Adsorption of Aniline Toxic Gas on a BeO Nanotube

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ABSTRACT: *Electrical sensitivity of a beryllium oxide nanotube (BeONT) was examined toward aniline (C_6H_5 NH_2) 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 aniline on the pristine nanotubes is about -19.06kcal/mol. However, when nanotube has been doped by P and S atoms, the adsorption energy of aniline molecule was decreased. The calculation showed that when the nanotube is doped by S, The adsorption energy is about -8.61kcal/mol and also the amount of HOMO/LUMO energy gap (E_g) will reduce significantly. As a conclusion, Beryllium oxide nanotube is a suitable adsorbent for aniline and can be used in different processes of aniline. It seems that nanotube (BeONT) is an appropriate semiconductor after being doped. The doped BeONT in the presence of aniline generates an electrical signal directly and therefore can be potentially used for aniline sensors.*

KEYWORDS: *Sensor; Nanotube; DFT; Aniline.*

INTRODUCTION

Aniline is one of the substances toxic to humans [1]. This compound used in various industries such as pharmaceutical, dyestuff, pesticide and etc. Because of the deleterious effects of aniline, removing that from the environment is considered seriously [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].

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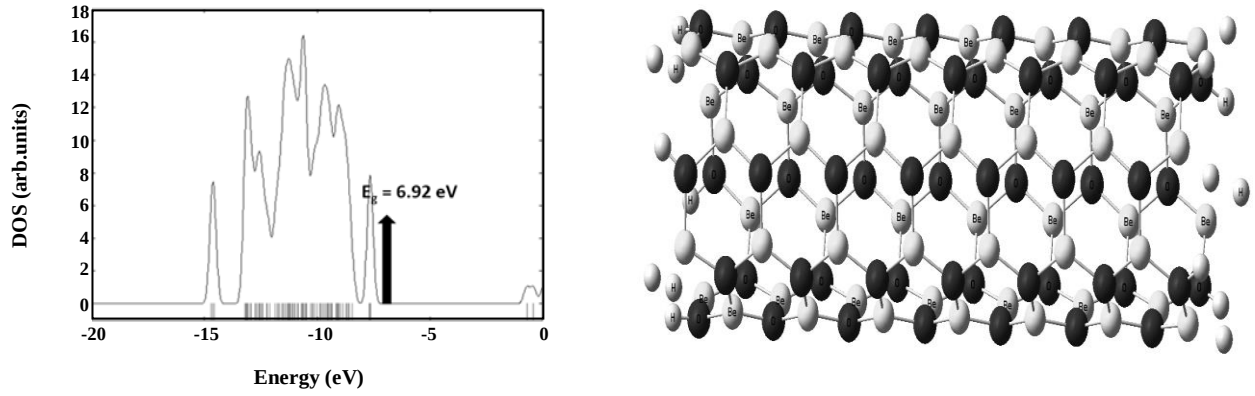

Fig. 1: BeONT and DOS diagram for E_g of the nanotube.

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 [6-8].

More recently, models of pristine beryllium oxide nanotubes (BeONT) were proposed and their structural, cohesive and electronic properties were predicted [9]. 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 [10]. Previously, adsorption of different molecules toward nanostructures has been studied [11-14]. In this study, the adsorption of aniline on the pristine BeONT and doped by S and P atoms have been investigated.

COMPUTATIONAL METHODS

We have optimized the aniline molecule and BeONT at the B3LYP/6-31G (d) level of theory [15-19]. BeONT is made up of 56O, 56Be atoms saturated by 16 hydrogen atoms which are located in initial and end part of the nanotube. The reason for utilizing this process is to decrease the boundary effects in the structure of the whole nanotube. (Fig. 1).

The BeONT that has been selected is armchair (4, 4) type and GAMESS software [20, 21] is used to perform these calculations. The B3LYP is demonstrated to be a reliable and commonly used functional in the study of different nanostructures [22-24]. We made aniline 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 Equation (1).

$$E_{ad} = E_{Nanotube+Aniline} - \left[E_{Aniline} + E_{Nanotube}\right] + \delta_{BSSE} \qquad (1)$$

According to the mentioned equation, $E_{Aniline}$ is aniline molecule's energy, $E_{Nanotube}$ is the nanotube energy and $E_{Nanotube+Aniline}$ is the nanotube's energy with aniline. In addition, δ_{BSSE} 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 aniline adsorption on the nanotube and conductivity which has been doped with S and P atoms.

