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Original Article

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ADSORPTION OF PYRIDINE BY USING BeO NANOTUBE: A DFT STUDY

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Abstract:

Electrical sensitivity of a beryllium oxide nanotube (BeONT) was examined toward (C_5H_5N) molecule by using density functional theory (DFT) calculations at the B3LYP/6-31(d) level, and it was found that the adsorption energy (E_{ad}) of pyridine on the pristine nanotubes is a bout -73.29kcal/mol. But when nanotubes has been doped with S and P atomes , the adsorption energy changed . Calculation showed that when the nanotube is doping by P, the adsorption energy is about -39.59kcal/mol and also the amount of HOMO/LUMO energy gap (E_g) will reduce significantly (Eg=2.55Ev). The BeONT doped with P is suitable semiconductor than the pristine BeONT.

Keywords: Nanotube, DFT, Pyridine

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1. Introduction:

Pyridine is a colorless, volatile, flammable, and toxic organic liquid that gives off an unpleasant order when present in wastewater. Pyridine is widely used as a solvent in paints and an intermediate in the manufacture of insecticides, herbicides, vitamins, colorants [1-3]. Pyridine and its derivatives are very toxic for aquatic and human life [2]. 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[8-9].More recently, models of pristine beryllium oxide nanotubes (BeONT) were proposed and their structural, cohesive and electronic properties were predicted [10-11].BeO compound often demonstrates different properties from the counterpart of C , BN and SiC because of the large iconicity of Be-O bond. For example, wurtzite BeO is an insulator with a wide band gap, high melting point, high thermal conductivity and large elastic constants [12] .Previously adsorption different molecules toward nanostructures has been studied [13-16]. In this study, the adsorption of pyridine on the pristine case BeONT while S and P atoms are in its structure has been investigated.

2. Computational methods:

Computation procedures are including the following**:**

We have optimized the pyridine molecule and BeONT at the B3LYP/6-31G (d) level of theory. BeONT is made up of 56O , 56Be atoms was saturated by 16 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 128 atoms (Fig.1).

