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Original Article

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Aniline adsorption on the surface of a BN nanotube: Computational study

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Abstract:

Electrical sensitivity of a boron nitride nanotube (BNNT) was examined toward aniline ($C_6H_5NH_2$) 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 a bout -19.03kcal/mol. But when nanotube has been doped with Si and Al atomes, the adsorption energy of aniline molecule was increase. Calculation showed that when the nanotube is doping by Al, the adsorption energy is about -27.73kcal/mol and also the amount of HOMO/LUMO energy gap (E_g) will reduce significantly. Boron nitride nanotube is a suitable adsorbent for aniline and can be used in separation processes aniline. It is seem that nanotube (BNNT) is a suitable semiconductor after doping, and the doped BNNT in the presence of aniline an electrical signal is generating directly and therefore can potentially be used for aniline sensors.

Keywords: Sensor, Nanotube, DFT, Aniline

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Introduction:

Aniline comes to light as a toxic compound for human [1,2]. It was reported that the amount of aniline that went into the environment has been estimated at 30000 tons annually [3], thus aniline detection and separation is very important. 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]. 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 [10-12]. An interesting case for studying about these BNNTs is investigating their composite type [13]. BNNTs unique properties including tensile strength, stiffness and deformation are the features of this nanotube [14-16]. Previously adsorption of different molecules toward nanostructures has been studied [17-20]. In this study, the adsorption of aniline on the pristine case BNNT while Si and Al atoms are in its structure has been investigated.

Computational methods:

Computation procedures are include the following:

We have optimized the aniline 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).

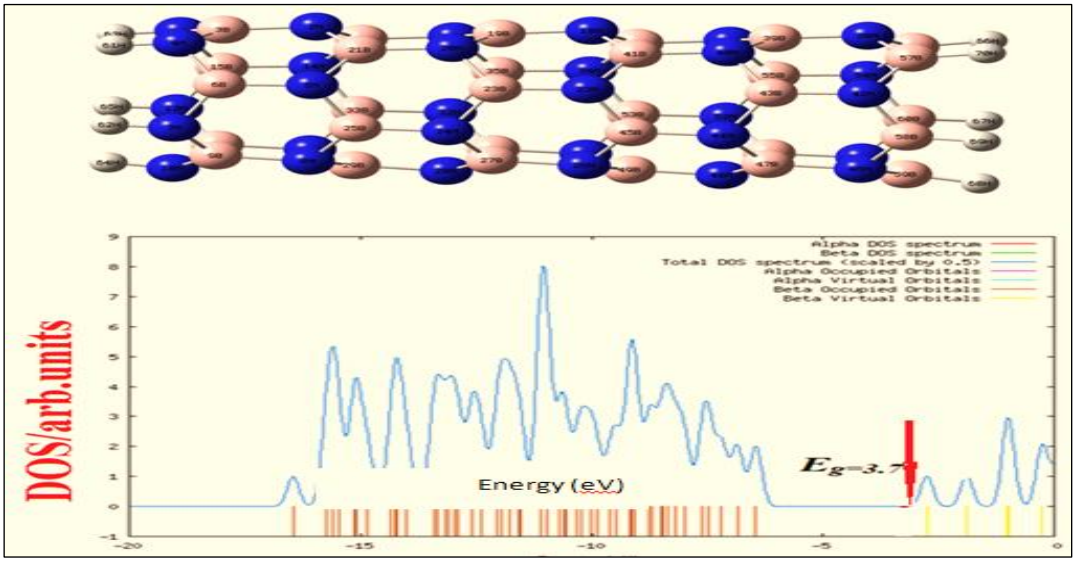

Figure1: BNNT and DOS diagram for E_g nanotube .

The BNNT that has been selected is zigzag (5,0) type and GAMESS software [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 anilie 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).

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

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 whit aniline. 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 aniline adsorption on the nanotube and conductivity that which is doping with Si and Al atoms.

