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Original Article

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Adsorption of ethanol by using BN nanotube: A DFT study

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Abstract:

Electrical sensitivity of a boron nitride nanotube (BNNT) was examined toward C_2H_5OH molecules by using density functional theory (DFT) calculations . It was founding that the adsorption energy(E_{ad}) of ethanol on the pristine nanotubes is about -51.5 kJ / mol, but when the nanotube has been doped with Si and Al atoms , the adsorption and recovery time changed and the sensitivity of nanotube toward ethanol was increased. Calculations showed that when the nanotube is doping ,the adsorption energy(E_{ad}) is about -20.2 kJ/mol that leads to decrease the recovery time and also due to doping the nanotube with Si , the amount of HOMO/LUMO energy gap (E_g) will reduce significantly . Therefore , when C_2H_5OH molecule toward to BBNT, the nanotube has produced electrical signals and it seems that these nanotubes can be used as adsorbents for the sensors which are sensitive about C_2H_5OH molecule.

Keywords: Sensor, nanotube, DFT

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Introduction:

Ethanol or ethyl alcohol with C_2H_5OH chemical formula is a flammability chemical material with specific smell. Ethanol has many industrial applications and it can exert both positive and negative actions (anti-anxiety) in humans. [1,2] In industry, ethanol is using as a solvent and chemical intermediate for the production of organic compounds . Recently carbon nanotubes (CNTs) have emerged as promising alternative for hydrogen storages, gas sensors, and others [2-4].Boron nitride nanotubes (BNNTs) have particular and unique properties and also have a semiconductor behavior. This behavior reason is the total atomic number of B and N [5-7], that an interesting case for studding about these BNNTs is investigating they composite types [8,9]. BNNT has different electronic properties by comparing with the CNT [1]. BNNT has a much wider energy, small band gap and finally it is a semiconductor which is a very interesting material to be applicative in nanoscale devices . Modifying electronic properties of nanotubes is an important issue for designing nanao base in nano instruments . BNNT has composed by of a single layer rotation of sp^2 . BNNT's unique properties including tensile strength, stiffness and deformation are the feature of this nanotube[10-12].Spiral structure around the pipe can cause the superconducting, conductors, semiconductors or insulators properties . In this study, the adsorption of ethanol on the pristine case BNNT while Al and Si atoms which are in its structure has been investigated.

Computational methods:

Computation procedures are include the following: We've optimized the ethanol molecule and BNNT at the B3LYP/ 6-31G(d) level of theory . BNNT which is made up of 30 N, 30 B atoms was 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 (Figure 1). The BNNT that has been selected is zigzag (5,0) type and GAMESS software is used to perform these calculations. B3LYP has been shown to be safe and reliable command line that usually used and studied for various nanostructures. We made ethanol molecule from different positions of the sites to be close to the nanotube and the it's adsorption has been calculated by using the equation 1.

$$E_{ad} = N_{anotube+Ethanol} - [E_{thanol} + N_{anotube}] + \delta_{BSSE} \qquad [1]$$