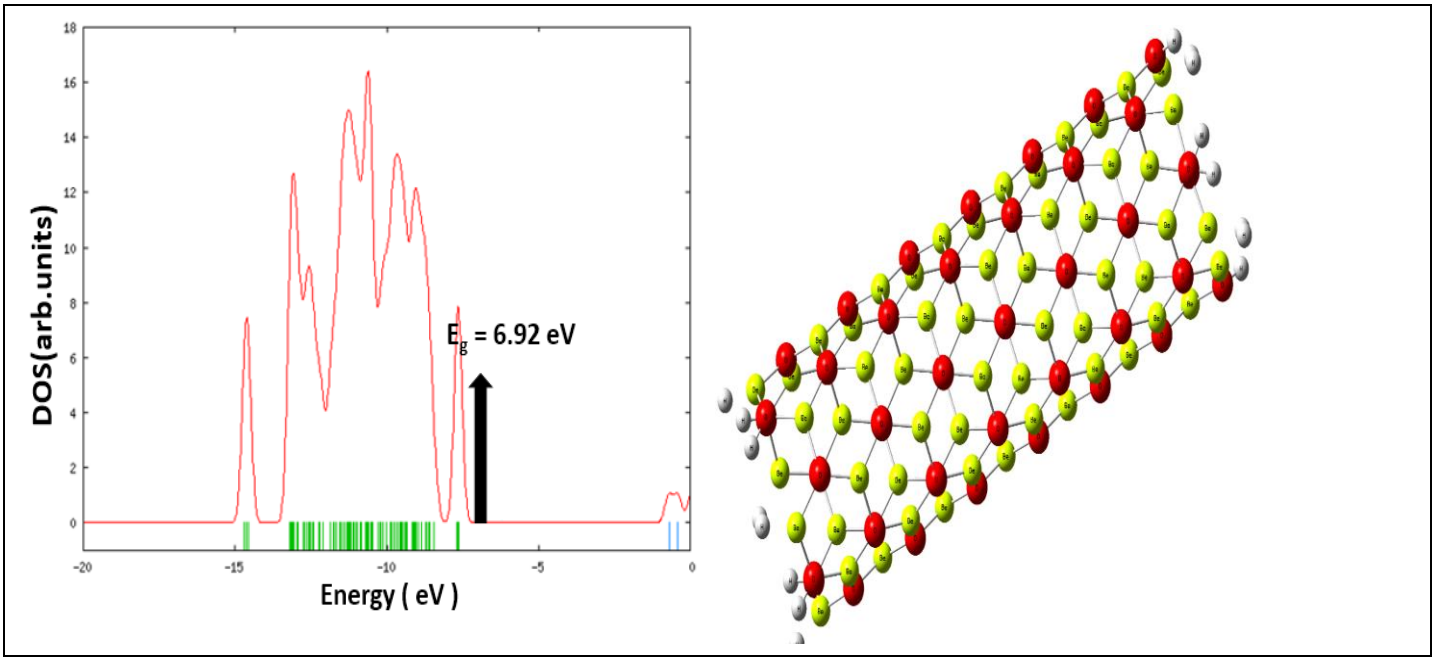

Figure1: BeONT and DOS diagram for E_g of nanotube.

The BeONT that has been selected is armchair (4, 4) type and GAMESS software [17] is used to perform these calculations. The B3LYP is demonstrated to be a reliable and commonly used functional in the study of different nanostructures [18-20].We made pyridine molecule from different positions of the site to be close to the nanotube and its adsorption has been calculated by using the equation 1.

$$E_{ad}=E_{Nanotube\ +Pyridine} - [E_{Pyridine} + E_{Nanotube}] + \delta_{BSSE} \qquad [1]$$

According to the mentioned equation EPyridine is pyridine molecule's energy, ENanotube is the nanotube energy and E Nanotube +Pyridine is the nanotube's energy whit pyridine. In addition, δBSSE is representing the basis set super position error. In the following steps S and P atoms in the nanotube structure have been doped to examine the pyridine adsorption on the nanotube and conductivity that which is doping with S and P atoms.

