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Functionalization of single-walled (n,0) carbon and boron nitride nanotubes by carbonyl derivatives (n=5,6): A DFT study

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Abstract

By using density functional theory calculations, chemical functionalization of finite-sized (5,0) and (6,0) carbon nanotubes (CNTs) and boron nitride nanotubes (BNNTs) by different carbonyl derivatives $-\text{COX}$ ($\text{X}=\text{H}$, CH_3 , OCH_3 , OH and NH_2) is studied in terms of geometrical and electronic structure properties. Also, the beneficial of local reactivity descriptors is studied in order to characterize the reactive sites of the external surface of the tubes. These local reactivity descriptors include the electrostatic potential $V_S(\mathbf{r})$ and average local ionization energy $\bar{I}_S(\mathbf{r})$ on the surfaces of these nanotubes. The estimated $\bar{I}_S(\mathbf{r})$ values show that the functionalized CNTs tend to activate the surface toward electrophilic/radical attack. Results show that chemical functionalization of CNTs leads to the reduction of $V_S(\mathbf{r})$ values and therefore enhancing the surface reactivity. On the other hand, BNNTs resist toward the chemical functionalization due to the negligible decrease in $V_{S,\min}$ and $\bar{I}_{S,\min}$ values. Generally, in contrast to BNNTs, chemical functionalization of CNTs can considerably improve their surface reactivity. In order to verify the surface reactivity pattern based on the chosen reactivity descriptors, the reaction energies for the interaction of an H^+ ion or H radical with external surface of the functionalized CNTs and BNNTs are calculated. A general feature of all studied systems is that stronger potentials are associated with regions of higher curvature.

Key words: functionalization; carbonyl derivatives; BNNT; CNT; electrostatic potential.

1. Introduction

Carbon-nanostructures, such as carbon nanotubes (CNTs) or nanowires have been recently attracted considerable attention in many scientific fields due to their outstanding structural, mechanical, and electronic properties [1-3]. The discovery of CNTs refers to 1991 when Ijima [4] found novel hollow carbon tubes by high-resolution electron microscopy which called multi-walled carbon nanotubes (MWCNTs). Two years later, single-walled carbon nanotubes (SWCNTs) were successfully synthesized with the same arc method [5]. After these discoveries, numerous studies have been focused on the CNTs to find the electronic and structural properties of these interesting novel materials [6,7]. These outstanding properties of CNTs make them potentially useful in an extended range of applications such as composite materials [8], energy storage [9], molecular sensing [9,10], nanoelectrical devices [11] functional nanodevices [12] and hydrogen storage [13]. The properties of CNTs are mainly dependent on their chirality and tubular diameter [14,15] which make them act as metals or semiconductors with an estimated diameter-dependent energy gap scaling [16]. Modification of CNTs by placing hetero-atoms, doping or defects leads to tremendous technological implications which has stimulated a lot of theoretical and experimental studies done on this topic [17,18]. For example, Xu et al. [19] compared the electrocatalytic activity of nitrogen-doped carbon nanotubes (NCNTs) with MWCNTs and indicated that NCNTs have a distinct electrocatalytic activity toward oxygen reduction reaction (ORR) in the alkaline condition. On the other hand, because the electronic properties of CNTs are related with their geometric structure, scientists have devoted considerable efforts to recognize favorable non-carbon-based materials which exhibit electronic properties independent of this factor [20,21].

In 1981, Ishii et al. [22] discovered one-dimensional boron nitride nanotubes (BNNTs) with a bamboo-like structure which named “BN whiskers”. These structures can be imagine as a rolled graphite-like BN sheet [23], in which carbon atoms are fully substituted by alternative layers consist of B and N atoms. Thus, the BNNTs can be regarded as isomorphic analogs of the CNTs with co-axial hexagonal boron nitride (h-BN) network [24]. However, a perfect tubular nanoscale BN was firstly predicted theoretically in 1994 [25] and after that it was synthesized experimentally by arc-discharge method in 1995 [26]. In the following few years, scientists have focused on the synthesis of BNNTs with a variety of methods such as laser ablation [27], ball-milling [28] or substitution reaction [29], but these methods provide BNNTs with different

purities. Because a large quantity of highly pure BNNTs were needed for chemical studies of BNNTs, thus the related works appeared only later during 2003-2005 [30]. In fact, in comparison with a limited number of experimental works, more papers were published theoretically about their electronic structures [25], property tuning [31], magnetic properties [32] and hydrogen storage [33]. The most important factor which makes BNNTs different from CNTs, is their conductivity. In contrast to CNTs, BNNTs act as permanent semiconductor with a wide band gap of about 5.5 eV, nearly independent of tubular diameter and chirality [34]. Other important advantages of BNNTs over CNTs are their higher surface reactivity, stability at high temperatures and facilitating sidewall decoration [35]. In contrast to non-ionic and hydrophobic CNTs, the BNNTs can be easily dispersed in water due to the ionic character of B-N bonds which make them exhibit significant ionic properties [36].

