Theoretical Study on Surface Modification of BN Nanotubes With 1, 2-diaminobenzenes

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Abstract

Functionalization of a boron nitride nanotube (BNNT) with 1,2 diaminobenzene (DAB) and its derivatives containing functional groups of –CN, –NO$_2$, –OH, and –NH$_2$ has been investigated using density functional theory in terms of energetic, electronic and geometric properties. DAB prefers to be adsorbed on B atoms of the BNNT via its amine head with the adsorption energy of –16.4 kcal/mol. Calculated density of states show that the HOMO-LUMO energy gap of the BNNT is little changed by chemical modification in the most stable states. The work function of BNNT is significantly decreased upon the functionalization with DAB molecules containing electron-donating groups of –OH and –NH$_2$ which will facilitate the field electron emission from the tube surface.

Keywords: Adsorption, DFT, Nanostructures, B3LYP

1. Introduction

Recently, numerous studies have been devoted to investigation of stable structures of different types of non-carbon nanotubes.[1–3] Boron nitride nanotubes (BNNTs) as semiconductors regardless of their diameter, chirality, or the number of tube walls have attracted a lot of research efforts in recent years.[4–7] They also possess high thermal conductivity and superb resistance to oxidation as well as excellent mechanical properties.[8–10] All these properties make BNNTs highly useful in nanotube-based materials and devices working in oxidative and hazardous environments or at high temperatures.[11] However, relatively large band gap and poor solubility in solvents have imposed great limitations to the applications of BNNTs.[12] Chemical functionalization is a commonly used method to tailor physical and chemical properties of nanotubes. However, low chemical reactivity of the surface of BNNTs hampers their chemical modification.[13] It has been already reported that covalent functionalization using adatoms, organic molecules, and functional groups can effectively change the electronic structures, magnetic properties, and solubility of the nanotubes.[14,15] Han and Zettl[16] have experimen-

tally reported the chemical functionalization of BNNT with semiconducting SnO$_2$ nanoparticles. Zhi et al.[17] have explored the covalent functionalization with long alkyl chains. On the other hand, theoretical calculations have also shown that BNNTs can be functionalized by various groups (such as H,[18] transition metals,[19] NH$_3$,[20] and CCl$_2$.[21] Mukhopadhyay et al. have investigated three amino acids on BNNT and they found that unlike to non-polar amino acid, polar amino acids strongly react with BNNT.[22] Same research group have shown that guanine adsorption on BNNT has higher Ead than other nucleobases. A higher Ead for guanine-BNNT conjugate appears to result from hybridization of the molecular orbitals of guanine and the BNNT.[23]

Compared with the above mentioned *covalent functionalization* of BNNTs (the hybridization type of the nanotube is changed upon functionalization), *noncovalent functionalization* (the hybridization type of the nanotube is unchanged upon functionalization) can do much to preserve their desired properties and keep them intact while significantly improving their solubilities or modifying their electronic properties.[24] Thus, noncovalent functionalizations of BNNTs by, for example, aromatic com-

pounds, surfactants, and polymers have attracted increasing attention due to their potential applications in development of novel biosensors, biofunctional materials, nanovectors for cell therapy, drug, and gene delivery.[25,26] However, altering the surface chemistry of the BNNTs is still in its early stages, and effective surface functionalization has remained a challenging task.

In the present work, we have investigated the functionalization of BNNTs by 1, 2-diaminobenzene (DAB) using density functional theory (DFT). DAB is an organic compound with the formula $C_6H_4(NH_2)_2$. This aromatic diamine is an important precursor to many heterocyclic compounds. It is used as a photographic developer and in making dyes. Furthermore, the effects of substituting two farthest H atoms of DAB by four different functional groups (–OH, –CN, –NH$_2$ and –NO$_2$) on geometrical structure and electronic properties of the BNNT and also on the adsorption behaviors were investigated. Recently, many efforts have been focused on designing and preparation of DAB-based CNTs/conducting polymer (CNTs/CP) composites not only because the CNTs can improve the electrical and mechanical properties of polymers,[27] but also because the composites possess the properties of individual components with a synergistic effect.[28,29]

