A FIRST PRINCIPLE STUDY ON THE ELECTRONIC PROPERTIES OF FUNCTIONALIZED CARBON NANOTUBES

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The electronic and structural properties of functionalized semiconducting and metallic single-walled carbon nano-tubes (SWNTs) were investigated using spin-polarized density functional theory. The selected systems were $SWNT-NH_2$, $SWNT-NH_2-OH$ and $SWNT-NH_2-OH-COOH$. Our results confirmed that, in metallic and semiconducting nanotubes with odd number of functional groups, an additional acceptor level is observed near the Fermi level, while systems functionalized with two groups retain their pure characteristic. The theoretical predictions reveal that the radical transfers from the functional groups to carbon atoms at the ortho and para sites of the six-membered ring. The calculated partial density of states and atomic polarizations confirmed this site dependence.

1. Introduction

\Since 1991, carbon nanotubes have attracted considerable attention due to their outstanding structural and electronic properties. The electronic properties of single wall carbon nanotubes (SWNTs) are remarkable as they can be either metallic or semiconducting depending on their chirality's and diameter [1]. Manipulation of electronic properties of SWNTs by covalent functionalization is one of the most encouraging areas as it can be used to convert metallic SWNTs into semiconducting one and vice versa upon proper selection of type and number of functional groups. There have been many experimental [2-8] and theoretical [9-14] studies in this area. Depending on targeted application of functionalized carbon nanotubes, different kinds of functional groups have been used. These functionalized tubes have many applications in polymer composites, catalysis, sensors, gas storage and clinical medicine [15-18]. The amino functionalization of SWNTs enable chemical covalent bonding between nanotubes and biological molecules such as proteins, peptides and amino acids makes these systems very promising in nanomedicine and nanobiotechnology. The carboxylic acid is an appropriate functional group as the carbon atom is covalently attached to the tube and the OH group can be replaced by different molecular groups allowing one to attach other molecules especially biological ones to the tube sidewall. In this paper, we study the effects of covalent functionalization on electronic and structural properties of metallic and semiconducting SWNTs using the -COOH, $-NH_2$, and -OH functional groups. We considered the simultaneity effects of different functional groups on electronic and struc-tural properties of SWNTs. Our ab initio results show that the functionalized systems are stabilized. The attachment of the functional groups to nanotube sidewall and charge transfer lead to significant change in the electronic properties of SWNTs, converting metallic tubes to semiconducting one and vice versa. We will show the detailed investigations of structural and electronic properties of these functionalized systems.

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2. Computational Details

The electronic and structural properties of functionalized metallic (5,5) and semiconducting (8,0) single-walled carbon nanotubes (SWNTs) were investigated using first principles methods. Total energy and electronic structure calculations were carried out utilizing the density functional theory (DFT) with a plane-wave basis set and pseudopotentials, as implemented in quantum-espresso ab initio simulation package [19, 20]. The ultrasoft pseudopotentials proposed by Vanderbilt were used to describe the ionic potentials [21]. For the exchange and correlation terms, the generalized gradient approximation was employed as described by Perdew, Berke and Ernzerhof (PBE) [22]. In order to evaluate the spin polarization in the systems with odd number of electrons, the spin polarized calculations were performed. A cut off energy of 160 Ry for the grid integration was used to represent the charge density. The Brillouin zone was sampled with 12 Monkhorst-Pack k-points in Γ-Z direction [23]. Periodic boundary condition and supercell approximation was used. To avoid the interaction between the functional groups in adjacent cells, a lateral separation of 20 Å between tube centres was used. The supercell has 80 atoms for a (5,5) armchair and 64 atoms for a (8,0) zigzag carbon nanotubes. All of the structures under study were fully optimized using the conjugate gradient method until the forces acting on atoms was smaller than 0.001 eV/Å [24]. The charge transfer was calculated by Lowdin analysis.

3. Results and discussion

In this study, three kinds of covalent sidewall functionalization of single wall carbon nanotubes are investigated. The selected systems are SWNT-NH$_2$, SWNT-NH2-OH and SWNT-NH$_2$-OH-COOH. Both the (5,5) metallic and (8,0) semiconducting SWNTs are considered. Considering the fact that the structural properties of the (8,0) and (5,5) functionalized SWNTs are the same, we will just discuss the details of the results of (5,5) functionalized systems, while the (8,0) systems are only listed in corresponding Tables for comparison. The optimized structures are shown in Fig.1.