Nonetheless, recent studies try to linking specific groups or molecules to the nanotubes in order to check the strong potential of chemical functionalization for enhancing the electronic properties of the tube [37-42]. Additionally, the separation of semiconductive tubes from metallic ones to purify nanotubes from carbonaceous impurities or to reduce the width of diameter dispersion may achieve by chemical functionalization [43]. For example, Chelmecka et al. [44] have studied the reactivity of zigzag CNTs toward carboxylation by adding 1 to 9 -COOH group(s) to the end of the tubes. In our previous work [45] we studied the electronic and structural properties of oxygen- and sulfur-terminated models of zigzag (6,0) CNT. We found that upon the O/S-doping at the tip(s) of pristine CNT, the electron density increase around the axial C-C bonds.

In the present work, functionalization of finite-sized (5,0) and (6,0) CNTs and BNNTs with carbonyl derivatives -COX (X=H, CH₃, OCH₃, OH and NH₂) are investigated in terms of geometric, energetic and electronic properties using density functional theory (DFT) calculations. In order to illustrate and give some insightful information about the surface reactivity of these nanotubes, the electrostatic potential, $V_S(\mathbf{r})$, and average local ionization energies, $\bar{I}_S(\mathbf{r})$, are further characterized in detail [46,47]. Previously, Politzer and co-workers [48,49] have developed several statistically defined quantities that explicitly reflect the magnitude of $V_S(\mathbf{r})$ at each point on the molecular surface. The different subsets of these quantities can be used to develop analytical representations of good accuracy for a variety of solution, liquid, and solid-phase properties that depend on noncovalent interactions [50-52]. Our

major goal in current study is to understand and compare the influence of different functionalization groups on the surface reactivity of CNTs and BNNTs. The surface reactivity of functionalized CNTs/BNNTs is verified via calculated chemisorptions energy for a single H^+ cation or H atom adsorption on the external surfaces of these tubes.

2. Theoretical aspects. In a molecule, the electrostatic potential $V(\mathbf{r})$ that is created by electrons and nuclei at any point $\mathbf{r}$ is given by [53]:

$$V(\mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|} - \int \frac{\rho(\mathbf{r}') d\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|} \quad (1)$$

in which Z_A is the charge on nucleus A, located at R_A , and $\rho(\mathbf{r})$ is the molecule's electronic density. Depending on the dominant contribution of the nuclei or electrons, $V(\mathbf{r})$ can be positive or negative in a given region. In order to find the most suitable sites for noncovalent interactions, $V(\mathbf{r})$ is usually computed on an appropriate molecular surface, and the results are labeled as $V_S(\mathbf{r})$. In contrast to $V(\mathbf{r})$, average local ionization energy, $\bar{I}(\mathbf{r})$, is given by [54]:

$$\bar{I}(\mathbf{r}) = \frac{\sum_i \rho_i(\mathbf{r}) |\varepsilon_i|}{\rho(\mathbf{r})} \quad (2)$$

In equation (2), ε_i is the energy of the i^{th} occupied atomic or molecular orbital and $\rho_i(\mathbf{r})$ is its electronic density. In fact, $\bar{I}(\mathbf{r})$ gives the average energy needed to remove an electron at a given point $\mathbf{r}$. Like $V_S(\mathbf{r})$, the computed $\bar{I}(\mathbf{r})$ are computed on the molecular surface and labeled $\bar{I}_S(\mathbf{r})$. The minima of $\bar{I}_S(\mathbf{r})$, $\bar{I}_{S,\min}$, refers to the least tightly-held or most easily ionized electrons, which should be the most reactive sites to an electrophilic or free radical attack [54].

The electrostatic potential over the molecular surface is usually characterized by several useful statistically defined global quantities, like:

(a) The positive, negative and overall average potentials on the molecular surface:

$$\bar{V}_S^+ = \frac{1}{m} \sum_{i=1}^m V_S^+(r_i) \quad , \quad \bar{V}_S^- = \frac{1}{n} \sum_{i=1}^n V_S^-(r_i) \quad , \quad \bar{V}_S = \frac{1}{m+n} \left(\sum_{i=1}^m V_S^+(r_i) + \sum_{i=1}^n V_S^-(r_i) \right) \quad (3)$$

In all cases, the summations are over the m positive and n negative points of a square surface grid, where $\bar{V}_S^+$ and $\bar{V}_S^-$ being their averages.