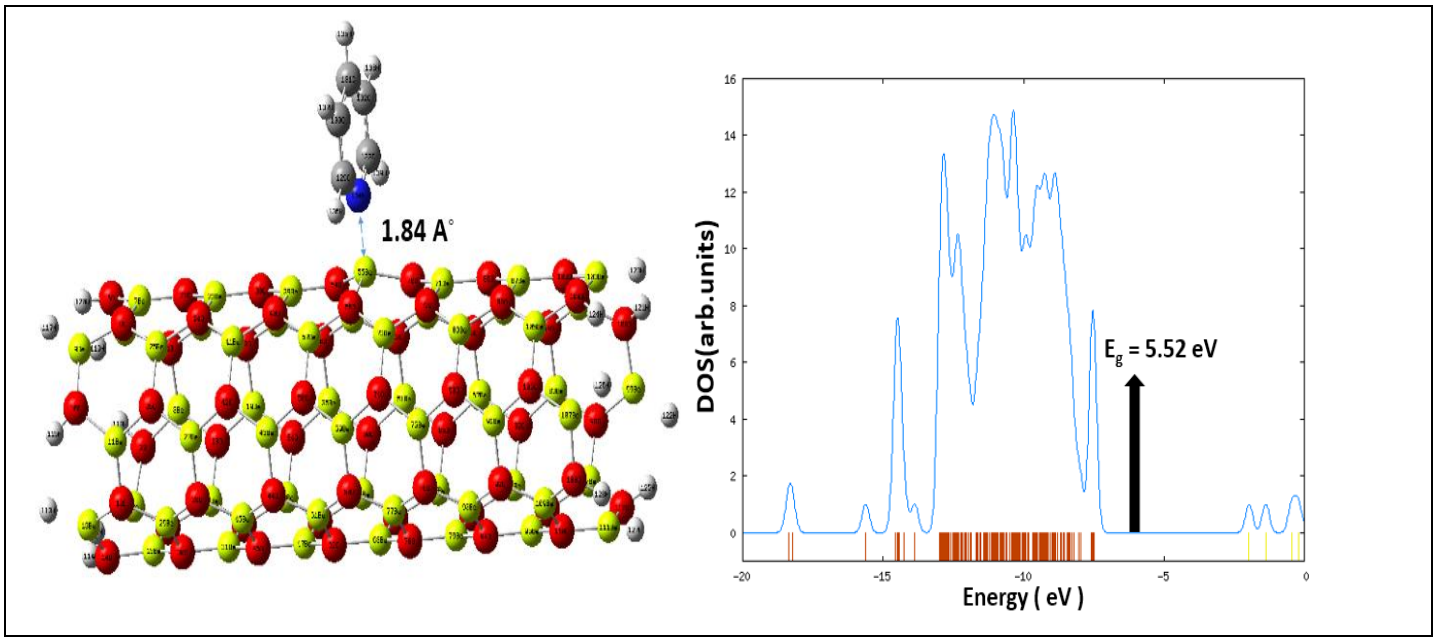

Figure 2: Pyridine adsorption on the BeONT and DOS diagram for observing E_g of nanotube.

3. Results and discussion:

In Figure 1, is showing the structure of beryllium oxide nanotube (BeONT), in order to obtain the most stable adsorption mode of C5H5N molecule on different position of BeONT, the most stable configuration has shown in Figure 2, that oxygen atom of pyridine is 1.84A0 far from beryllium atom of the nanotube .Entailed information of the structure and electronic properties of the BeONT including the HOMO/LUMO energy gap (Eg) is shown in table 1. In which adsorption energy (Ead) for mentioned configuration of pyridine and nanotube is about -73.29kcal/mol and then we calculated the HOMO/LUMO energy gap (Eg) for pristine nanotube since the pyridine 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. E_{ad} (kcal/mol),eV for the others

System	E_{ad}	E_{HOMO}	E_{LUMO}	E_g
BeONT	-	-7.62	-0.7	**6.92**
BeONT-Pyr	-73.29	-3.56	-1.96	**5.52**
BeO(O,S)	-	-7.63	-0.73	**6.90**
BeO(O,S)Pyr	-55.65	-7.26	-1.94	**5.32**
BeO(O,P)	-	-1.87	-0.68	**2.55**
BeO(O,P)Pyr	-39.59	-5.53	-1.32	**4.21**

3.1 Adsorption of C_5H_5N on P doped BeONT:

To examine the sensitivity of the adsorption of BeONT of C5H5N as an adsorbent for C5H5N examining has been done two times, once Be atom doped by P atom and other time O atom by P atom has been doped. Doped calculation of P on BeONT shows that the value of Eg is less than the pristine nanotube (Fig.3). DOS diagram clearly shows that when P doped on the BeONT it will become a semiconductor. The BeONT is a suitable absorbent for pyridine molecule. But when BeONT doped by P the adsorption energy is less than when we just use the pristine BeONT .If Ead is significantly increased then it expect that recovery will be so long, meanwhile according to transition state theory and recovery time can be explain as equation[2].

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

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 table1 show that the recovery time and adsorption energy is suitable level. (Fig.4)