Table 1. Structural optimization results of pure and functionalized (5,5) SWNT (C^1 is related to –COOH group).

System	d$_{C-C}$ (Å)	d$_{C-N}$ (Å)	d$_{C-C^1}$ (Å)	d$_{C-O}$ (Å)	a$_{C-C-C}$ (°θ)	a$_{C-C-N}$ (°θ)	a$_{C-C-C^1}$ (°θ)	a$_{C-C-O}$ (°θ)
(5,5) SWNT	1.42	-	-	-	119.2	-	-	-
(5,5) SWNT-NH$_2$	1.51	1.50	-	-	109.7	107.7	-	-
(5,5) SWNT-NH$_2$-OH	1.51	1.49	-	1.47	109.6	109.9	-	109.2
(5,5) SWNT-NH$_2$-OH-COOH	1.52	1.49	1.51	1.47	108.7	109.2	109.9	109.2

As the Figure shows, due to the attachment of the functional groups, local distortions are occurred along the radial direction on the nanotube sidewall. These distortions are caused by local rehybridization of nanotube carbon atoms from sp^2 to sp^3 hybrid upon C-C (Fig. 1a), C-N (Fig. 1b) and C-O (Fig. 1c) bond formation with the functional groups. The calculated average bond lengths and angles of the pristine and functionalized tubes confirm this rehybridization (Fig.2 and Table 1). To evaluate the chemical stability of the structures, the binding energies are calculated using Eq. (1).

$$E_b = E(SWNT / X) - E(SWNT) - E(X) \qquad (1)$$

Where E(SWNT/X) is the energy of the functionalized carbon nanotube, E(SWNT) is the energy of the SWNT and E(X) is the energy of the functional group. The calculated binding energies indicate that the functionalized carbon nanotubes are stabilized. As the values listed in Table 2 show, the binding energies always increase with increasing the number of attached functional

groups. To determine the most stable configurations, we consider different possible distributions of two and three addend functional groups on the nanotube sidewall. Our results show that, adsorption of the second and third functional groups on the tube sidewall exhibit strong site dependence [14]. The resulted binding energies show that the second and third functional groups favour the ortho and para sites of the six-membered ring that the first or second functional group is chemisorbed (Fig. 3). As values listed in Table 2 show, we can see that the functionalized metallic (5,5) SWNTs have larger binding energies in respect to those of functionalized semiconducting (8,0) SWNT. This is due to the existence of finite charge density at the Fermi level of the metallic one, that cause to stabilize formed charge complex between tube and functional group [25].
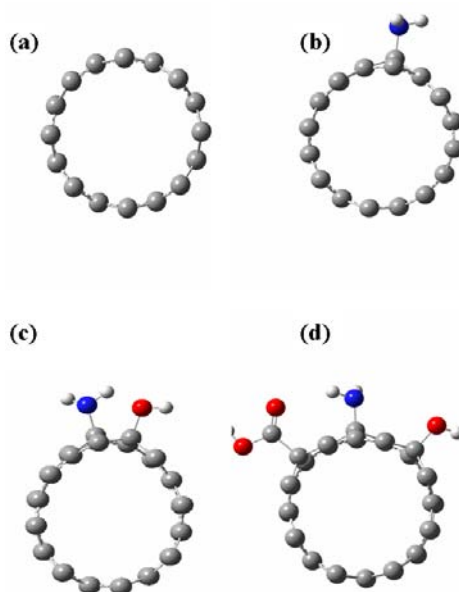

Fig. 1. Optimized structures for: (a) pure (8,0) SWNT; (b) (8,0) SWNT-NH_2; (c) (8,0) SWNT-NH_2-OH; and (d) (8,0) SWNT-NH_2-OH-COOH.