2. Computational Methods

Geometry optimizations, natural bond orbital (NBO), and density of states (DOS) analyses were performed on a (5, 0) zigzag BNNT (constructed of 30 B and 30 N atoms), and different DAB/BNNT configurations at B3LYP/6-31G (d) level of theory as implemented in GAMESS suite of program.[30] This level of theory is a popular approach which has been commonly used for nanotube structures.[31–36] It has been previously demonstrated by Tomic *et al.*[37] that the B3LYP provides an efficient and

robust basis for calculations of III–V semiconductors, capable of reliably predicting both the ground state energies and electronic structure. The length and diameter of the optimized pure BNNT have been computed to be about 11.42 Å and 4.23 Å, respectively. Avoiding boundary effects, atoms at the open ends of the tube have been saturated with hydrogen atoms. The adsorption energy (E_{ad}) of different adsorbate is defined as follows:

$$E_{ad} = E \text{ (adsorbate /BNNT)} - E \text{ (BNNT)} - E \text{ (adsorbate)} \quad (1)$$

where E (adsorbate/BNNT) is the total energy of the complex (adsorbed molecule on the BNNT surface), and E(BNNT) and E(adsorbate) are total energies of the pristine BNNT and the adsorbate molecule, respectively. Negative value of E_{ad} indicates the exothermic character of the adsorption. The canonical assumption for Fermi level is that in a molecule (at T = 0 K) it lies approximately in the middle of the HOMO-LUMO energy gap (E_g), which is in fact the chemical potential. Since the chemical potential of a free gas of electrons is equal to its Fermi level as traditionally defined, herein, the Fermi level of the considered systems is at the center of the E_g.

3. Results and Discussion

3. 1. Adsorption of DAB With BNNTs

A partial structure of the optimized BNNT and its DOS plot are shown in Fig. 1, indicating that the tube is a semiconductor with an E_g of 3.70 eV. After structure optimization, the B atoms relax inward while the N ones relax outward of the tube surface. Thus, the relaxed zigzag BNNT can be characterized by two coaxial cylindrical tubes with an outer N cylinder and inner B cylinder. Two types of B-N bonds can be found, one with the length of 1.44 Å
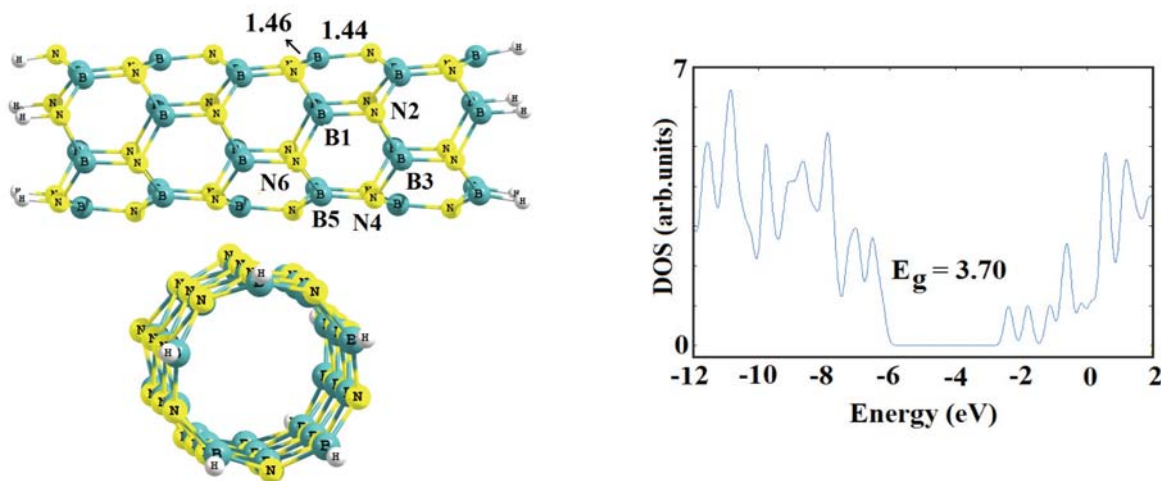