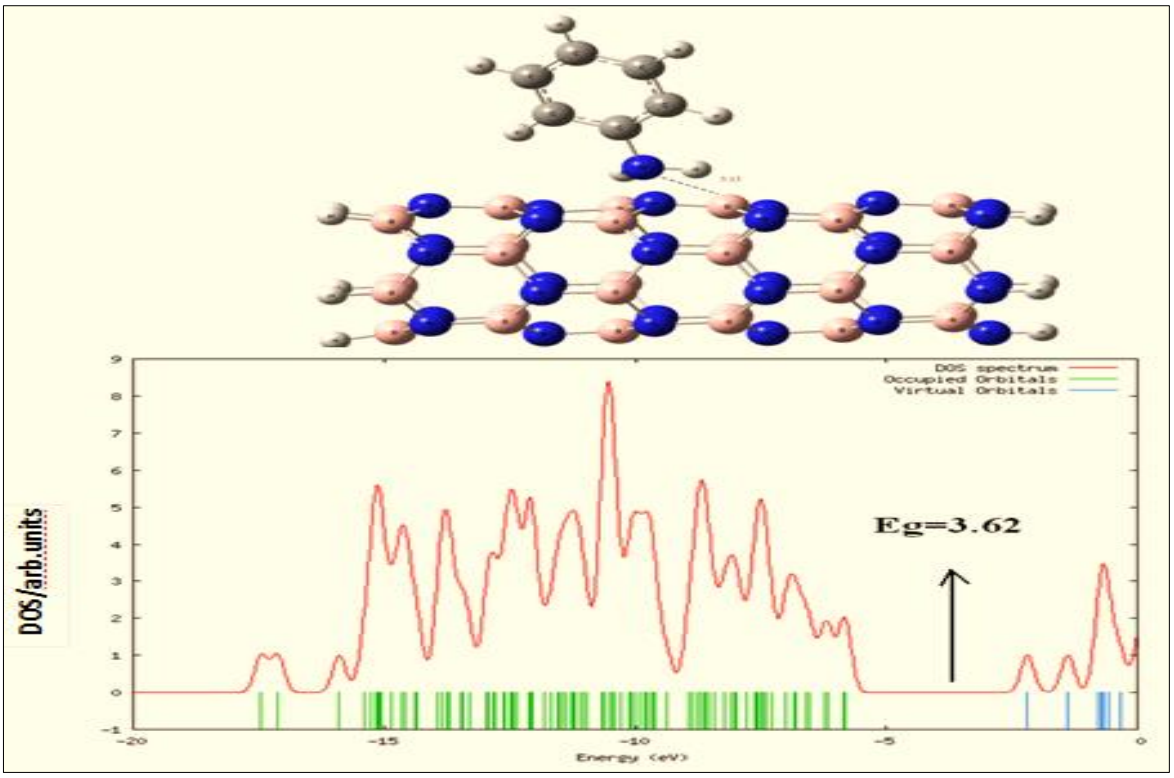

Figure 2: Aniline adsorption on the BNNT and DOS diagram for observing E_g of nanotube. Distance is in Å

Results and discussion:

Fig.1, shows the structure of boron nitride nanotube (BNNT), in order to obtain the most stable adsorption mode of aniline molecule on different positions of BNNT, the most stable configuration is shown in Fig.2, that nitrogen atom of aniline is 3.13 Å far from born atom of the nanotube. Detailed information of the structure and electronic properties of the BNNT including the HOMO/LUMO energy gap (E_g) are shown in Table1 in which adsorption energy (E_{ad}) for mentioned configuration of aniline and nanotube is about –

19.03kcal/mol and then we calculated the HOMO/LUMO energy gap (E_g) for pristine nanotube since the aniline molecule is adsorbed on the nanotubes (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.

Table1. E_{ad}(kcal/mol), eV for the others

System	E_{ad}	E_{HOMO}	E_{LUMO}	E_g
BNNT	-	-6.45	-2.76	**3.69**
Ani/BNNT	-19.03	-5.81	-2.19	**3.62**
Si_N-Ani	-24.91	-5.19	-2.36	**2.89**
Si_B	-	-5.75	-2.68	**3.07**
Si_B-Ani	-10.85	-5.06	-2.55	**2.51**
Al_N	-	-5.54	-3.00	**2.54**
Al_N-Ani	-27.73	-4.94	-2.27	**2.67**
Al_B	-	-6.42	-2.67	**3.75**
Al_B-Ani	-47.75	-6.12	-2.28	**3.84**

Adsorption of C6H5NH2 on Al doped BNNT:

To examine the sensitivity of the adsorption of BNNT of $C_6H_5(NH)_2$ as an adsorbent for $C_6H_5(NH)_2$ 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.2) and the best adsorption energy (E_{ad}=-47.75kcal/mol) is obtained when Al sitting instead of N and aniline has been adsorbed. When Al is doped on BNNT 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 Al is doped on the BNNT (Fig.3), it will become a semiconductor E_g=2.67eV. Optimization of these types of interactions is desirable for gas detection because such strong interaction means that the BNNT is a suitable absorbent for aniline molecule (Fig.4). If E_{ad} 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 Eq.(2)

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

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.