RESULTS AND DISCUSSION

Fig. 1, shows the structure of beryllium oxide nanotube (BeONT), in order to obtain the most stable adsorption mode of aniline molecule on different positions of BeONT, the most stable configuration is shown in Fig. 2, that carbon atom of aniline is 1.89Å far from oxygen atom of the nanotube.

Detailed information of the structure and electronic properties of the BeONT including the HOMO/LUMO energy gap (E_g) are shown in Table 1 in which adsorption energy (E_{ad}) for mentioned configuration of aniline and nanotube is about -19.06kcal/mol. We calculated the HOMO/LUMO energy gap (E_g) for pristine nanotube since the aniline molecule is adsorbed on the nanotube (Table 1). The 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
BeONT	-	-7.62	-0.70	6.92
Ani/BeO	-19.06	-7.01	-0.80	6.21
BeO/ (O,S)	-	-7.63	-0.73	6.90
BeO/(O,S)Ani	-8.61	-5.63	-0.71	4.92
BeO/(O,P)	-	-6.55	-4.00	2.55
BeO/(O,P)Ani	-9.29	-5.76	-3.88	1.88

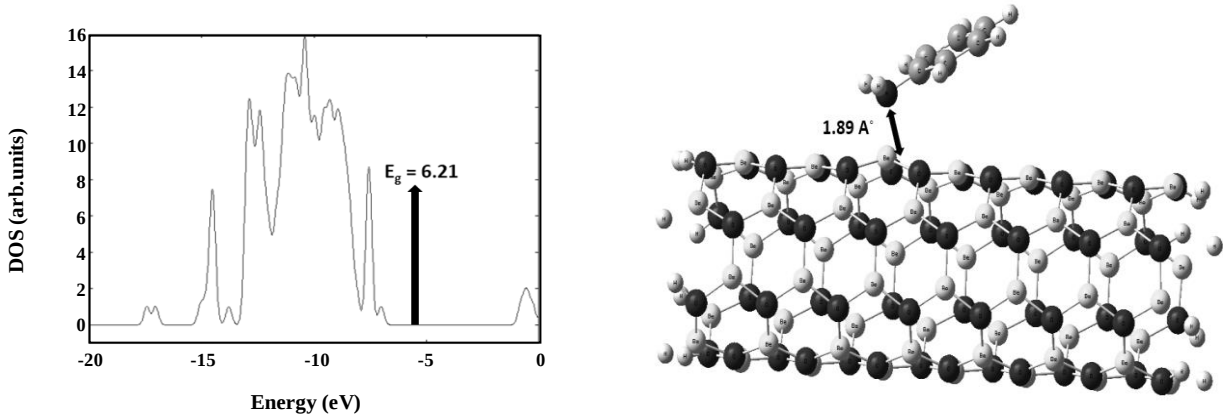

Fig. 2: Aniline adsorption on the BeONT and DOS diagram for observing E_g of the nanotube. Distance is in Å.

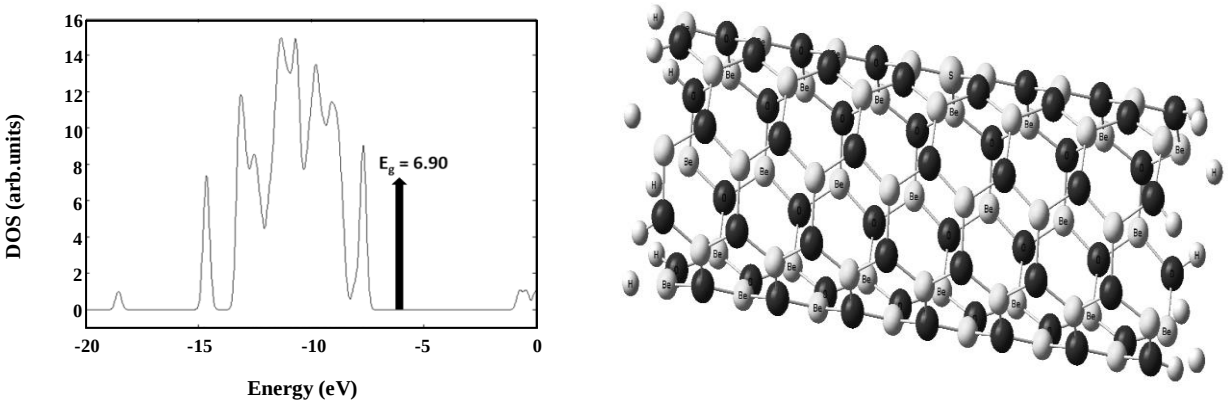

Fig. 3: Doped nanotube by S and DOS diagram for E_g of the nanotube.