Fig 1. Partial structure of optimized BNNT and its density of states (DOS) plot. Distances are in Å.
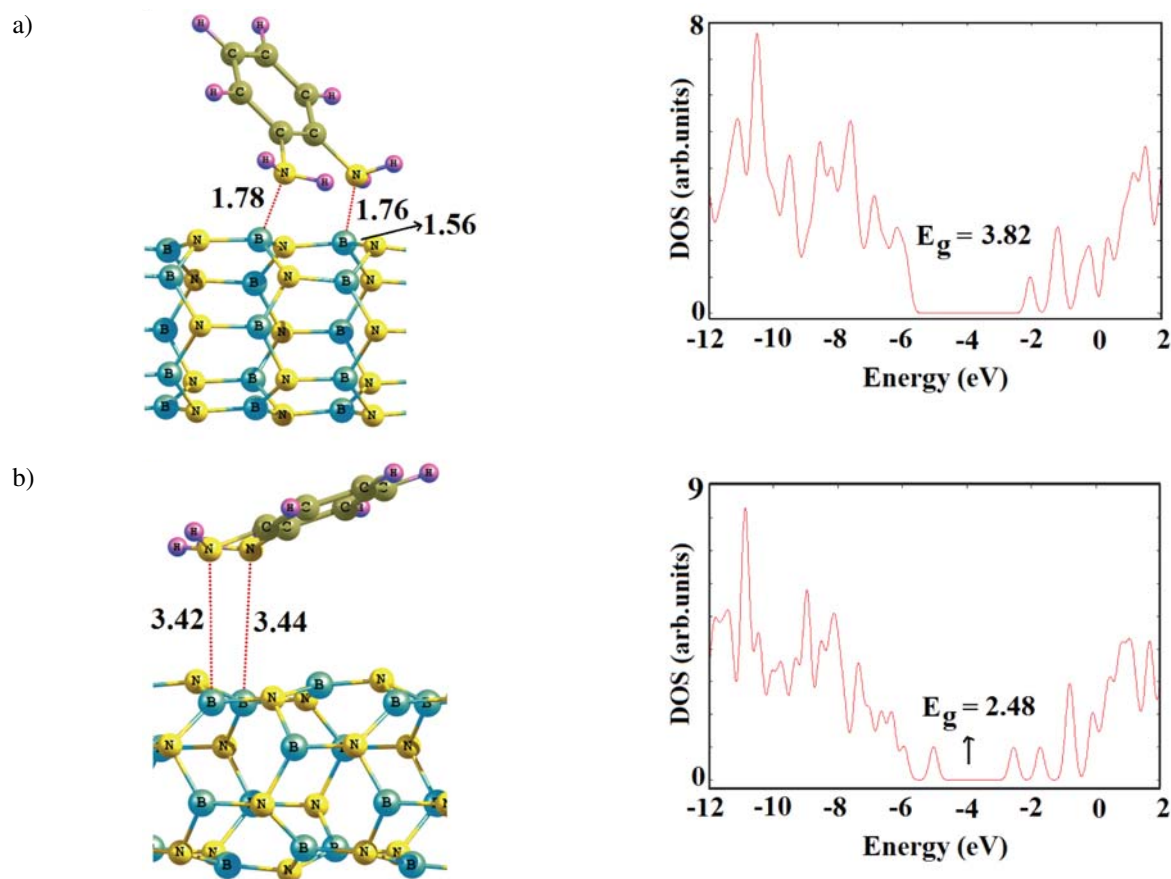
Fig 2. Configurations **A** and **B** for adsorption of DAB on the BNNT and its density of states (DOS) plots. Distances are in Å.

which is in parallel with the tube axis (the B*1*N2 bond), and another with the bond length of 1.46 Å, but not in parallel with the tube axis (the B*1*N6 bond). A DAB molecule has been considered to be adsorbed on the outside surface of the BNNT. In order to find stable configurations (local minima), we have probed a number of different adsorption sites on the tube surface including 1, 2 addition to parallel or diagonal bond, 1, 3 addition on two B or two N atoms of a hexagonal ring, and diagonal or parallel 1, 4-addition. After relax optimizations, it has been found that only those configurations which have undergone 1, 3 addition, converged to a local minimum. Figure 2 shows the most and the second most stable configurations.