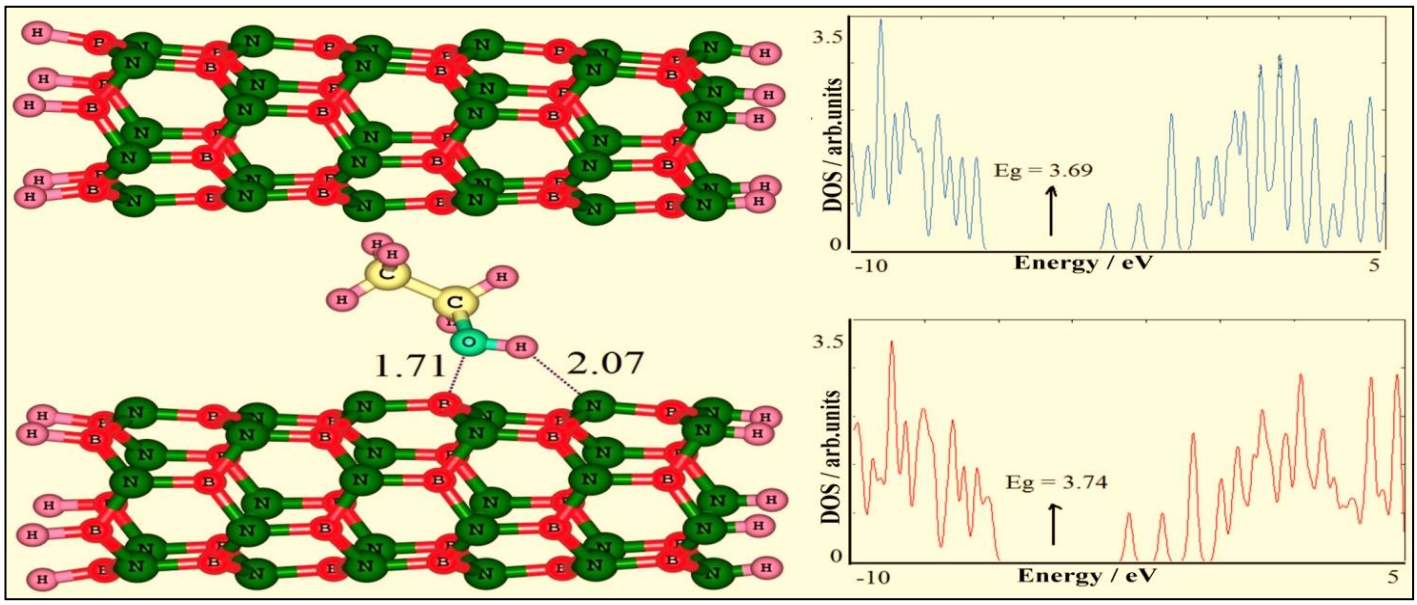

Figure 1: Ethanol adsorption on the BNNT and DOS diagram for observing E_g of Nanotube

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

Results and discussion:

Figure 1 is showing the structure of boron nitride nanotube. In order to obtain the most stable adsorption mode of C_2H_5OH molecule on different positions of BNNT ,the most stable case has shown in Figure 1 ,oxygen atoms of ethanol is 1.71A° far from boron atom of the nanotube and hydrogen atom of ethanol is 2.07A° far from nitrogen atom of the nanotube.Detailed information of the structure and electronic properties of BNNT including adsorption energy (E_{ad}) has been shown in Table 1. That the adsorption energy for mentioned configuration of ethanol and nanaotube is about E_{ad} = - 51.5 kJ/mol. The HOMO/LUMO energy gap (E_g) has been calculated (Table 1) and the diagram which shows E_g has been obtained by using DOS(density of state) software.

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

System	E_{ad}	E_{HOMO}	E_{LUMO}	E_g	$\Delta E_g(\%)$
BNNT	-	-6.45	-2.76	3.69	-
E-BNNT	-51.5	-6.21	-2.47	3.74	**+1.3**

Adsorption of C2H5OH on Al-doped BNNT:

To examine the sensitivity of the adsorption of boron nitride nanotube of ethanol as an adsorbent for ethanol it examining has done tow times, once B atom doped by Al atom and other time N atoms by Al has been doped . Doped calculations of Al on BNNT shows that the value of E_g is less than the pristine nanotube (Fig.2) and the best E_{ad} is when Al sitting instead of B and ethanol has been adsorbed. DOS diagram clearly shows that when Al is doped on BNNT it will become a semiconductor. Then the investigation of C_2H_5OH adsorption for doped Al on boron nitride nanotube from oxygen side of ethanol has been studied (Fig.3). Optimization of these types of interactions are desirable for gas detection because such strong interactions means that the BNNT is a suitable adsorbent for ethanol molecule. If E_{ad} is significantly increased then it expect that recovery time will be so long that according to transition state theory and recovery time can be explain equation 2.