(b) The average deviation of $V_S(\mathbf{r})$:

$$\Pi = \frac{1}{m+n} \sum_{i=1}^{m+n} |V_S(r_i) - \bar{V}_S| \quad (4)$$

According to Politzer et al. [54], Π is an indicator of the internal charge separation in the molecule and it is present even in highly symmetric molecules like CO [55].

and (c) The total variance, σ_{total}^2 :

$$\sigma_{total}^2 = \sigma_+^2 + \sigma_-^2 = \frac{1}{\alpha} \sum_{j=1}^{\alpha} [V_S^+(r_i) - \overline{V_S^+}]^2 + \frac{1}{\beta} \sum_{k=1}^{\beta} [V_S^-(r_k) - \overline{V_S^-}]^2 \quad (5)$$

3. Computational details. All DFT calculations were carried out with the GAMESS electronic structure package [56]. The geometries of all pristine and functionalized CNTs/BNNTs were optimized using the M06-2X/6-31G* level of theory. A finite-sized (6,0) zigzag nanotube, having 72 C atoms for CNT, and 36 B and 36 N atoms for BNNT, was considered for the pristine CNT/BNNT while the length (diameter) of these tubes were 13.53 (4.55) and 13.64 Å (5.18 Å), respectively. Both ends of the truncated CNTs and BNNTs were capped with hydrogen atoms to saturate dangling bonds. Also, in order to investigate the curvature effect, a finite-sized (5,0) CNT/BNNT having 60 C atoms for CNT, and 30 B and 30 N atoms for BNNT, was chosen with the length (diameter) of 13.48 (4.07) and 13.58 Å (4.19 Å), respectively. Then, different functionalization over these tubes was studied in detail. The M06-2X/6-31G* level of theory was used for the frontier molecular orbitals (FMOs) analysis. The optimized structures were used to compute the $V_S(\mathbf{r})$ and $\bar{I}_S(\mathbf{r})$ over grids covering both the inner and outer 0.001 au surfaces of the tubes. The surface $V_S(\mathbf{r})$ and $\bar{I}_S(\mathbf{r})$ quantities were computed at the M06-2X/6-31G* level using WFA code of Politzer and co-workers [49].

4. Results and discussions

The purpose of this study is to investigate the effect of chemical functionalization on the electronic structure and surface reactivity of the finite-sized (5,0) and (6,0) zigzag CNTs and BNNTs. In order to achieve this purpose, these nanotubes are functionalized by carbonyl derivatives. Different -COX (X=H, CH₃, OCH₃, OH and NH₂) groups are individually attached to the C-tips of CNTs and B- or N-tips of BNNTs. In the following sections, we will first discuss about the geometric structures, FMO analysis and total density of states (TDOS) of the pristine and functionalized CNTs/BNNTs in detail. Next, in order to gain insights about the surface reactivity of these tubes, the $V_S(\mathbf{r})$ and $\bar{I}_S(\mathbf{r})$ are thoroughly studied.

4.1. Structural parameters, FMO and TDOS analysis

The optimized structure of finite-sized pristine (6,0) zigzag CNT is illustrated in Figure 1. As evident, the possible orientations of the C-C bonds relative to the tube axis result in two

nonequivalent types of bonds, i.e. zigzag or axial, which are shown in Figure 1 with A and Z prefixes, respectively. The calculated Z and A bond lengths in the pristine (6,0) CNT are 1.43 and 1.42 Å, respectively. These are in good agreement with those of other related theoretical studies [15,45]. To better understand the electronic structure of pristine CNT, TDOS, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of this tube are also considered. According to Figure 1, the HOMO of pristine CNT is mainly localized at C–C pair along the tube axis, while the LUMO is localized on carbon atoms located at the tips. The high coefficient of wave function for these carbon atoms in the LUMO reveals the large probability of these sites to undergo a nucleophilic attack. The small band gap of 1.85 eV shows that the pristine (6,0) CNT can act as a semiconductor (Table 1).