We also calculated the band structures of the pure and functionalized tubes as shown in Figs. 4 and 5. As the Fig. 4a shows, the bare (5,5) armchair nanotube is a metal with a zero band gap and (8,0) tube is a semiconducting tube with a band gap about 0.5 eV (Fig. 5a). Considering the fact that there are odd numbers of electrons in our systems with the odd number of functional groups, spin-polarized DFT calculations are used. We can see that after the functionalization with functional groups, significant change is occurred in the band structure of the pristine tubes. In (5,5) tube, due to the attachment of NH_2, symmetry of the system is reduced and the two bands crossing over the Fermi level are separated (Fig. 4b). As a result, a half filled band is appeared near the Fermi level. Figures 4b and 4c show the spin-polarized band structure of the (5,5) SWNT-NH_2 system. As shown in the Figure, the half filled band observed at the Fermi level, splits in two bands with a very small gap of 0.7 eV due to the exchange interaction. The band of spin up electron (Fig. 4b) is appeared bellow the Fermi level and therefore it is an occupied band, while the band of spin down electron (Fig 4c) is located upper the Fermi level, therefore, it is an empty conducting band. So, the metallic tube is converted to a semiconducting tube. The Lowdin analysis indicate that the 0.11 e transfer from the nanotube to NH_2. Calculated charge transfers are listed in Table 2.
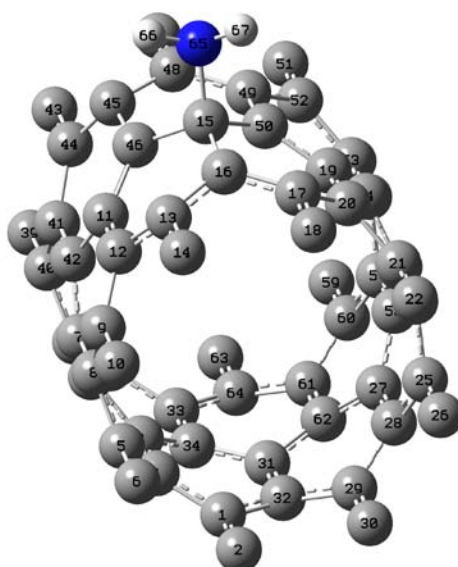
Fig 2. Position of different carbon atoms in (8,0) SWNT-NH$_2$.

Table 2. The calculated charge transfers, the magnetic moment, the band gap, and the binding energy values for functionalized nanotubes. The negative sign indicates charge transfers from the functional group to the nanotube.

System	Charge transfer (electron)	Magnetic moments (μ_B/cell)	Band gap (eV)	Binding energy (eV)
(5,5) SWNT	-	-	0.0	-
(5,5) SWNT-NH$_2$	0.11	1.94	0.3	1.35
(5,5) SWNT-NH$_2$-OH	0.11, 0.2	-	0.0	3.59
(5,5) SWNT-NH$_2$-OH-COOH	0.11, 0.2, -0.034	1.86 -	0.4 0.5	4.69 -
(8,0) SWNT	-	1.82	0.2	0.92
(8,0) SWNT-NH$_2$	0.11	-	0.5	3.16
(8,0) SWNT-NH$_2$-OH	0.11, 0.2	1.71	0.3	4.46
(8,0) SWNT-NH$_2$-OH-COOH	0.11, 0.2, -0.04			