In the most stable configuration (**A**, Fig. 2), two N atoms of DAB are close to individual B*1* and B*3* sites (Fig. 1) of the BNNT, with distances of 1.76 and 1.78 Å, respectively. Moreover, in this configuration, two hydrogen atoms of the amino groups are involved in H-bonding with N sites of the BNNT with corresponding bond lengths of 2.10 and 2.62 Å. In this functionalized BNNT, a local structural deformation can be observed on both the DAB molecule and the BNNT. The H–N–H bond angle of the DAB molecule is significantly decreased from 114° and 107° in the free molecule to 108° and 105° in the ad-

sorbed state. Mulliken population analysis shows a net charge transfer of 0.306 *e* (Table 1) from the adsorbate to the tube. The B atoms bonded to DAB molecule are both lifted up so that the lengths of B*1*–N2 and B*1*–N6 bonds are slightly increased from 1.44 and 1.46 Å in the pristine nanotube to 1.47 and 1.56 Å in configuration **A**, respectively. Calculated DOS plot (Fig. 2A) shows that the DAB adsorption through this configuration has no sensible effects on the electronic properties of the BNNT so that the E_g of the tube has slightly increased from 3.70 to 3.82 eV.

In the second most stable configuration (**B**, Fig. 2), two nitrogen atoms of the DAB molecule are near to B*1* and B*5* atoms. It can be seen that the amino heads of the adsorbate are bonded to the B atoms of the BNNT in both the most and the second most stable configurations. Major difference between the two configurations is the orientation of one of the amino groups, which is toward B*1*…B*3* and B*1*…B*5* along the BNNT for the most and the second most stable configurations, respectively. Adsorption process in configuration **B** is obviously weaker (E_{ad} = –1.1 kcal/mol) than configuration **A** (–16.1 kcal/mol). Why is the reaction of DAB molecule with BNNT in configuration **B** less favorable than that of the configuration **A**? The favorability of each configuration is related to the distance

of two adsorbed B sites in the hexagonal ring of the BN-NT. Our geometrical analysis shows that B*1*…B*3* and B*1*…B*5* distances are about 2.49 and 2.31 Å, respectively, and the N…N distance in DAB is about 2.78 Å. It suggests that the interaction of DAB with BNNT in configuration **B** will result in formation of a new ring with more strain than the one which is formed in configuration **A**.

From inspection of the DOS plot (Fig. 2B) it is revealed that the conduction level of the BNNT in complex **B** is similar to that of the pristine BNNT, whereas an impurity peak has been appeared at –5.03 eV in DOS plot of the functionalized BNNT, reducing the E_g of the BNNT from 3.70 to 2.48 eV. Appearance of this peak indicates that after adsorbing the DAB molecule, the complex **B** becomes more semiconductor-like, with a drop in the DOS near the Fermi level, and thus a significant increase in conductance is expected, compared to the pristine tube. The phenomenon can be explained by the following relation:[38]

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

where σ is the conductance and k is the Boltzmann's constant. According to the equation, smaller E_g values lead to the higher conductance at a given temperature. The considerable change of about 33% (Table 1) in the E_g value demonstrates the high sensitivity of the electronic properties of the BNNT towards the DAB adsorption on its surface.