Adsorption of $C_6H_5NH_2$ on BeONT doped by S

To examine the sensitivity of the adsorption of BeONT of $C_6H_5NH_2$ as an adsorbent for $C_6H_5NH_2$ its examining has been done, The oxygen atom doped by S. Doped calculation of S on BeONT shows that the value of HOMO/LUMO energy gap (E_g=4.92eV) is less than the pristine nanotube with E_g=6.90eV (Fig. 3) and the best adsorption energy (E_{ad}=-8.61kcal/mol) is obtained when S sitting instead of O and aniline has been adsorbed. When S doping on BeONT in the presence of aniline electrical signal is generation directly and therefore can potentially be used for aniline sensors. DOS diagram clearly shows that when S is doped on the BeONT (Fig. 3) it will become a semiconductor (E_g=6.90eV).

Optimization of these types of interactions is desirable for gas detection because such strong interactions mean

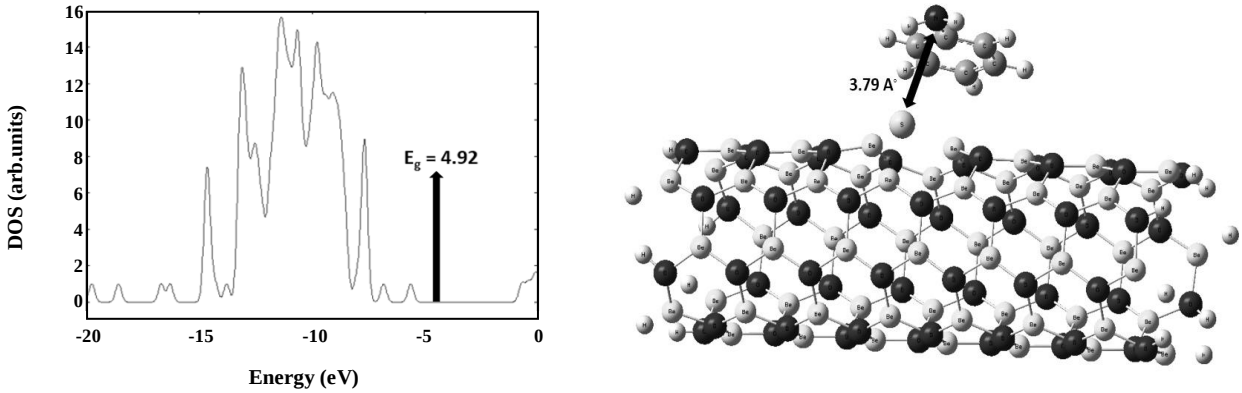

Fig. 4: Aniline adsorption on doped nanotube by S and DOS diagram for observing Eg of the nanotube.