Therefore, the resulted systems show the characteristic of the p-type doped semiconductor. In (8, 0) tube, after functionalization with NH$_2$ the band gap is reduced (about 0.3 eV) and conduction of the tube is increased. In the case of (8,0) tube, as (5,5) tube, the charge transfers from nanotube to amine group (Table 2). As a result, (8,0) amine-functionalized tube, behaves as a p-type semiconductor. The resultant systems, both (5,5) SWNT-NH$_2$ and (8,0) SWNT-NH$_2$, show similar band gaps and therefore similar semiconducting characteristics. The band structures of (8,0) amine-functionalized tube are very similar to that of (5,5) functionalized tube (Fig 5). To determine the origin of the half-filled bands observed at the Fermi level, for both (5,5) and (8,0) tubes, some partial DOS calculations are carried out for N, H and C atoms at ortho, para and meta positions of the six-membered ring that the NH$_2$ group is adsorbed (Fig. 6 parts b and c). The results demonstrate that the 2p orbitals of carbon atoms at the ortho and para sites have significant contributions in these bands (Fig. 6b). The contributions of the carbon atom at the meta position is minute.
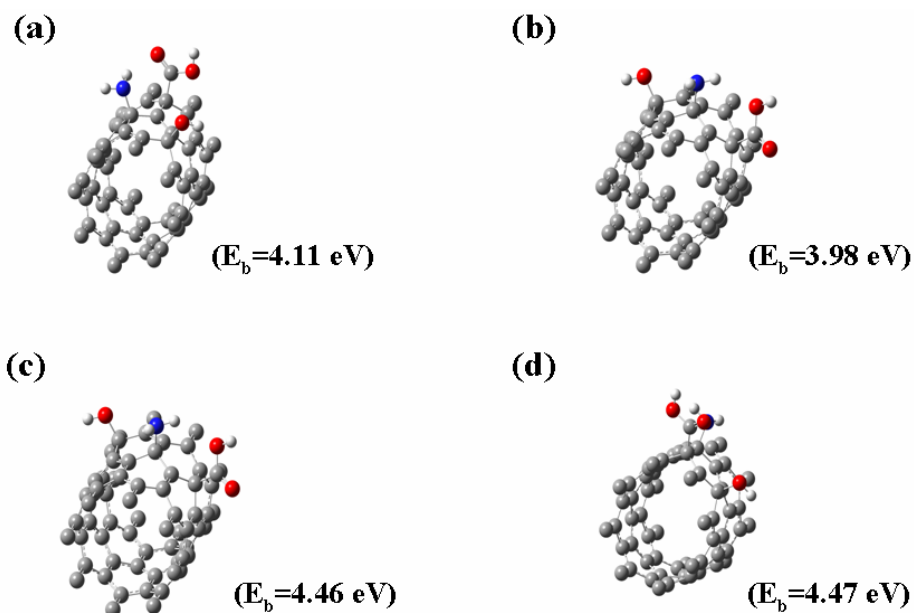
Fig 3. Optimized structures for different distributions of func-tional groups on the (8,0) SWNT sidewall at (a, b) meta; (c) para; and (d) ortho position.

As the Fig. 6c shows, the states of nitrogen and hydrogen atoms are located far from the Fermi level and have no contributions in these bands. We also calculated the magnetic moments of the systems with odd number of electrons (Table 2).
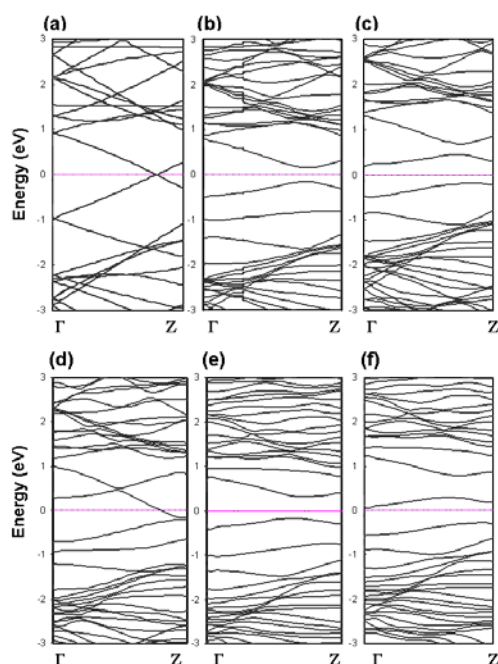

Fig. 4. Electronic band structures for: (a) pure (5,5) SWNT; (b) (5,5) SWNT-NH$_2$ (spin up); (c) (5,5) SWNT-NH$_2$ (spin down); (d) (5,5) SWNT-NH$_2$-OH; (e) (5,5) SWNT-NH$_2$-OH-COOH (spin up); and (f) (5,5) SWNT-NH$_2$-OH-COOH (spin down). The Fermi level is referred to the zero energy.