Although after functionalization of CNT with different carbonyl derivatives, the shape of the tube changes significantly, but the total A and Z bond lengths have a negligible change in comparison with the pristine CNT. This can be explained as the geometrical structure of sp^2 -carbon networks is not changed after functionalization. It is found that after introducing the –COX functional group to the CNT, the C atom of –COX is covalently bonded to the C-tip of the CNT with the C–C bond lengths in the range of 1.42 to 1.45 Å. The corresponding charge-transfer (q_{CT}) values from the CNT to –COX group are listed in Table 1. The relative magnitude order of q_{CT} for different functional groups is as follows:

$$-\text{CONH}_2 < -\text{COOCH}_3 < -\text{COCH}_3 < -\text{COOH} < -\text{COH} \quad (6)$$

As seen, the lowest q_{CT} corresponds to the case of CONH_2 with the value of 0.15 e (Table 1). This is expected, since the resonance possibility of $-\text{CONH}_2$ group allows it to act as a weaker electron-withdrawing substituent. The same trend is also seen in the case of $-\text{COOCH}_3$, $-\text{COCH}_3$, $-\text{COOH}$ and $-\text{COH}$ functional groups. In addition, value of dipole moment in the functionalized CNTs increases with respect to the pristine tube, which can be attributed to the charge separation between CNT and –COX group (Table 1). The data of Table 1 also indicate that upon the functionalization of CNT, the band gap of the tube is slightly changed compared to the pristine tube and all the chemically functionalized CNTs are still semiconductors with the calculated band gap (E_g) value in the range of 1.67–1.79 eV. Also, the TDOS plots of different functionalized CNTs are shown in Figure S1 of Supporting Information. One can see that the contribution of the functional groups in the TDOS plots is largely away from the Fermi level.

Hence, the chemical functionalization of the CNT with -COX groups has a little effect on the Fermi level energy of the tube.

The optimized structure of finite-sized (6,0) BNNT is shown in Figure 1 with the A and Z bond length of 1.45 and 1.46 Å, respectively. The Mulliken population analysis shows that the nitrogen atoms of pristine BNNT are negatively charged by about -0.51 e, and the boron atoms are positively charged with the same magnitude. Therefore, unlike nonpolar case of pristine CNT, the dipole moment of pristine BNNT is nonzero due to alternate layers of B and N atoms. The FMO analysis shows that the HOMO of the pristine BNNT is mainly accumulates around the N-tip and neighboring B/N atoms of the tube while its LUMO is mostly localized around the B-tip and nearest B/N atoms of the surface. The estimated HOMO-LUMO gap is about 7 eV, which is larger than the experimentally measured band gap for bulk h-BN (5.8 eV) [26].

According to Figure 1, the pristine BNNT consists of a regular pattern of B and N atoms. So, in order to study the functionalization of BNNT, the functional groups are introduced in B- or N-tip of pristine BNNT, separately (see Figures S2 and S3). Upon introduction of -COH group in both mentioned tips, the B-C and N-C bond lengths are formed with amount of 1.61 and 1.38 Å, respectively. Other functionalization groups form the covalent B-C and N-C bonds in the range of 1.60-1.62 Å and 1.37-1.39 Å, respectively (see Table 1). In comparison with B-tip functionalized BNNTs, the stronger binding occurs between the -COX group and N-tip of nanotube due to the larger electronegativity and smaller covalent radius of nitrogen. Also, in the B- and N-tip functionalized BNNTs a net charge-transfer is occurred from the BNNT to the -COX and vice versa (Table 1). The amount of these net charges are negligible, especially in N-tip functionalized BNNT, except in the case of N-tip functionalization with -COOCH₃ (-0.38 e). The calculated TDOS plots for different chemically modified BNNTs are depicted in Figures S2 and S3. It is seen that the presence of -COX does not considerably affect the DOSs near the Fermi level. Hence, the HOMO-LUMO energy gap of the functionalized tubes is slightly changed compared to the pristine tube. The largest change of E_g belongs to the -COH in which E_g of the BNNT is decreased by 3.1%. Generally, it can be concluded that chemical functionalization of pristine (6,0) BNNT by -COX groups can't considerably improve its electrical conductivity and surface reactivity.

Along with these functionalizations, another question arises whether the diameter of the nanotube can affect the binding distances and electronic structure properties of functionalized

tubes. To find the answer of this question, the curvature effect on different functionalized CNTs/BNNTs is investigated carefully. Table S1 of Supporting Information is reported the geometric parameters of these five different functional groups over the (5,0) CNT/BNNT. In comparison with (6,0) CNT (BNNT), the E_g of (5,0) CNT(BNNT) is increased (reduced) from 1.85 (7.05) to 1.92 eV (6.24 eV). The E_g of functionalized CNTs show an increase from 1.92 eV in pristine (5,0) CNT to 2.42 eV in the functionalized tube with $-\text{COH}$ group, while, like the (6,0) BNNT, the E_g of functionalized BNNT do not change significantly. It should be noted that other structural values such as bond length or charge-transfer of the functionalized CNTs/BNNTs are similar to those on (6,0) CNT/BNNT (see Table S1).