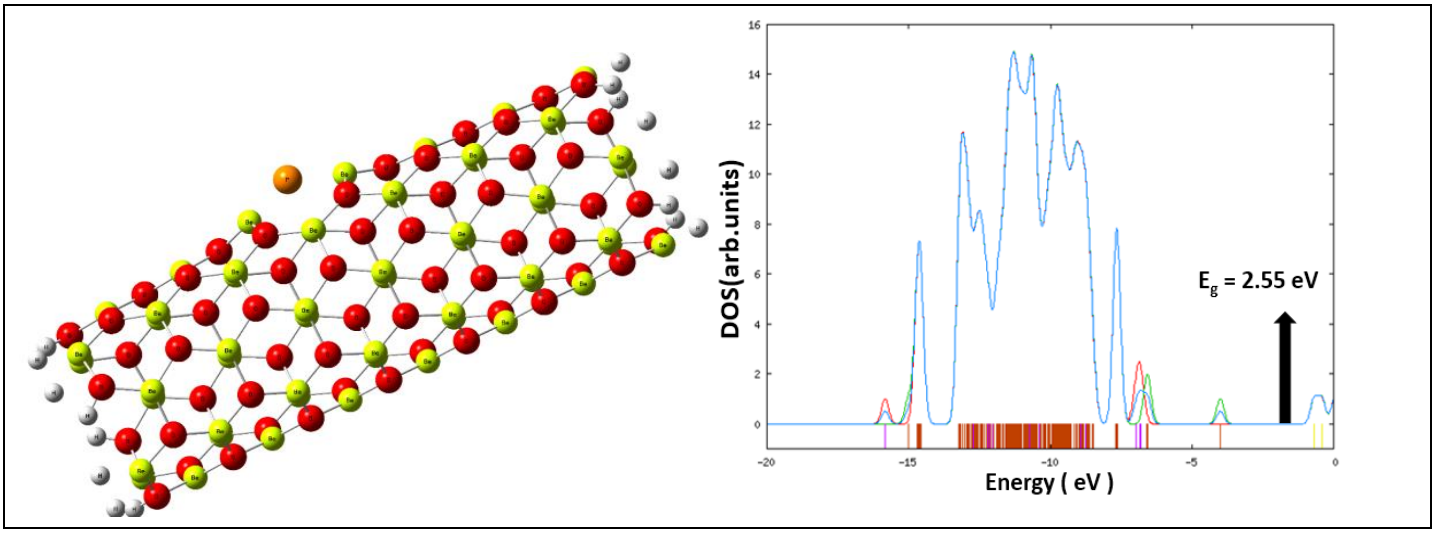

Figure 3: Doped nanotube by p and DOS diagram for E_g of nanotube.