3. 2. Influence of Different Functional Groups on the Adsorption of DAB

Furthermore, the effect of substituting the two farthest H atoms of 1,2-diaminobenzene in the most stable configuration (**A**) by different functional groups (including –OH, –CN, –NH$_2$, and –NO$_2$) on the geometrical structure and electronic properties of the functionalized BNNT has been investigated (Fig. 3). We have found that all of the adsorbates can be chemically adsorbed on the BNNT sidewall and bond with boron atoms. The corresponding E_{ad} and charge transfer from the four adsorbates have been summarized in Table 2. Relative magnitude order of the E_{ad} for different functional groups is as follows: –NH$_2$ > –OH > –H > –CN > –NO$_2$

The least negative E_{ad} belongs to the group of –NO$_2$ with the value of –11.8 kcal/mol. This phenomenon may be explained by noting the fact that the –NO$_2$ group is an electron withdrawing functional and limits the electron transfer to the BNNT surface. This behavior is also predicted in the case of –CN so that the E_{ad} is about –13.2 kcal/mol and a net charge of 0.178 *e* is transferred to the tube from the adsorbate. In contrary, the DAB molecule with the functional of –NH$_2$ has relatively the most negative E_{ad} in comparison with the other cases. Calculated E_{ad} value for this structure is about –19.6 kcal/mol and a net
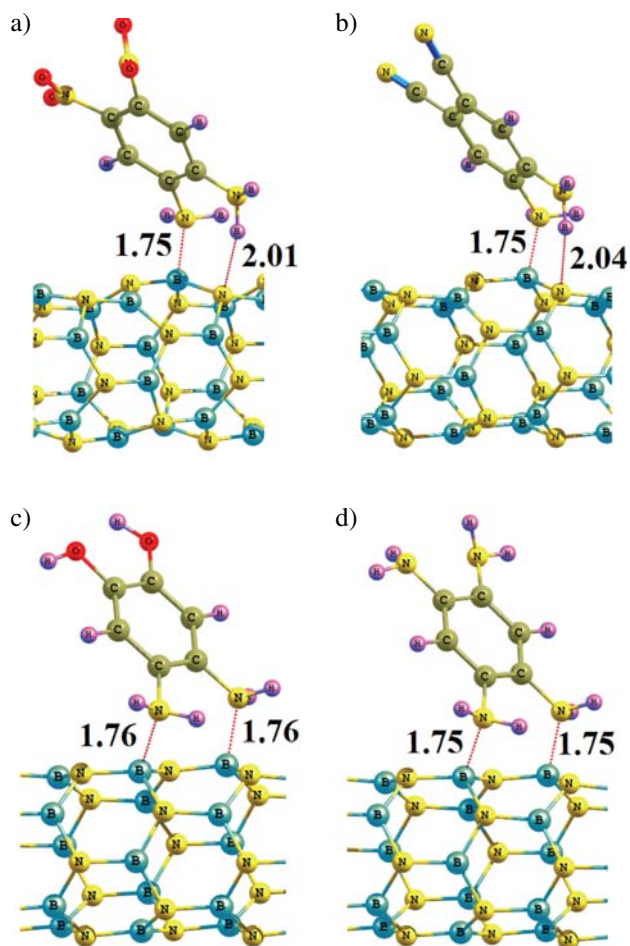

Fig. 3. Optimized structures of functionalized BNNT with different DAB. (a) –NO$_2$; (b) –CN; (c) –OH and (d) –NH$_2$. Distances are in Å.

Table 1. Calculated adsorption energies (E$_{ad}$, kcal/mol), an also HOMO energies (E$_{HOMO}$), LUMO energies (E$_{LUMO}$), HOMO-LUMO energy gap (E$_g$) and Fermi level energy (E$_{FL}$) of systems in eV (Fig. 2).

System	E$_{ad}$	^{a}Q$_T$ (e)	E$_{HOMO}$	E$_{FL}$	E$_{LUMO}$	E$_g$	$^b\Delta$E$_g$(%)
BNNT	–	–	–6.45	–4.60	–2.75	3.70	–
A	–16.4	0.306	–5.86	–3.95	–2.04	3.82	3.1
B	–1.1	0.043	–5.03	–3.79	–2.55	2.48	32.9

^{a} Q$_T$ is defined as the average of total Mulliken charge on the DAB molecule.
^{b} The change of HOMO-LUMO gap of BNNT after DAB adsorption