4.2. Surface electrostatic potentials

It has been proved that the electrostatic surface potential is a valuable tool for analyzing and predicting surface reactivity of different nanotubes [7,15,57,58]. Figure S4 displays the evaluated $V_S(\mathbf{r})$ on the 0.001 au surface of the pristine and functionalized (6,0) CNTs. In this figure, the location of the most positive and negative $V_S(\mathbf{r})$, designated as $V_{S,\text{max}}$ and $V_{S,\text{min}}$, is clearly specified. In the pristine (6,0) CNT, the ending hydrogen atoms with an electron-donating property, make the outer carbon surfaces negative (blue color), with a $V_{S,\text{min}}$ value of -16.6 kcal/mol. These negative $V_{S,\text{min}}$ values show the attractive channels for the electrophilic or free radical attack. Besides, the positive regions (red color) are mostly concentrated at the tips of CNT which are associated by hydrogen atoms with the $V_{S,\text{max}}$ of about 29.9 kcal/mol. The positive and negative surface areas (A_S^- , A_S^+) for pristine CNT and the corresponding surface parameters such as $V_S(\mathbf{r})$, σ_{total}^2 and local polarity or internal charge separation (π) are listed in Table 2. It should be noted that because of the delocalized π electrons, weak positive and negative regions occur above/below the rings and above the C-C bonds of the surface, respectively. The greater variation in the surface potentials of the pristine CNT can be achieved from the Π (12 kcal/mol) and σ_{total}^2 (213 (kcal/mol)²) values. These values are much larger than fullerene-like systems [56], short-length open CNTs [15] and are in close agreement with other related finding values for pristine (6,0) CNT [59].

The introduction of functional groups into the CNT structure changes its local electronic environment. After adding five different carbonyl derivatives to the tips of (6,0) CNT, the characteristic surface patterns and evaluated surface quantities are significantly changed (Table 1). The overall patterns of $V_S(\mathbf{r})$ for functionalized CNTs are shown in Figure S4. In all cases,

the lowest (more negative) value of $V_{S,min}$ is associated with the carbon atom attached to the –COX group. Starting from the –COH functionalized group, the $V_{S,min}$ changes from -16.6 kcal/mol in pristine CNT to -20.0 kcal/mol after functionalization, which makes the negative regions associated with the C atoms stronger than before. Substitution of the hydrogen atom of –COH group by CH_3 , OCH_3 , OH and NH_2 groups further increases the absolute value of $V_{S,min}$. Relative magnitude order of absolute value of $V_{S,min}$ for different functional groups is as follows:

$$-COH < -COCH_3 < -CONH_2 < -COOCH_3 < -COOH \quad (7)$$

The increase in the absolute value of $V_{S,min}$ of carbon atoms regarding the pristine tube reveals the stronger tendency of the carbon atoms to be susceptible to nucleophilic attack than those of the pristine one. Also, $V_{S,max}$ increases from 29.9 kcal/mol in the pristine CNT to the range of 39.5–43.2 kcal/mol in the functionalized CNTs. In addition, the surface potentials of chemically modified CNTs show considerably more variation than those of the pristine tube, as can be seen by comparing the estimated σ^2_{total} and Π values.

The importance of curvature effect on the surface electrostatic potentials of pristine and functionalized (5,0) CNTs is also studied (Table S2). As a result, the absolute value of $V_{S,min}$ is increased with the reduction of the CNT diameter, which is consistent with those results of politzer and co-workers [60]. Also, the $V_{S,max}$ value enhances from 29.9 kcal/mol in pristine (6,0) CNT to 34.4 kcal/mol in (5,0) CNT. After functionalization, the amounts of $V_{S,min}$ and $V_{S,max}$ are increased in which the –COH and –COOH groups has the higher value than others, respectively. Moreover, there is no regular trend for the magnitudes of Π from the (6,0) tube to the (5,0) tube, while the σ^2_{total} is increased with the reduction of the tube diameter.

The surface electrostatic potential of (6,0) BNNT is quite interesting. In all part of the surface a regular pattern of positive and negative potentials, which are associated with B and N atoms, is seen (Figures S5 and S6). In contrast to the pristine CNT, H atoms of BNNT can be either positive or negative which depends on the attachment of hydrogen atoms to the B- or N-tip of BNNT. Moreover, the positive regions which exist above the B atoms are stronger than the negative areas above the N atoms. The most positive regions are associated with hydrogen atoms located at the N-tip with the $V_{S,max}$ of about 53.3 kcal/mol, which is in good agreement with our previous work [15]. This large amount of $V_{S,max}$ can be due to the great electronic charge transfer from the H atoms to the capped N atoms of the BNNT. It can be seen from the σ^2_{total} value (243 (kcal/mol)²) that there is a greater difference between the surface potential of pristine BNNT and

CNT (213 kcal/mol). The entire surfaces, both inner and outer, are negative $A_S^- > A_S^+$. Moreover, it can be seen that there is a local B^+H^- polarity at one tip and NH^+ at the other tip of the tube (see Figures S5 and S6).