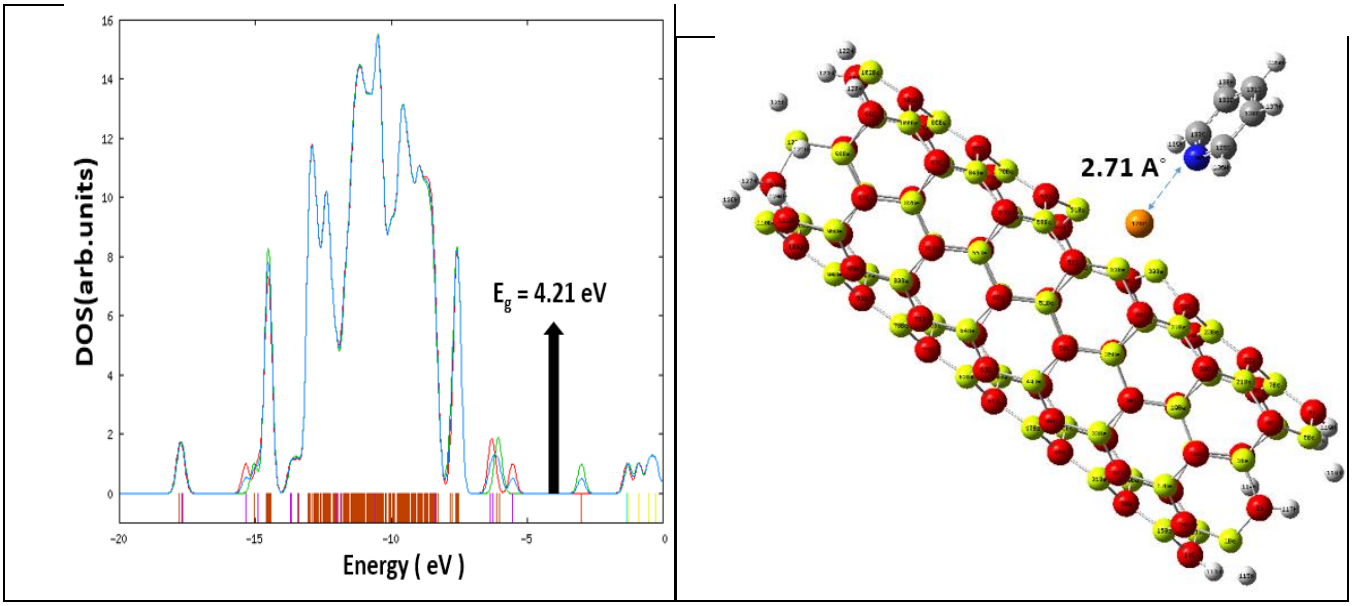

Figure 4: Pyridine adsorption on doped nanotube by P and DOS diagram for observing E_g of nanotube.

3.2 Adsorption of C_5H_5N on S doped BeONT:

At this stage doping have been studied with another element. First, instead of Be atom in the beryllium oxide nanotube a S atom and then instead of O atom in the S atom replaced in a nanotube(Fig.5), and then geometrical structures and electronic properties of BeONT has been doped and its adsorption behavior have been studied. Computations showed that when S replaced by Be in BeONT the Eg will become less (Fig.6).When S is sitting of O and Be, and the adsorption energy of pyridine on nanotube is less than when we just use the pristine nanotube (not doped). After adsorption of C5H5N on the mentioned nanotube that has doped by P the HOMO/LUMO energy gap (Eg) will decrease and therefore a substantial increasing will happen in conductivity that this phenomenon can be explain as equation 3,[21]

$$\sigma \propto \exp(-E_g /2kT) \qquad [3]$$

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.