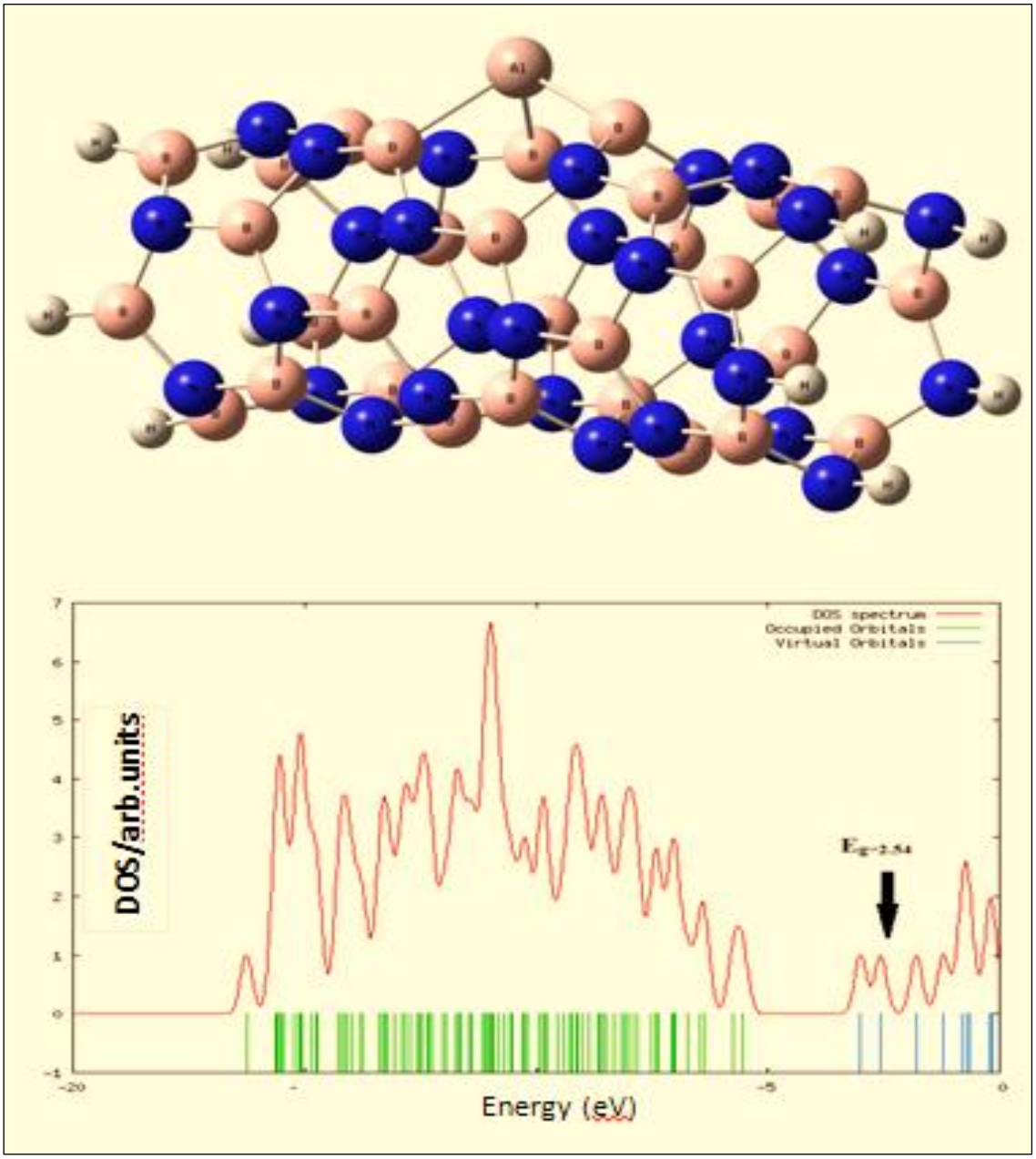

Figure3: Doped nanotube by Al_N and DOS diagram for E_g. Distance is in Å.