Figures S2 and S3 display the overall patterns of $V_S(\mathbf{r})$ for B- and N-tip functionalized (6,0) BNNTs, respectively. Upon the addition of $-COH$ group to the B-tip of BNNT, the $V_{S,min}$ ($V_{S,max}$) values change from -19.4 (53.3) kcal/mol in the pristine tube to -18.6 (54.4) kcal/mol in the $-COH$ functionalized one (Table 2). Also, in the N-tip functionalized BNNT, the $V_{S,min}$ ($V_{S,max}$) value is about -19.5 (53.9) kcal/mol. Generally, after functionalization, the $V_{S,min}$ values change in the range of -18.6 to -20.3 kcal/mol for B-tip and -19.5 to -22.0 kcal/mol in N-tip functionalized BNNTs (Table 2). The corresponding change in $V_{S,max}$ value are in the range of 52.8 to 54.4 and 51.3 to 53.9 kcal/mol, respectively. As it is clear, the σ_{total}^2 values are shown an increase and decrease in B- and N-tip BNNTs, respectively, which show the difference of surface reactivity of these chemically modified BNNTs.

To verify the surface reactivity pattern based on the surface electrostatic potentials discussed above, the chemisorption energies for interaction of an H^+ cation with external surface of different (6,0) CNTs and BNNTs were calculated. It is evident that the reaction energies predict the reactive sites as that of the $V_{S,min}$ values. The chemisorption energy becomes more negative as $V_{S,min}$ increases for both CNTs and BNNTs. Figure 2 shows the correlation of $V_{S,min}$ with H^+ chemisorption energies. Good correlation coefficients with an R^2 value of 0.957 (CNTs) and 0.924 (BNNTs) are found between H^+ interaction energies and $V_{S,min}$ values, which suggests that the surface electrostatic potential can provide a useful method to evaluate the surface reactivity of finite-sized CNTs and BNNTs.

The curvature effect on the surface electrostatic potentials of pristine and functionalized (5,0) BNNTs show that with the reduction of tube diameter, the $V_{S,min}$ value enhances (becomes more negative) while the $V_{S,max}$ value has not a significant alteration (Table S2). After functionalization, the amounts of $V_{S,min}$ are increased while this is more visible in B-tip functionalized BNNTs than N-tip types. In addition, like zigzag CNTs, there is no regular trend for the magnitudes of Π from the (6,0) tube to the (5,0) tube, while the σ_{total}^2 is decreased from 243 kcal/mol in (6,0) BNNT to 224 kcal/mol in (5,0) BNNT.

4.3. Surface average local ionization energies

Another local property which is related to the surface activity is the average local ionization energies, $\bar{I}_S(\mathbf{r})$. The $\bar{I}_S(\mathbf{r})$ map which plotted on the 0.001 au molecular surface of the pristine (6,0) CNT is illustrated in Figure S4. As it is clear, there are many $\bar{I}_{S,\min}$ and $\bar{I}_{S,\max}$ on the surface of this tube which are mainly located above each C atom and center of the ring, respectively. The estimated $\bar{I}_{S,\min}$ is 8.6 eV (Table 2), which is in close agreement with other related studies [15,61]. These sites correspond to the weakly hold electrons that make them the most reactive sites to the radical attack. After adding the $-\text{COH}$ functional group to the C-tip of CNT, the $\bar{I}_{S,\min}$ value decreases from 8.6 in the pristine to 7.8 eV in functionalized CNT (Figure S4). The $\bar{I}_{S,\min}$ values for other different functionalized CNTs are depicted in Table 2 which show a total reduction in the range of 0.5 to 1.0 eV in different functionalized CNTs. Similar to $V_{S,\min}$ values, the main reduction relates to the functionalized CNT with $-\text{COOH}$ group. This reduction in the $\bar{I}_{S,\min}$ values shows that the reactivity of the tube surface increase after functionalization. On the other hand, the $\bar{I}_{S,\max}$ value in the functionalized CNT with $-\text{COH}$ group is 16.4 eV, which increases in comparison with pristine CNT (13.8 eV). Generally, the $\bar{I}_{S,\max}$ values increase in the range of 16.2 to 16.4 eV in other functionalized CNTs.