Table 2. Calculated adsorption energies (E_{ad}, kcal/mol), and also HOMO energies (E_{HOMO}), LUMO energies (E_{LUMO}), HOMO-LUMO energy gap (E_g) and Fermi level energy (E_{FL}) of systems in eV (Fig. 4).

| System	E_{ad}	[a]Q_T (e)	E_{HOMO}	E_{FL}	E_{LUMO}	E_g	[b]ΔE_g(%)–
BNNT	–	–	–6.45	–4.60	–2.75	3.70	–
–NO$_2$	–11.8	0.140	–6.51	–4.71	–2.92	3.59	2.9
–CN	13.2	0.178	–6.49	–4.56	–2.64	3.85	4.0
–OH	–17.1	0.353	–5.82	–3.93	–2.04	3.78	4.8
–NH$_2$	–19.6	0.391	–5.70	–3.82	–1.95	3.75	1.3

[a] Q_T is defined as the average of total Mulliken charge on the DAB molecule.
[b] The change of HOMO-LUMO gap of BNNT after DAB adsorption

charge of 0.391 *e* is transferred to the tube, which is higher than others (Table 2). An identical trend is also predicted in the case of –OH so that the E_{ad} is about –17.1 kcal/mol. Thus, as a general rule, electron donating groups which can give more negative charges to the tube will result in a stronger reaction, as seen here. As can be seen in Fig. 3 (panels a and b), one of the amino groups has re-oriented so that a weak H-bond formed (with corresponding bond lengths of 2.01 and 2.04 Å for the –CN and –NO$_2$ groups, respectively) instead of the strong B-N bond. The findings are in agreements with Zeng *et al*. work.[39] They found that adsorption of amino with electron withdrawing functional group has lower E_{ad} than other amino groups.

DOS plots have been shown in Fig. 4, indicating that upon the functionalization, the electronic properties of the tube have no obvious change compared to the pristine tube and all of the chemically modified BNNTs are still semiconductors with a wide E_g (3.59–3.87 eV) close to that of the pristine BNNT. It is noteworthy to say that as shown in Fig. 5, although the change of E_g in DAB with electron donating groups (–NH$_2$ and –OH) does not follow a definite trend but the DOS near the HOMO and LUMO levels has changed in comparison with that of the pristine tube which would result in a Fermi level enhancement from –4.60 eV to –3.82 and –3.93 eV, respectively in the cases of –NH$_2$ and –OH. This phenomenon leads to a decrement in the work function that is important in field emission applications. An interesting phenomenon is that calculated profiles of HOMO (Fig. 5) demonstrated that the HOMO shifted on the DAB groups in all of

a)

b)

c)