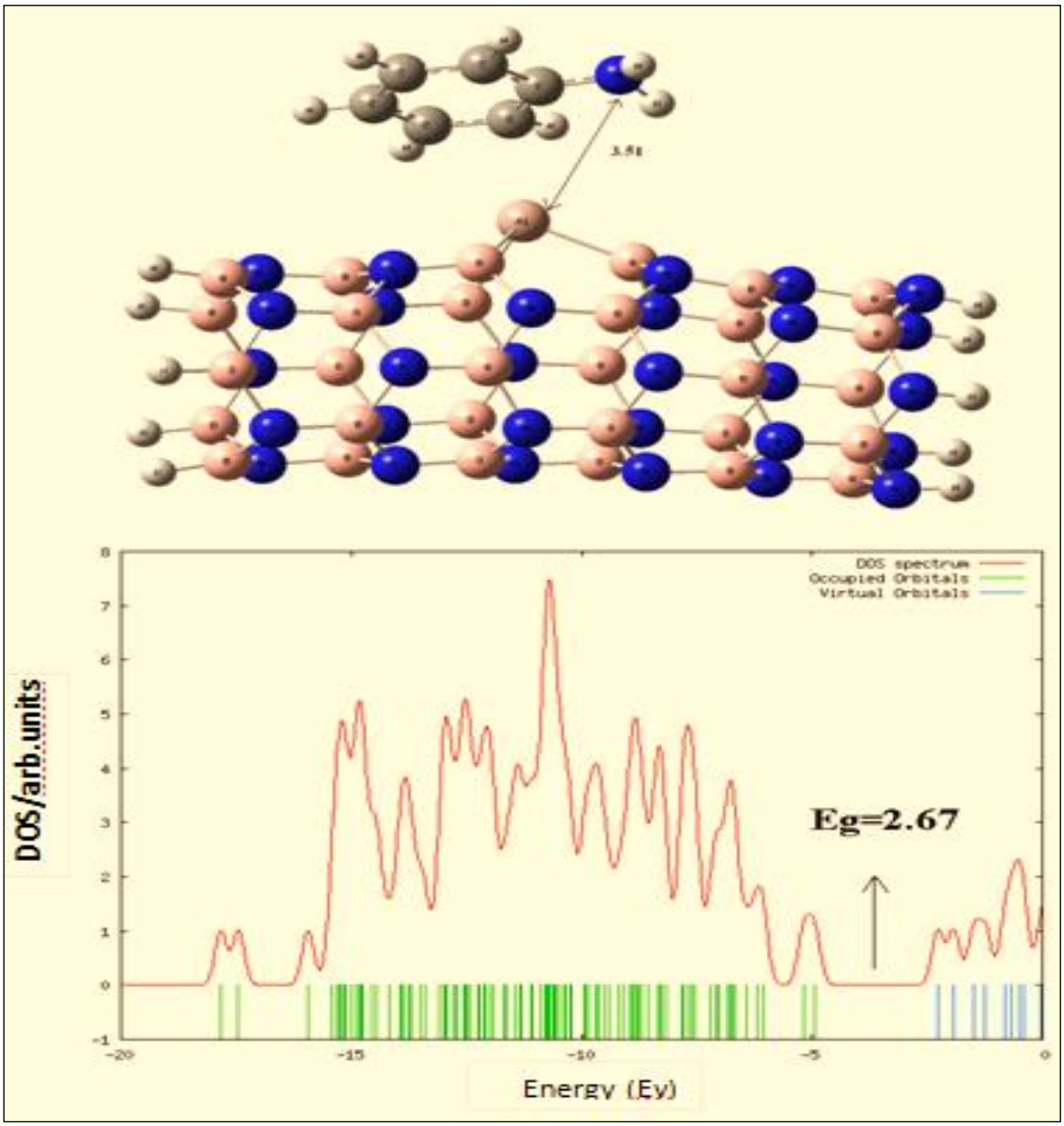

Figure 4: Aniline adsorption on doped nanotube by Al_N and DOS diagram for observing E_g of nanotube. Distance is in Å.

Adsorption of C6H5NH2 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 (Fig.5). Computations showed that when N is replaced by Si in BNNT the HOMO/LUMO energy gap will become less of E_g=2.54eV. When Si is sitting of N, and the adsorption energy of aniline on nanotube is more (E_{ad}= -24.91kcal/mol) than when we just use the pristine nanotube (E_{ad}= -19.03kcal/mol). After adsorption of $C_6H_5(NH)_2$ on the mentioned nanotube that has been doped by Si the HOMO/LUMO energy gap (E_g=2.89eV) will be decrease the pristine of nanotube and therefore a substantial increase will occur in conductivity and this phenomenon can be explain as Eq.(3), [22]

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

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 it can be concluded that therefore Si is a not suitable for doping in BNNT.