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

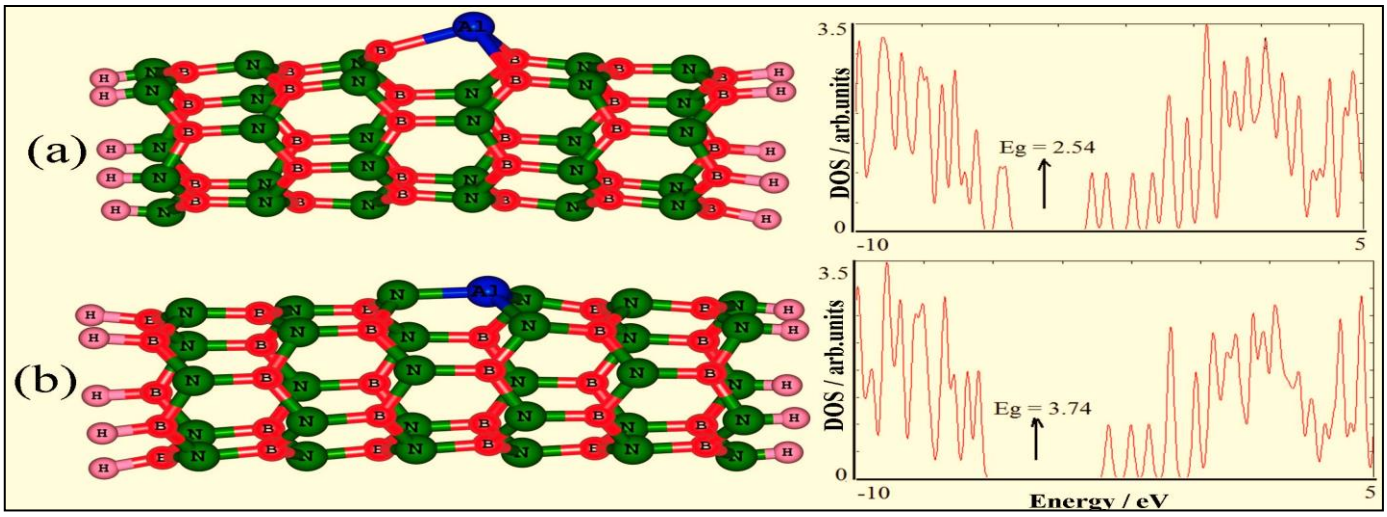

Figure 2: Doped nanotube by Al and DOS diagram for observing E_g nanotubes

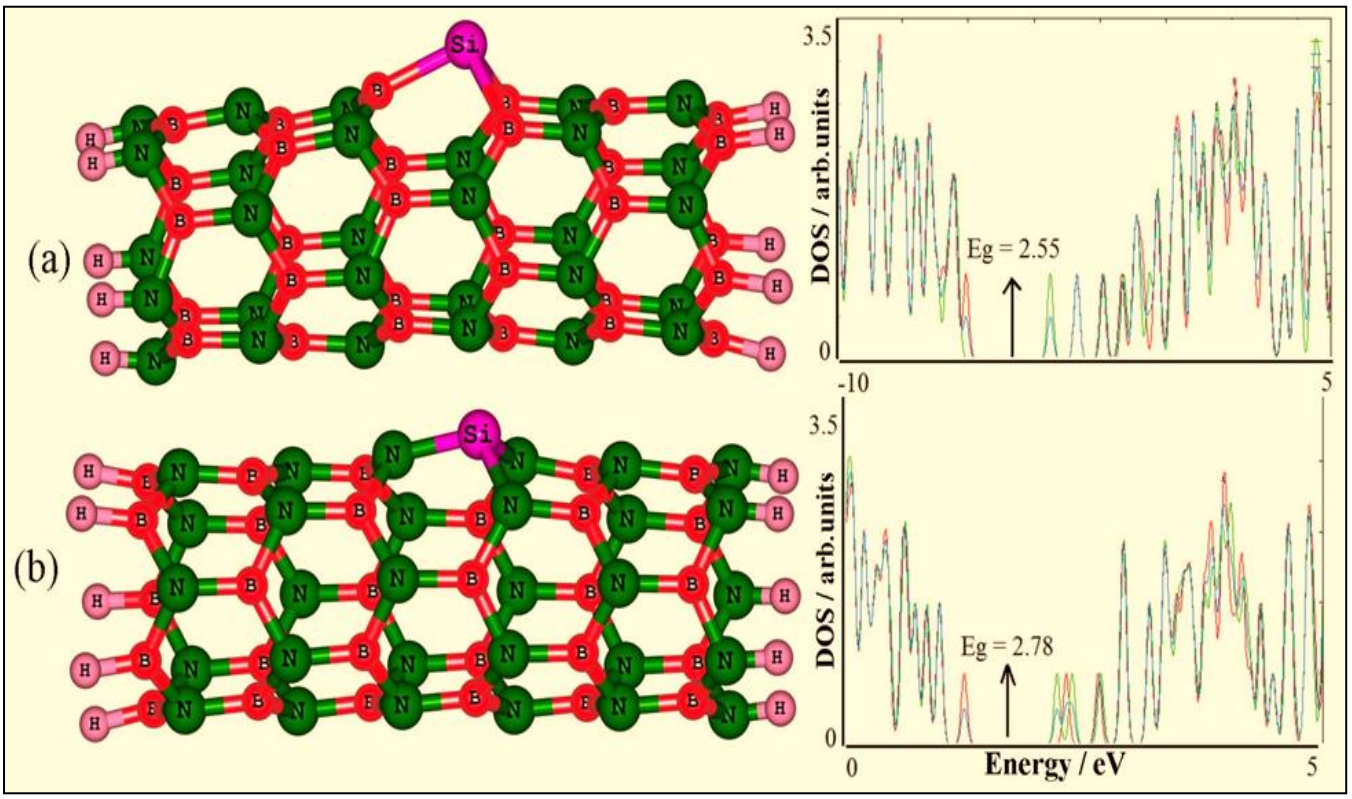

Figure 3: Doped nanotube by Si and DOS diagram for observing E_g nanotubes

That in this equation τ represents the recovery time ,T is temperature ,k is Boltzman constant and υ_0 is attempt frequency .According to this equation as often as adsorption energy is increasing the recovery time becomes longer and computations in Table 2 show that the recovery time and absorption energy is in suitable level. After computations we got it that when Al is sitting instead of N on BNNT the E_g will decrease(Fig.4).