d)
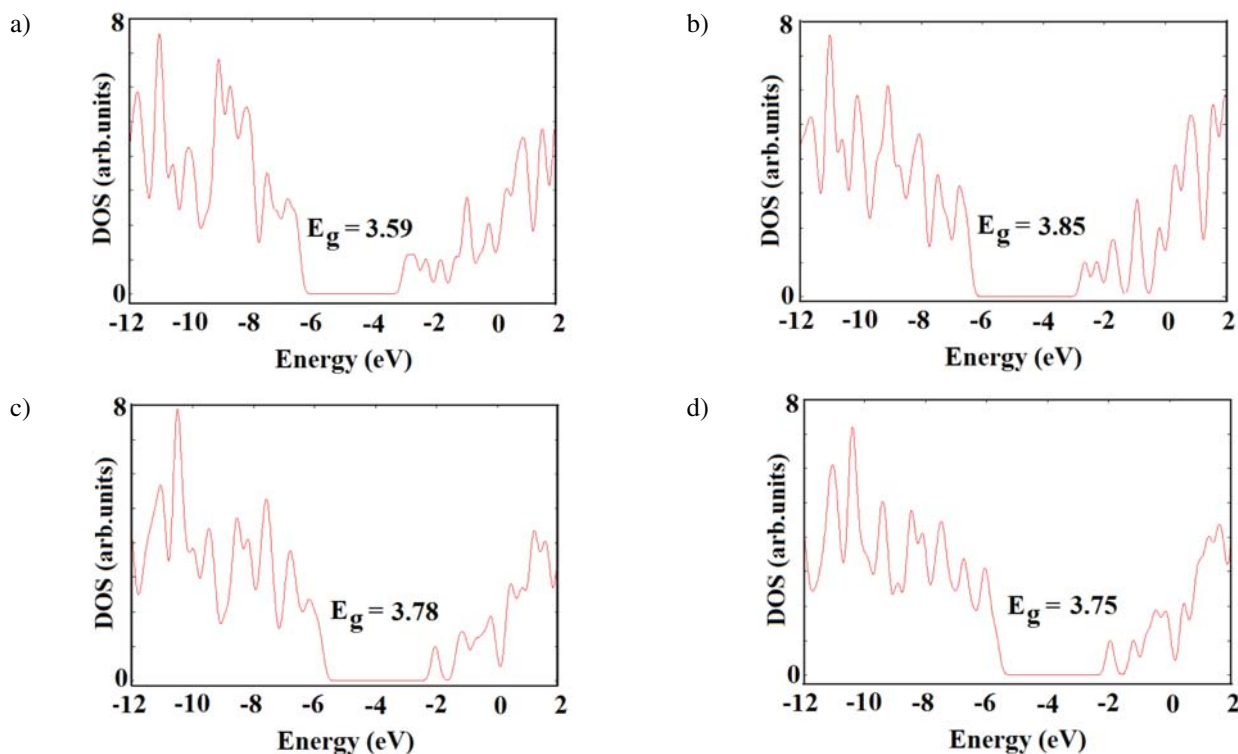
Fig 4. Density of states (DOS) plots for different DAB/BNNT complexes. The E_g is donated to HOMO/LUMO energy gap of system. (a) –NO$_2$; (b) –CN; (c) –OH and (d) –NH$_2$.
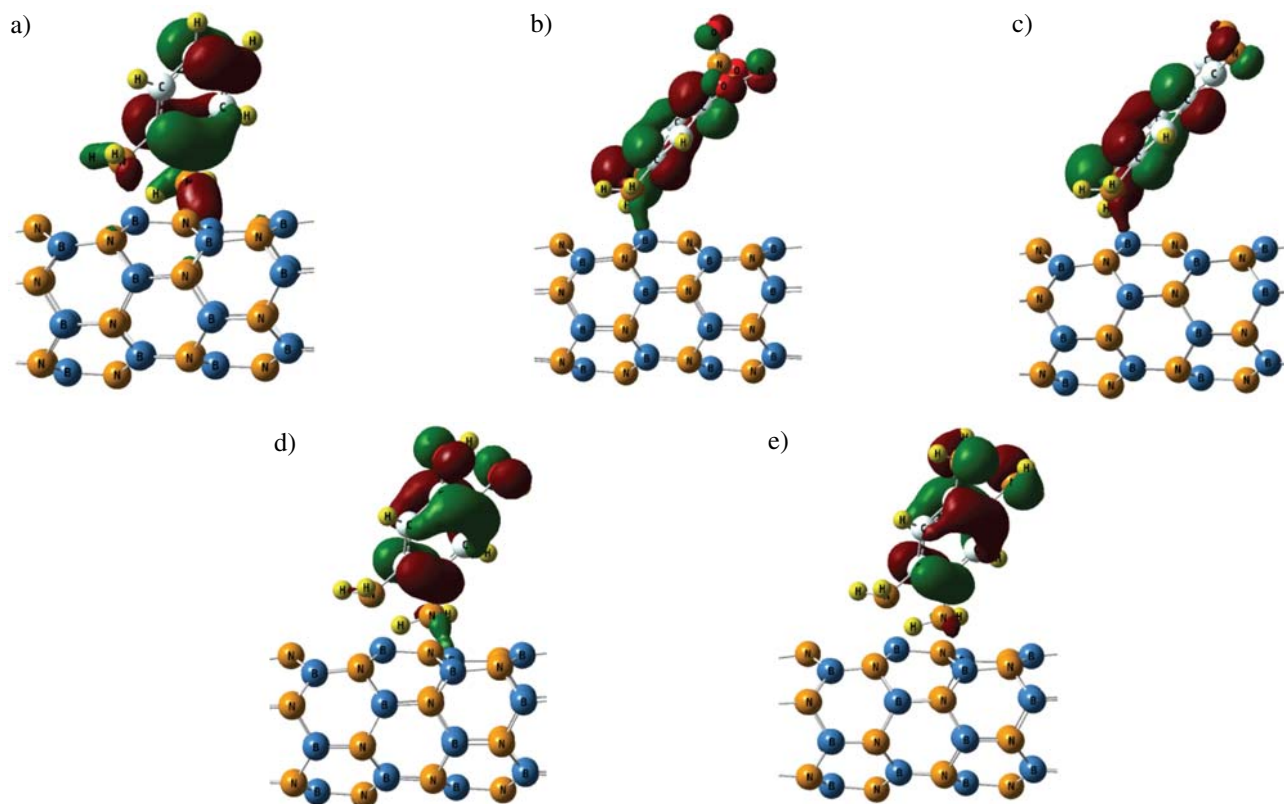
Fig. 5. HOMO profiles for different DAB/BNNT complexes. (a) –H; (b) –NO$_2$; (c) –CN; (d) –OH and (e) –NH$_2$.