As the Figure 6a shows, the DOS of up spin states at the Fermi level are larger than that of the down spin states for (5,5) SWNT-NH$_2$. This is the origin of the magnetic moments. The magnetic moments are calculated using Eq. (2).

$$\xi = \frac{n_\uparrow - n_\downarrow}{n_\uparrow + n_\downarrow} \qquad (2)$$

Where $n_\uparrow$ and $n_\downarrow$ represent the spin density of electrons with up and down spin direction in the unit cell. Based on the above results, the second functional group is chemisorbed at the para site of the six-membered ring that the NH$_2$ group is located. With adsorption of the second functional group, the system energetically becomes favourable (Table 2).
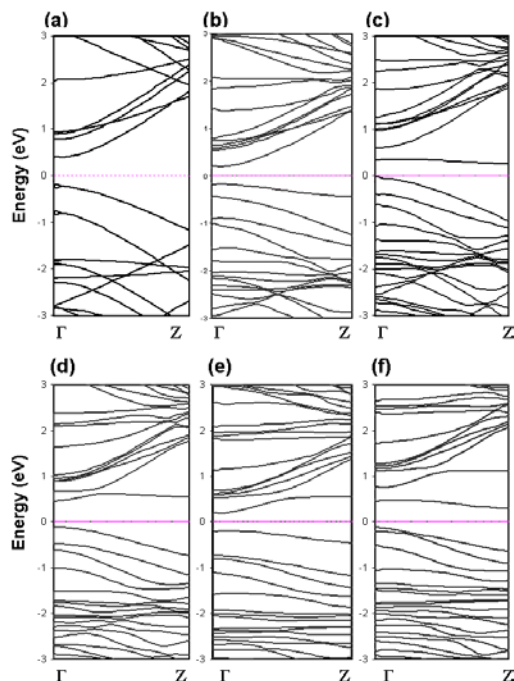

Fig. 5. Electronic band structures for: (a) pure (8,0) SWNT; (b) (8,0) SWNT-NH$_2$ (spin up); (c) (8,0) SWNT-NH$_2$ (spin down); (d) (8,0) SWNT-NH$_2$-OH; (e) (8,0) SWNT-NH$_2$-OH-COOH (spin up); and (f) (8,0) SWNT-NH$_2$-OH-COOH (spin down). The Fermi level is referred to the zero energy.

Table 3. The polarization values of carbon atoms for (8,0) SWNT-NH$_2$ system.

Atom	Position	Polarization
C_{15}	ortho	0.1042
C_{17}	para	0.1244
C_{19}	ortho	0.1068
C_{45}	para	0.0968
C_{49}	ortho	0.2249
C_{53}	para	0.1002
Other atoms	Non-ortho/para	< 0.06