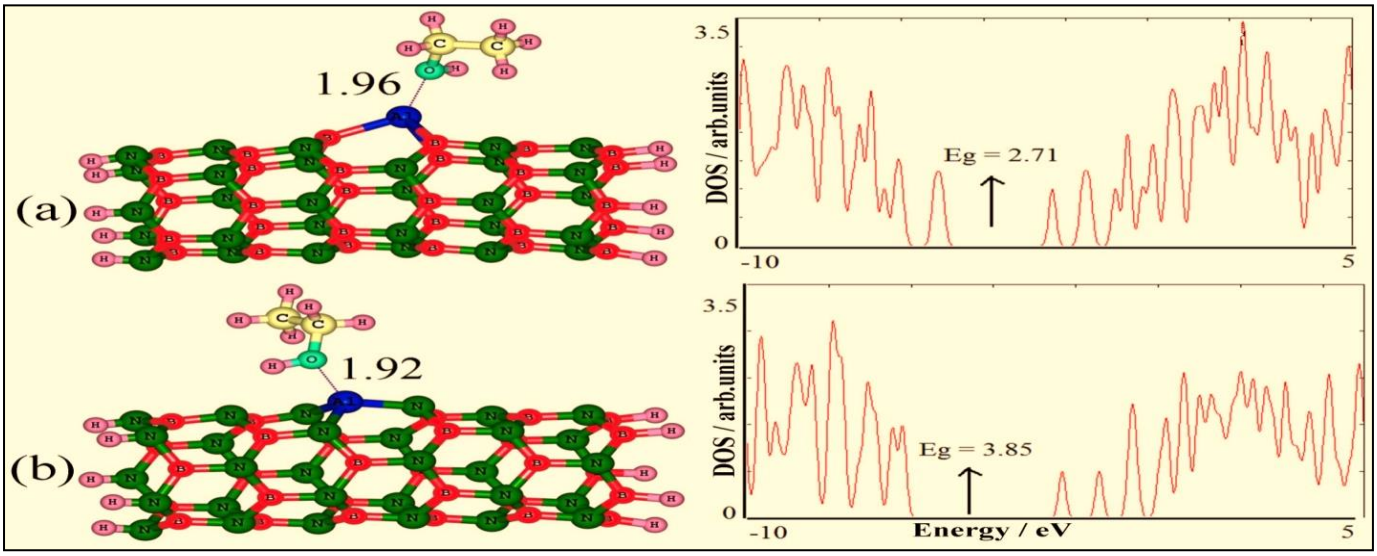

Figure 4: Ethanol molecule adsorption by the AL doped nanotube and DOS diagram for observing E_g of nanotubes

Adsorption of C2H5OH on Si-doped BNNT :

At this stage doping of nanotube has been studied with other 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 (Figure 3), and then geometrical structures and electronic properties of BNNT has been doped and its adsorption behavior has been studied. Computations showed that when Si replaced by N in BNNT the E_g will become less (Fig.5).

