (Ead=-24.29kcal/mol) than when we just use the pristine nanotube (Ead=-16.37kcal/mol). After adsorption of C5H6N on the mentioned nanotube that has doped by Si the HOMO/LUMO energy gap (Eg=3.39ev) will decrease and therefore a substantial increase will occur in conductivity and this phenomenon can be explain as Eq.(3),[24]

$$\sigma \propto \exp(-Eg /2kT) \quad [3]$$

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

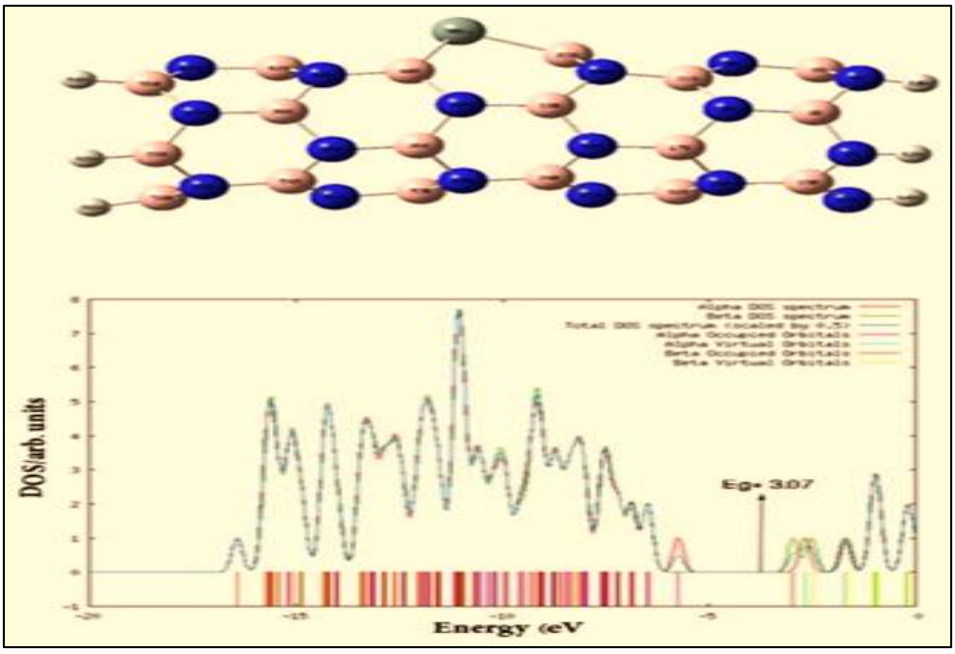

Figure 5: Doped nanotube by Si and DOS diagram for E_g nanotube.

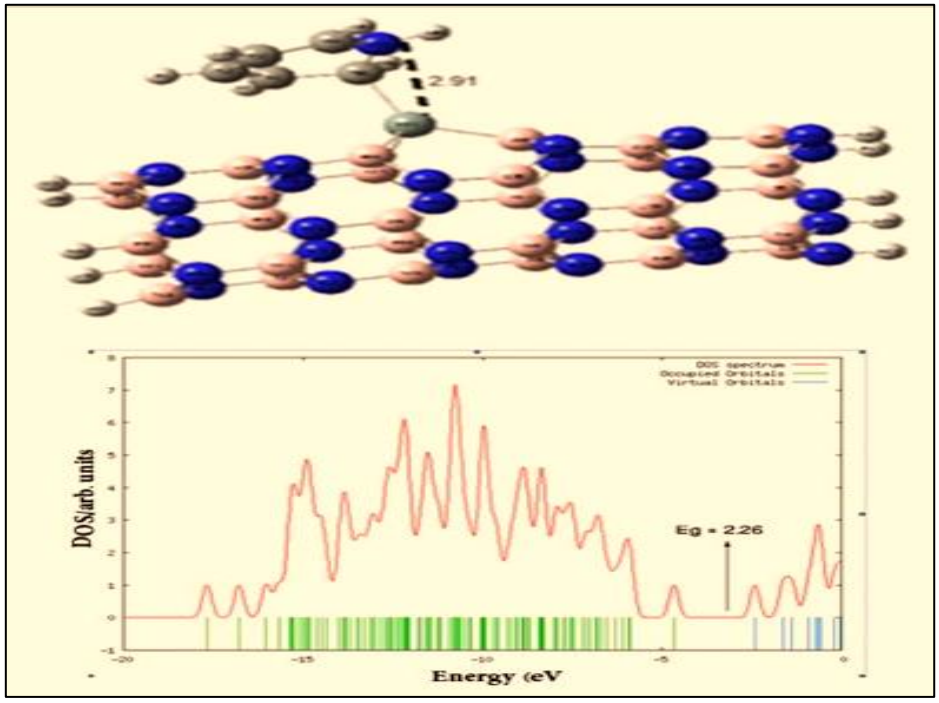

Figure 6: Pyrrole adsorption on doped Si nanotube and DOS diagram for observing E_g nanotube.

4. Conclusion:

The adsorption of an pyrrole(C5H6N) molecules on the surface of BNNT (boron nitride nanotube) has been 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 modify the nanotubes as an effective adsorbent of pyrrole molecule in gas sensors which are sensitive about pyrrole. 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.

Acknowledgment:

We are appreciating and thanking Islamic Azad University of Mahshahr in advance due to their financial supports.

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