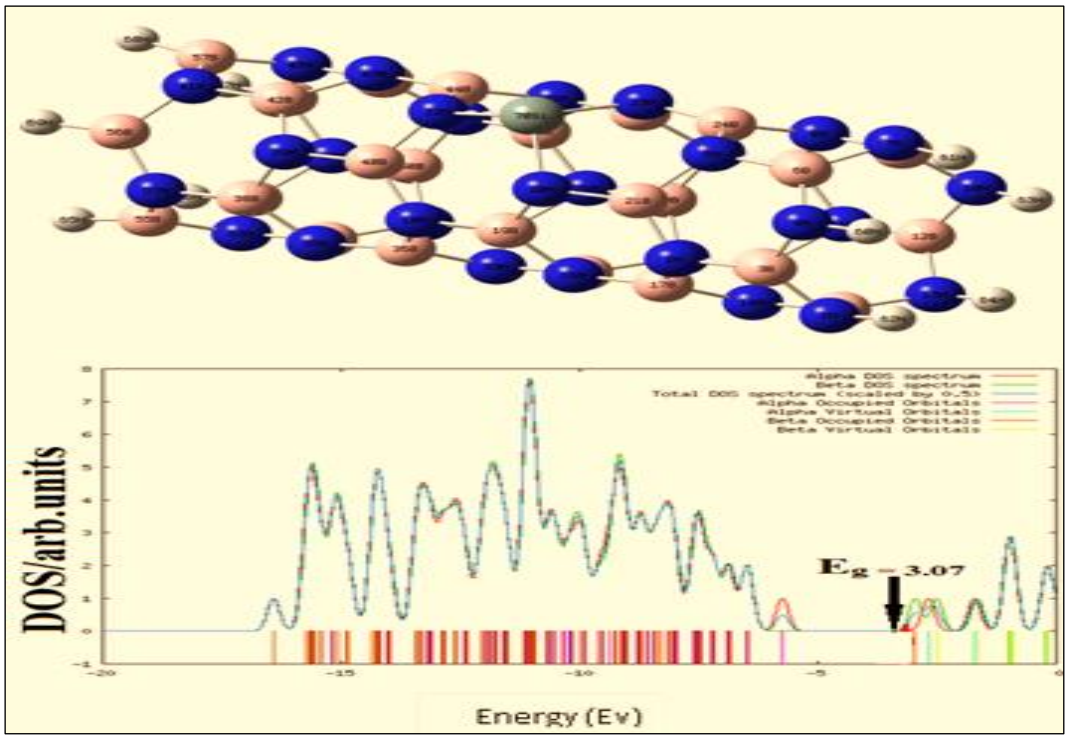

Figure 5: Doped nanotube by Si_B and DOS diagram for E_g of nanotube.