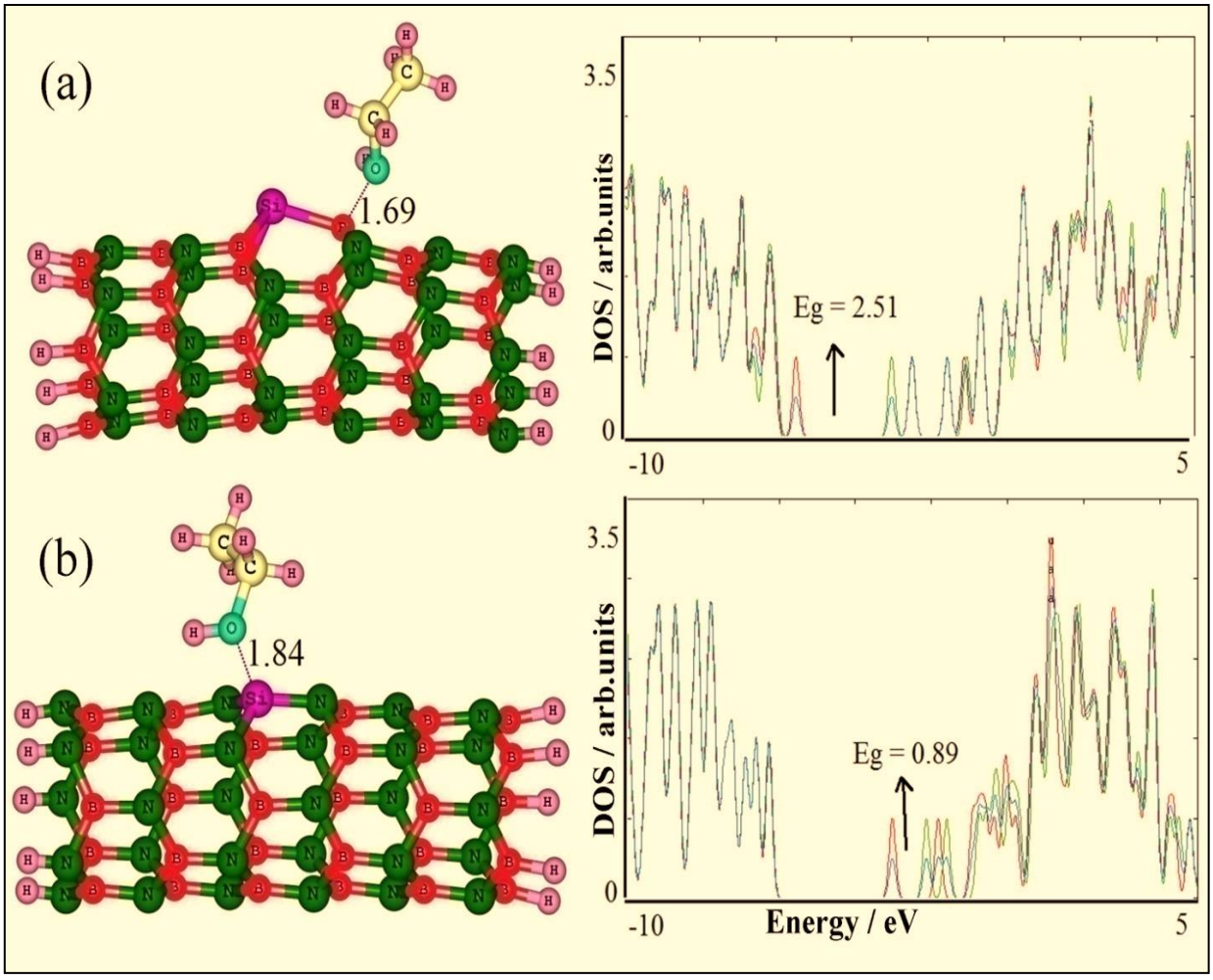

Figure 5: Ethanol molecule adsorption by the Si doped nanotube and DOS diagram for observing E_g of nanotubes

When Si is sitting instead of N and B atoms in BNNT the adsorption energy of ethanol on nanotube is less than when we just use the pristine nanotube and the same result is when Al is sitting instead of N and B (Table 2) . Therefore due to less adsorption energy lead to shorter recovery time and shows that BNNT that has been doped by Si is a suitable adsorbent for ethanol gas sensors which are sensitive about ethanol. After adsorption of C_2H_5OH on the mentioned nanotube that has doped by Si the E_g will decrease and therefore a substantial increasing will happen in conductivity meanwhile this phenomenon can be explained as equation 3 .

$$\sigma \propto \exp\left(\frac{-E_g}{2kT}\right) \qquad [3]$$

Where σ is conductance , T is temperature , k is the Boltzmann constant and according to this equation 3 as often as E_g is smaller it leads the conductivity to be more. It can be concluded that when Si is doping on BNNT in the presence of C_2H_5OH an electrical signal is generating directly and therefore can potentially be used for C_2H_5OH sensors.

Table2. E_{ad} (kJ/mol), eV for the others

System	E_{ad}	E_{HOMO}	E_{LUMO}	E_g	$^{*}\Delta E_g(\%)$
Si_N	-	-6.06	-3.51	2.55	-
Si_N-E	-40.8	-5.47	-2.96	2.51	-1.7
Si_B	-	-5.73	-2.95	2.78	-
Si_B-E	-20.2	-3.02	-2.13	0.89	-68.0
Al_N	-	-5.54	-3.00	2.54	-
Al_N-E	-145.0	-5.03	-2.32	2.71	+6.7
Al_B	-	-6.41	-2.67	3.74	-
Al_B-E	-171.8	-6.18	-2.33	3.85	+2.9

Conclusion:

The adsorption of an ethanol (C_2H_5OH) molecule on the surface of BNNT(boron nitride nanotube) has studied by using density functional theory (DFT)calculations, and then we doped the Si and Al atoms in the structure of the nanotube ,the results show it is clearly possible to modifying nanotubes as an effective adsorbent of ethanol molecule in gas sensors which are sensitive about C_2H_5OH.These results may be open a new gate to chemically modifying the nanotubes in a way to expand the fields of its applications in industry and technology.

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