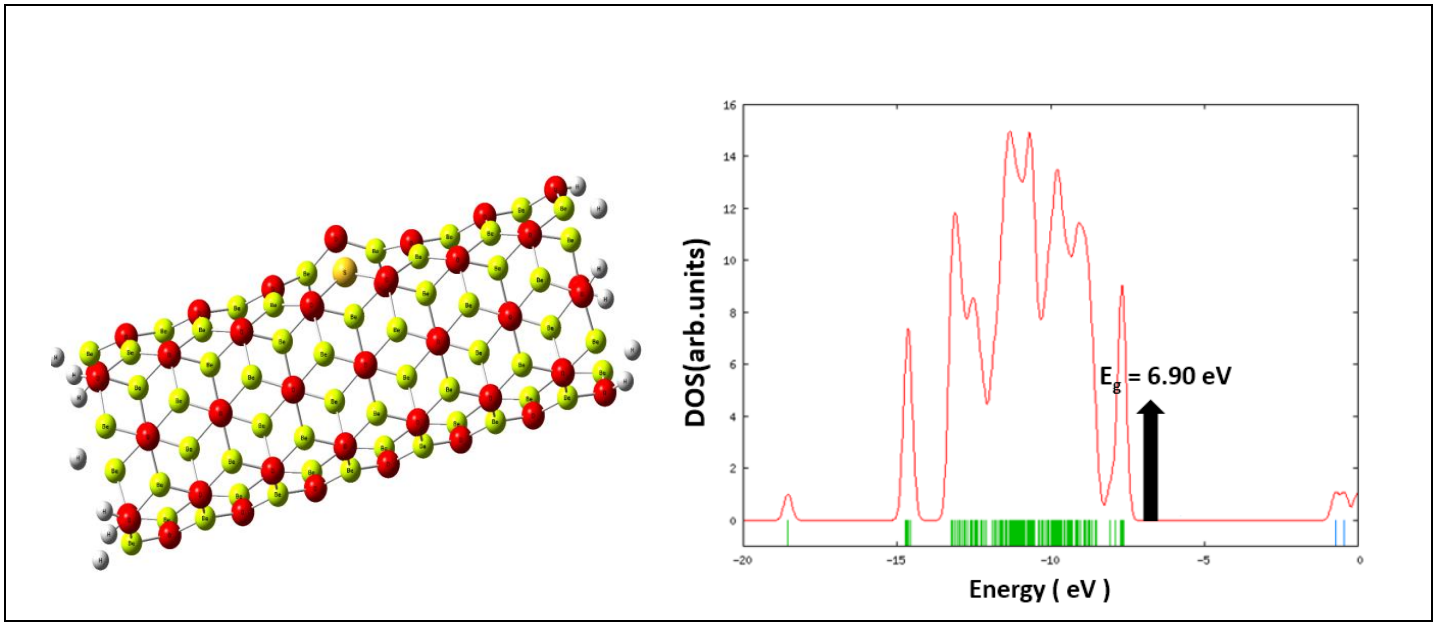

Figure 5: Doped nanotube by S and DOS diagram for Egnanotube.

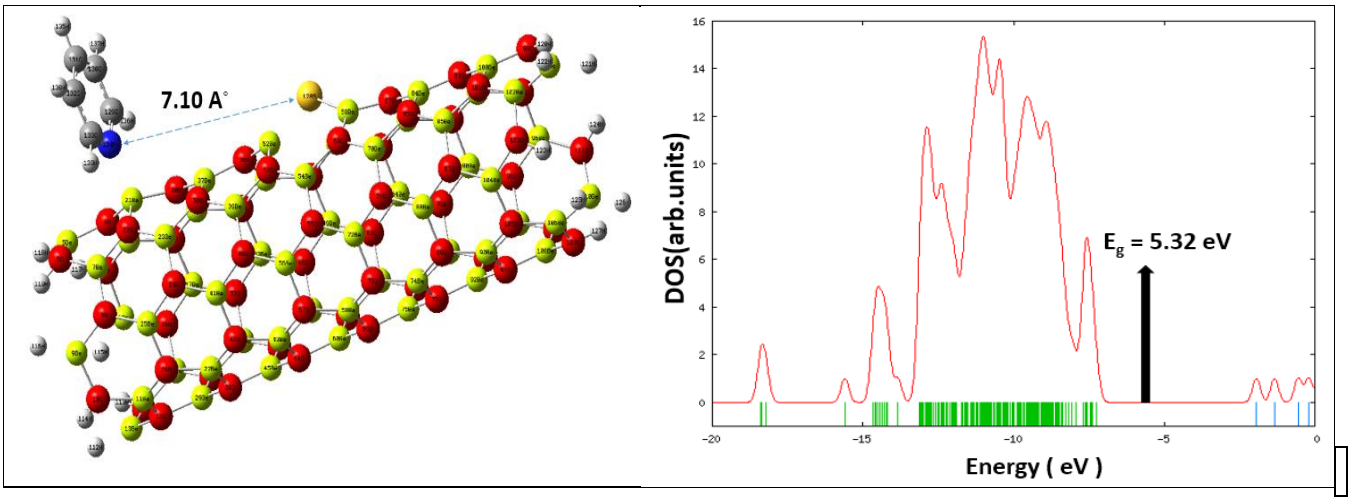

Figure 6: Pyridine adsorption on doped S nanotube and DOS diagram for observing E_g nanotube.

4. Conclusion:

The adsorption of an pyridine (C5H5N) molecules on the surface of BeONT (beryllium oxide nanotube) has studied by using density functional theory (DFT) and then we doped the S and P atoms in the structure of the nanotube, the results show it is clearly possible to modifying the nanotube is not suitable adsorbent of pyridine molecule in gas sensors. When P is doped on BeONT the Eg is less than piristine BeONT and it lead to more conductivity. The BeONT doped with P is a suitable semiconductor than the piristine BeONT. These results may be open a new gate to chemically modifiing the nanotubes in away to expand the fields of its applications in industry and technology.

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