DAB-functionalized BNNT, while; the LUMO remained in BNNT surface.

Theoretical investigations have shown that introducing adsorbates at the surface of BNNTs might effectively modify the field emission properties,[40] and can be potentially used in designing efficient field emission displays (FED). The work function can be found using the standard procedure by calculating the potential energy difference between the vacuum level and the Fermi level, which is the minimum energy required for one electron to be removed from the Fermi level to the vacuum. The decrement in the work function indicates that the field emission properties of the BNNTs are facilitated upon the adsorption of mentioned adsorbates. Furthermore, this results in reduced potential barrier of the electron emission for the nanotube, facilitating the electron emission from the BNNT surface. These changes can lead researchers to design of new and different BNNT structures which have unique surface properties and make them suitable for microelectronics technology.

4. Conclusion

Functionalization of a BNNT with DAB and its derivatives containing functional groups of –CN, –NO$_2$, –OH, and –NH$_2$ has been investigated by employing DFT met-

hod. It has been found that DAB prefers to be adsorbed on B atoms of the BNNT via its amine head with the adsorption energy of –16.4 kcal/mol. Relative magnitude order of the E$_{ad}$ for different functional groups is found to be as follows: –NH$_2$ > –OH > –H > –CN > –NO$_2$, indicating that the adsorption behavior depends on the electron-withdrawing or -donating capability of the subgroups within the derivatives. Chemical modification of BNNT by the studied groups results in little changes in the electronic properties of the tube and may be an effective way for the purification of BNNTs. The work function of BNNT is significantly decreased upon the functionalization with DAB molecules with electron-donating groups of –OH and –NH$_2$ which will facilitate the field electron emission from the tube surface.

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Povzetek

Z uporabo funkcionalne gostotne funkcionalne teorije smo raziskovali energetske, elektronske in geometrijske lastnosti nanocevk borovega nitrida (BNNT) z 1,2 diaminobenzenom (DAB) in njegovimi derivati s funkcionalnimi skupinami –CN, –NO₂, –OH in –NH₂. Ugotovili smo, da je DAB preferenčno adsorbiran na borovem atomu BNNT preko amino skupine; energija adsorpcije znaša –16.4 kcal/mol. Izračunana gostota stanj kaže, da je HOMO-LUMO energijska vrzel BNNT le malo spremenjena s kemijsko modifikacijo v najbolj stabilnem stanju. Funkcionilizacija BNNT z DAB molekulami, ki vsebujejo elektron-donorske skupine –OH in –NH₂ signifikantno zmanjša delovno funkcijo nanocevk.