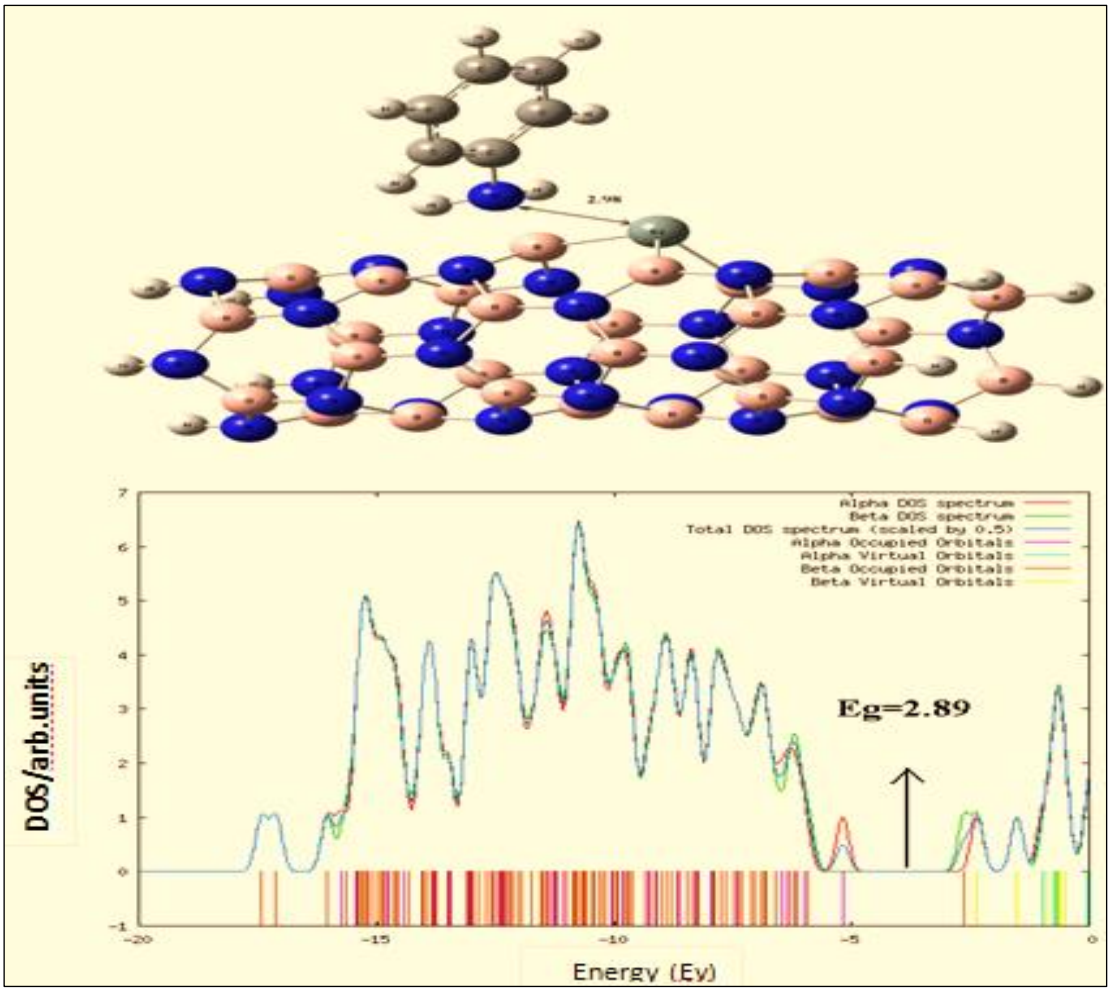

Figure 6. Aniline adsorption on doped nanotube by Si_N and DOS diagram for observing of E_g nanotube. Distance is in Å.

Conclusion:

The adsorption of an aniline ($C_6H_5NH_2$) molecules on the surface of BNNT (boron nitride nanotube) has been studied by using density functional theory (DFT) and then we doped the Al atom in the structure of the nanotube, the results show it is clearly possible to modify the nanotube as an effective adsorbent of aniline molecule in gas sensors which are sensitive about aniline. These results may be open a new gate to chemically modify the nanotubes in a way to expand the fields of their applications in industry and technology.

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References:

[1]E. Brillas and J. Casado, Aniline degradation by electro-fenton and peroxi-coagulation processes using a flow reactor for wastewater treatment, Chemosphere, 47,241(2002).

[2]S.H. Gheewala and A.P. Annachhatre, Biodegradation of aniline, Wat. Sci. Technol. 36,53 (1997).

[3]Y. Wu, W. Zhang, W.Sun and D. Yin, Microcosm study on aniline degradation in weihe riverbed sediments under denitrification conditions, J. North-west. Polytech. Univ. 23,652 (2005).

[4]S.Iijima, Science of Fullerenes and carbon nanotubes,Nature354,56(1991).

[5]G.Hummer,Water, protonund ion transport:from nanotubes to proteins ,Mol.Phys.105,201(2007)

[6]B.E. Zhu,Z.Y. Pan,M.Hou,D.Cheng,andY.X.Wang Melting behavior of gold nanowires in carbon,Mol.Phys.109,527(2011)

[7]F.R. Hung, G. Dudziak, M. Sliwinska-Barthkowiak, and K.E.Gubbins,Freezing/melting behavior within carbon nanotubes. Mol.Phys.102,223(2004).

[8]D.W.H. Fam, Al. Palaniappan, A.I.Y. Tok, B.Liedberg, and S.M.Moochhala,Sens. Areview on technological aspects in fluencingcommercializatior of carbon nanotube sensors. Actuators B: Chem.157, I (2011)

[9]I.Cabria, M.J.Lopez, and J.A.Alonso, Comp. Mater. Density Functional calculations of hydrogen adsorption on boron nanotubes and boron sheets. Sci.35, 238(2006).

[10] S.Hou, Z.Shen, J. Zhang, X.Zhao, and Z.Xue, Abinitio calculations on the ope