The $\bar{I}_S(\mathbf{r})$ of pristine (6,0) BNNT in comparison with CNT, is more interesting. The $\bar{I}_{S,\min}$ value of pristine (6,0) BNNT (10.5 eV) is much larger than that of CNT (8.6 eV) which shows the higher surface reactivity of the CNT toward the radical attack than BNNT. The lowest values of $\bar{I}_{S,\min}$ are for nitrogen atoms which are located at N-tip of BNNT, while the largest values of $\bar{I}_{S,\max}$ belong to hydrogen atoms located at B-tip (Figure S5). Upon chemical functionalization on B- or N-tip of BNNT, the $\bar{I}_{S,\min}$ and $\bar{I}_{S,\max}$ values do not change significantly (Table 2). For example, the $\bar{I}_{S,\min}$ and $\bar{I}_{S,\max}$ value in B-tip functionalized BNNT with $-\text{COH}$ group are 10.6 and 16.4 eV, respectively, which are slightly different from those of pristine tube. Generally, the magnitudes of $\bar{I}_{S,\min}$ lie in the range of 10.5 to 10.6 eV in B-tip and from 10.4 to 10.6 eV in N-tip functionalized (6,0) BNNT, respectively. Also, the calculated $\bar{I}_{S,\max}$ values in B- and N-tip functionalized BNNT are in the range of 16.3 to 16.4 eV and 16.4 to 16.6 eV, respectively. As it is clear, these values have not a significant difference with pristine BNNT. This emphasize on the resistance of BNNTs, in contrast to CNTs, toward the chemical functionalization by $-\text{COX}$ group.

Figure 3 represents the linear correlation between $\bar{I}_{S,\min}$ and atomic hydrogen adsorption energies on the (6,0) CNTs and BNNTs. As evident, an acceptable correlation was found, with

an R^2 value of 0.976 (CNTs) and 0.939 (BNNTs), indicating that $\bar{I}_{S,\min}$ can provide an effective tools for rapidly and economically assessing the relative surface reactivity of finite-sized functionalized CNTs and BNNTs.

Finally, in order to identify the contribution of curvature effects to the surface ALIE properties of the pristine and functionalized CNTs/BNNTs, the $\bar{I}_{S,\min}$ and $\bar{I}_{S,\max}$ values were evaluated for pristine and functionalized (5,0) CNTs/BNNTs (Table S2). It is clear that the reduction of tube diameter do not considerably affect the reactivity of tubes toward a radical/electrophile attack.

5. Conclusion

We have studied the chemical functionalization of finite-sized (5,0) and (6,0) CNTs and BNNTs with different carbonyl derivatives including $-\text{COX}$ ($X=\text{H}$, CH_3 , OCH_3 , OH and NH_2) by using DFT calculations. It is found that after introducing the $-\text{COX}$ functional group to the CNTs, the C atom of $-\text{COX}$ is covalently bonded to the C-tip of the CNTs with the C-C bond lengths in the range of 1.42 to 1.45 Å. The relative magnitude order of q_{CT} for different functional groups attached to the (6,0) CNT is as follows: $-\text{CONH}_2 < -\text{COOCH}_3 < -\text{COCH}_3 < -\text{COOH} < -\text{COH}$. Similarly, after functionalization of (6,0) BNNT, the covalent B-C and N-C bonds of the B-tip and N-tip functionalized BNNTs change in the range of 1.60-1.62 Å and 1.37-1.39 Å, respectively. Our results indicated that chemical functionalization of pristine BNNTs by $-\text{COX}$ groups can't considerably improve its electrical conductivity and surface reactivity. Based on the computed electrostatic potentials, it is found that the characteristic surface patterns and evaluated surface quantities are significantly increased in CNTs in contrast to BNNTs. Due to the chemical functionalization, the negative regions associated with carbon atoms are stronger than before, which means that the attached $-\text{COX}$ group tends to activate the CNT surface toward an electrophilic or free radical attack. Also, good linear correlations were found between chemisorptions energies of H^+ cation and $V_{S,\min}$ values indicating that $V_{S,\min}$ can provide an effective tool for rapidly and economically assessing the relative surface reactivity of finite-sized functionalized CNTs and BNNTs. The small diameter (5,0) CNT/BNNT has notably stronger and more variable positive and negative regions. This can be due to the high degree of curvature on the sides and at the caps.

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Figure Captions:

Figure 1. Geometric structures and TDOS plots of pristine CNT and BNNT

Figure 2. Correlation between H^+ chemisorption energies and $V_{S,min}$ values of CNTs and BNNTs

Figure 3. Linear correlation between hydrogen atom chemisorption energies and $\bar{I}_{S,min}$ values of CNTs and BNNTs

Draft

Figure 1.

Figure 2.

Figure 3.