The second functional group that attached to the nanotube sidewall is a hydroxile group. After the functionalization with the OH group, (5,5) SWNT became metallic with the band crossing over the Fermi level as pure tube (Fig. 4d), and (8,0) tube band gap was 0.5 eV as pure tube (Fig. 5d). Partial DOS calculations show that the bands appeared near the Ferrmi level are mainly composed from the 2p orbitals of carbon atoms near the adsorption site, especially those that are located at ortho and para sites respect to OH or NH$_2$ groups. Thus the third functional group, a -COOH group, chemisorbed at one of those para sites. The calculated spin polarized band structures in both tubes functionalized with three addend groups, as shown in Figures 4 and 5 (parts e and f), are similar to that of (5,5) SWNT-NH$_2$ and (8,0) SWNT-NH$_2$. The corresponding band gaps are also near to those of tubes functionalized with amine group (Table 2). The PDOS analysis of the half filled band appeared at the Fermi level indicate that these bands are composed mainly from the 2p orbital of carbon atoms at the ortho and para sites.
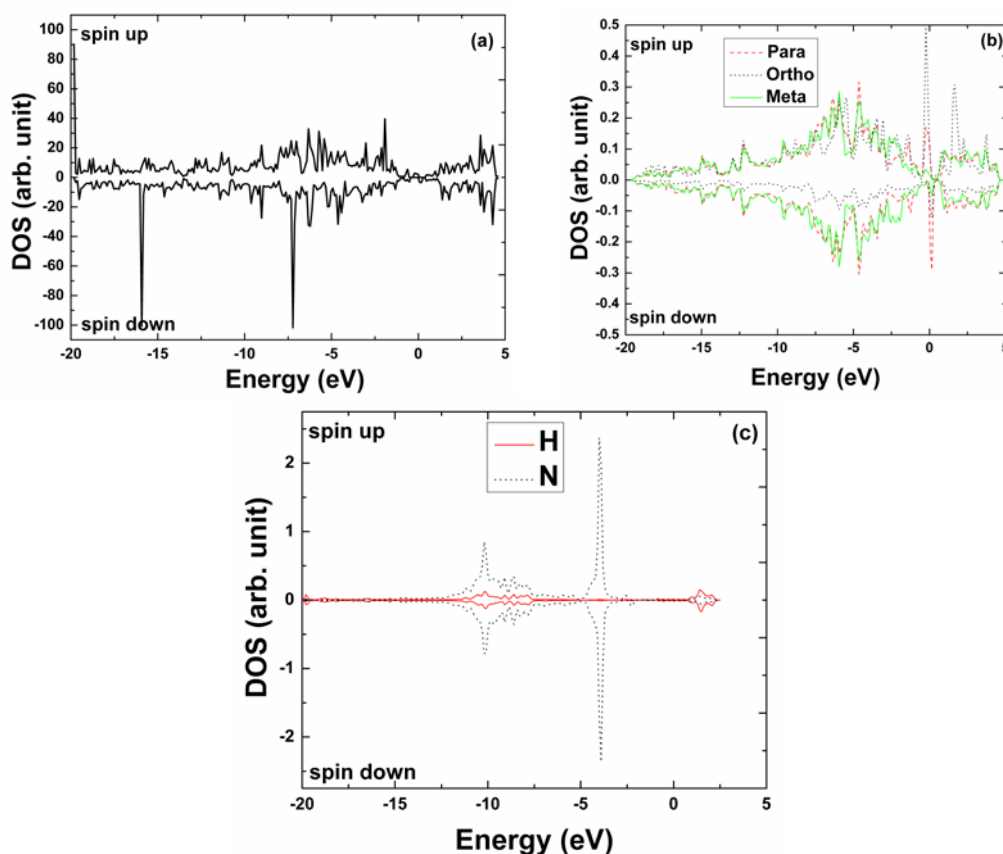
Fig. 6. (a) Total DOSs of (8,0) SWNT-NH$_2$; (b) partial DOSs of different C atoms, and (c) partial DOSs of N and H atoms for (8,0) SWNT-NH$_2$. The Fermi level is referred to the zero energy.

For the (5,5) and (8,0) functionalized SWNTs with one and three functional groups, the bands appeared at the Fermi level are flat and hardly distributed. Flatness of these bands indicates that the magnetic moments are localized near the adsorption site. The atomic polarizations are also calculated for all atoms contained in our systems with the spin polarization (Table 3). The results show that the carbon atoms located at the ortho and para positions (Fig. 3) have larger polarization than other non ortho- para atoms. This conclusion confirms the previous results obtained from energy and DOS calculations. From the Lowdin population analysis we conclude that the carbon nanotube act as an electron donor for -NH$_2$ and -OH groups and electron acceptor for -COOH group. The transferred charges in (5,5) tube are 0.11, 0.2 and -0.03 for the -NH$_2$, -OH and -COOH groups, respectively. The corresponding results for (8,0) functionalized tubes are listed in Table 2. The negative sign indicate that the charge is transferred from the -COOH group to the nanotube. Thus the electron withdrawing power of the carbon nanotube is limited.

4. Conclusion

In summary, using the first principle calculations, we have studied the effects of covalent functionalization on electronic and structural properties of the metallic and the semiconducting SWNTs. Our results show that attachment of odd number of functional groups lead to appearance of a half-filled acceptor level at the Fermi level in both the metallic and semiconducting tubes. In attachment of two functional groups to the nanotube sidewall, the electronic characteristic of pure nanotube is observed in both the metallic and semiconducting SWNTs. The result of charge transfer calculations show that the charge transfers from the nanotube to -OH and -NH$_2$ groups, and from the -COOH group to the nanotube. Due to charge transfer mechanism, carbon nanotubes show the characteristic of p-type semiconductor. More interestingly, both metallic and semiconducting nanotubes, show similar electronic band structures. Therefore upon proper

treatment it can be possible to tune the electronic properties of both metallic and semiconducting tube to the desire one.

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