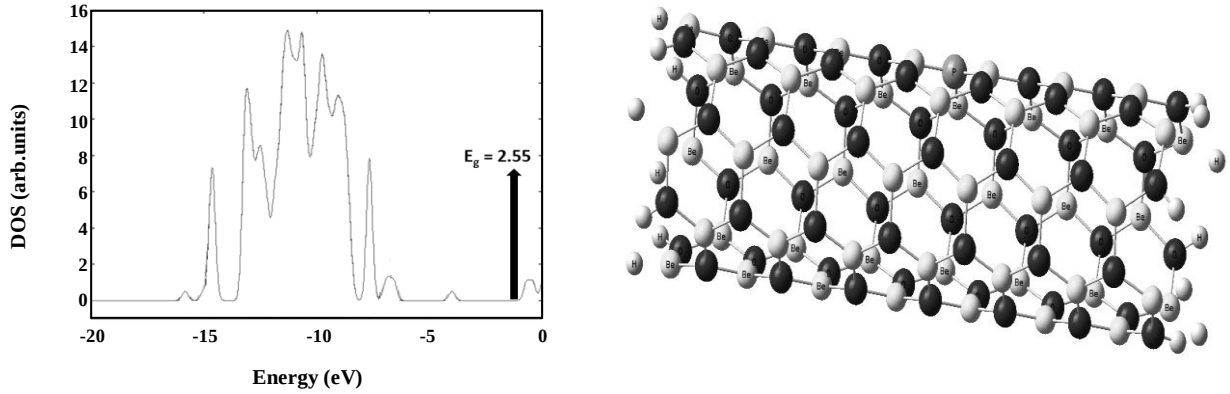

Fig. 5: Doped nanotube by P and DOS diagram for E_g of the nanotube.

that the BeONT is a suitable absorbent for aniline molecule (Fig. 4).

Adsorption of $C_6H_5NH_2$ on BeONT doped by P

At this step, doping is studied with other elements. First, O atom is replaced by a P atom in the beryllium oxide nanotube (Fig. 5). Then geometrical structures, electronic properties and adsorption behavior of BeONT and doped Nanotube are studied (Fig. 5).

Computations showed that when O replaced by P in BeONT, the HOMO/LUMO energy gap (e.g. E_g=2.55eV) will become less than pristine nanotube's. (Fig. 5).

When p is replacing O, the adsorption energy of aniline on nanotube is -9.29kcal/mol that is less than the pristine nanotube's (E_g=-19.06kcal/mol).

After adsorption of $C_6H_5NH_2$ on the mentioned nanotube that has doped by P, the HOMO/LUMO energy gap is obtained 1.88eV which is less than the pristine nanotube (Fig. 6) and therefore a substantial increase will occur in conductivity and this phenomenon can be explained as Equation (2).

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

Where σ is conductivity, T is temperature and k is Boltzmann constant. According to this equation, while E_g decreases; the conductivity will increase. Therefore P is a suitable element for being doped in BeONT.

CONCLUSION

The adsorption of an aniline ($C_6H_5NH_2$) molecule on the surface of BeONT (beryllium oxide nanotube) has been studied by using Density Functional Theory (DFT) and then we doped the S atom in the structure of the nanotube, the results show that it is clearly possible to modify the nanotube as an effective adsorbent of aniline molecule in gas sensors which are sensitive to aniline.

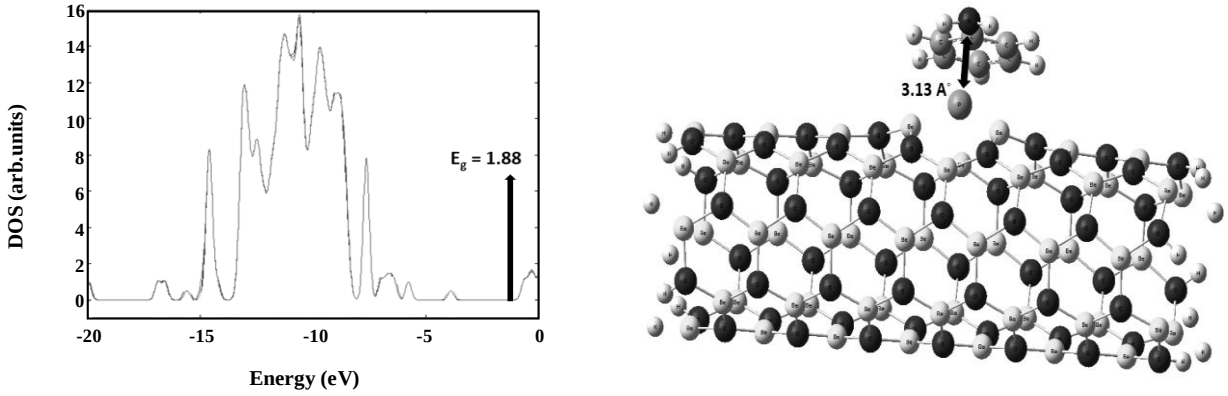

Fig. 6: Aniline adsorption on doped nanotube by P and DOS diagram for observing of E_g nanotube.

These results may open new doors to chemically modify the nanotubes thereby expand the fields of their applications in industry and technology.

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