Table 1. Calculated binding distances (R), charge-transfer (q_{CT}), dipole moment (μ), HOMO (E_{LUMO}) and LUMO energy (E_{LUMO}), band gap (E_g) and its change relative to pristine tube ($\% \Delta E_g$) for pristine and –COX functionalized CNTs/BNNTs

surface	$R_{C-C/B-C/N-C}$ (Å)	q_{CT}	μ (Debye)	E_{HOMO} (au)	E_{LUMO} (au)	E_g (eV)	$\% \Delta E_g$
<i>Pristine CNT</i>	-	-	0.00	-0.155	-0.087	1.85	-
-COH	1.42	-0.26	13.59	-0.168	-0.105	1.72	-7.0
-COCH ₃	1.43	-0.23	12.88	-0.166	-0.105	1.67	-9.7
-COOCH ₃	1.44	-0.21	9.99	-0.166	-0.101	1.75	-5.4
-COOH	1.43	-0.25	11.88	-0.166	-0.105	1.68	-9.2
-CONH ₂	1.45	-0.15	8.62	-0.164	-0.098	1.79	-3.2
<i>Pristine BNNT</i>	-	-	8.02	-0.300	-0.041	7.05	-
B-tip BNNT							
-COH	1.61	-0.12	9.85	-0.302	-0.051	6.83	-3.1
-COCH ₃	1.61	-0.13	7.19	-0.298	-0.033	7.21	+2.3
-COOCH ₃	1.60	-0.38	6.24	-0.298	-0.033	7.21	+2.3
-COOH	1.62	-0.14	8.58	-0.301	-0.046	6.94	-1.6
-CONH ₂	1.61	-0.07	9.63	-0.300	-0.044	6.97	-1.1
N-tip BNNT							
-COH	1.38	0.01	4.49	-0.305	-0.046	7.06	+0.1
-COCH ₃	1.39	0.06	5.37	-0.303	-0.044	7.04	-0.1
-COOCH ₃	1.38	0.06	6.71	-0.301	-0.043	7.04	-0.1
-COOH	1.37	0.02	6.08	-0.303	-0.044	7.04	-0.1
-CONH ₂	1.39	0.09	6.40	-0.301	-0.043	7.02	-0.4

Table 2. Calculated surface electrostatic potentials and average ionization energies for different models of (6,0) CNTs/BNNTs ^{a,b}

Tube	A_S^+	A_S^-	$\bar{V}_S^+$	$\bar{V}_S^-$	σ_{total}^2	Π	$V_{S,min}$	$V_{S,max}$	$I_{S,min}$	$I_{S,max}$
<i>Pristine CNT</i>	185	333	17	-10	213	12	-16.6	29.9	8.6	13.8
-COH	221	309	17	-10	321	13	-20.0	43.2	7.8	16.4
-COCH ₃	218	328	17	-10	309	13	-20.6	42.8	7.7	16.3
-COOCH ₃	226	331	15	-11	279	13	-28.9	41.1	7.8	16.2
-COOH	215	321	17	-11	316	14	-32.4	42.5	7.6	16.3
-CONH ₂	214	325	16	-11	279	13	-21.4	39.5	8.1	16.2
<i>Pristine BNNT</i>	232	303	17	-7	243	12	-19.4	53.3	10.5	16.3
B-tip BNNT										
-COH	275	278	16	-8	272	12	-18.6	54.4	10.6	16.4
-COCH ₃	252	305	15	-9	254	12	-20.2	52.8	10.5	16.3
-COOCH ₃	243	325	16	-8	247	12	-20.3	52.8	10.5	16.3
-COOH	256	304	17	-8	283	13	-19.0	53.7	10.6	16.4
-CONH ₂	267	297	17	-9	307	13	-18.9	54.2	10.6	16.4
N-tip BNNT										
-COH	284	269	14	-6	206	11	-19.5	53.9	10.6	16.6
-COCH ₃	288	282	14	-7	194	11	-20.4	52.5	10.5	16.
-COOCH ₃	281	301	15	-7	195	11	-20.9	51.3	10.5	16.4
-COOH	267	293	15	-7	215	11	-20.0	51.9	10.5	16.5
-CONH ₂	269	294	15	-7	211	11	-22.0	49.4	10.4	16.4

^a The A_S^- and A_S^+ values are $\text{\AA}^2$. Also, the $\bar{V}_S^+$, $\bar{V}_S^-$, Π , $V_{S,max}$ and $V_{S,min}$ magnitudes are in kcal/mol. σ_{total}^2 values are in $(\text{kcal/mol})^2$. ^b The $I_{S,min}$ and $I_{S,max}$ values are in eV.