

A Computational NMR Study for Chemisorption of Oxygen-doped on the Surface of Single-Walled Carbon Nanotubes

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Abstract: In this study computational Nuclear Magnetic Resonance (NMR) study and chemisorptions are performed to investigate the electronic structure properties of arm-chair (4, 4) and zig-zag (5, 0) Single-Wall Carbon Nanotubes (SWCNTs). First-principles of Density Function Theory (DFT) have applied in calculations on properties of molecular oxygen-doped (O-doped) SWCNTs. The results show dramatic differences between two types, (5, 0) zigzag and (4, 4) arm chair, of carbon nano-tubes. Structural models are optimized and chemisorption energies are obtained to investigate the Nuclear Magnetic Resonance (NMR) parameters for O-doped (5, 0) zigzag and (4, 4) armchair single-walled carbon nanotubes based on calculations using DFT. The chemical-shielding (σ_{ii}) tensors were converted to isotropic chemical-shielding (iso) and anisotropic chemical-shielding ($\Delta\sigma$) and asymmetric (μ_j) parameters of ^{17}O and ^{13}C atom for the optimized structures. We found that introduction oxygen does significantly change the structure of the SWCNT and thus the bonding mode of the structure is remarkably altered. Comparing the results of the zigzag and armchair models and calculated chemical shielding, electric field gradient tensors at the sites of carbon reveal that O_2 chemisorption has a dramatic effect on the electronic structure of SWCNTs.

Keywords: Anisotropic, chemical shielding, DFT, gaussian98, isotropic, NMR, oxygen-doping

INTRODUCTION

Calculation by computational methods has a long history in the study of materials used in energy technologies. As the number of articles in this field suggest, these methods continue to play a substantial role which is, moreover, likely to grow in the future (Catlow *et al.*, 2010). Carbon Nano-Tubes (CNT) are nano structures derived from rolled grapheme planes (Fig. 1) (Ijima and Ichihashi, 1993) whose electronic properties can be controlled. Zhao *et al.* (2002) studied the absorption of various gas molecules (NO_2 , O_2 , NH_3 , N_2 , CO_2 , CH_4 , H_2O , H_2 and Ar) on both single SWNT and SWNT bundles using first principles method. The Self-Consistent Field (SCF) electronic structure calculations are performed based on Density Functional Theory (DFT) (Schimizu and Tsukada, 1993; Lynch and Hu, 2000; McClenaghan *et al.*, 2000; Zhang and Hu, 2000; Noguera, 2001). Jhi *et al.* (2000) theoretically studied the effect of oxygenation on the electronic and magnetic properties of SWNT, their calculation for the density of states shows that weak coupling between carbon and oxygen leads to conducting states near the band gap. One possible way to modify the electronic and vibronic properties is a charge transfer during their intercalation and fictionalization (Barros *et al.*, 2007). Depending on their diameter and felicity it was predicted that they can be semiconductors or densities (Avouris *et al.*, 2000) and their electrical

properties can be modified by doping (Lee *et al.*, 1997). The conductance of a single oxygen doped (6, 6) nano-tube decreases by about 30% with respect to that of the perfect nano-tube (Lang and Avouris, 1998). (Ulbricht *et al.*, 2002) concluded that no evidence for a more strongly bound chemisorbed species or for dissociative oxygen absorption was found. The effects of oxygen chemisorption on a nano-tube based field effect transistor have been controversial as to whether it induces oxygen-doping of the nano-tube body or the work function increase in the semiconductor electrode. The doping effect could be more influential in devices with longer nano-tubes (Babanejad *et al.*, 2010; Ashrafi *et al.*, 2010). In this study, two contributions to the resistance of nano-tubes were investigated. First, we calculate the contact from oxygen chemisorption on a nano-tube with model semiconductor (5, 0) zig-zag and (4, 4) arm chair single-walled carbon nano-tubes (Fig. 2). Then we concentrate on the resistance produced by substitutional defects. We show the chemical-shielding (σ_{ii}) tensors were converted to isotropic chemical shielding (iso) and anisotropic chemical-shielding ($\Delta\sigma$) and asymmetric (μ_j) parameters of ^{17}O and ^{13}C atoms for the optimized structures (Table 1 and 2) (Saito *et al.*, 1992; Mintmire *et al.*, 1992).

They can also sustain large current the study of electronic and structural properties of oxygen-doped single wall nano-tubes have been performed (Mirzaei and Hadipour, 2006). The calculation of NMR (Ghasemi

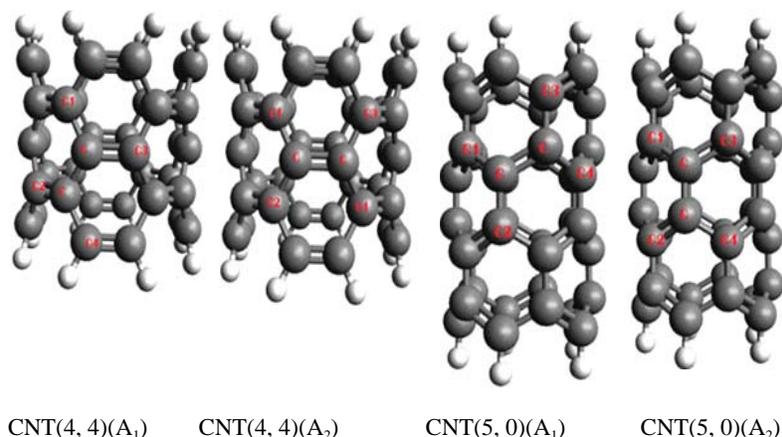


Fig. 1: (A₁&A₂) the (5, 0) and (4, 4) SWCNT

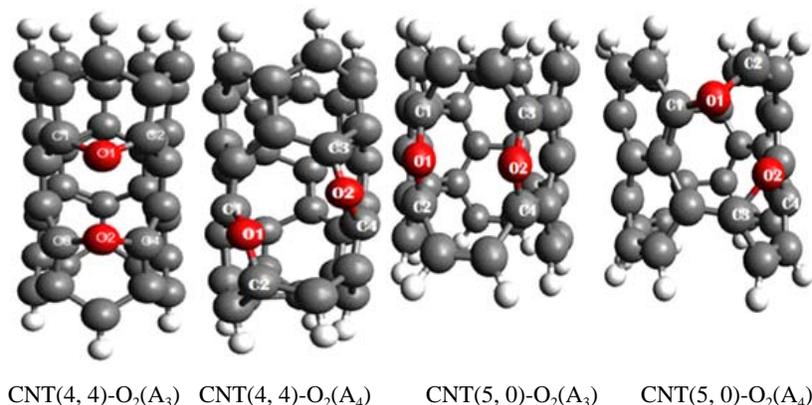


Fig. 2: Chemisorption configurations of an O₂ molecule (The sites A₃, A₄ of (4, 4) and (5, 0) SWCNT-O₂, respectively)

Table 1: Calculated ¹⁷O NMR parameters for CNT, O₂-CNT (4, 4) systems^a

Model ¹⁷ O (configuration)	Atoms	σ_{11}	σ_{22}	σ_{33}	σ_{iso}	$\Delta\sigma$	η_n
CNT(4,4) - (A ₁)	C ₁	-1.1600	-1.1600	163.8700	53.8495	165.0308	0.0000
	C ₂	-1.1600	-1.1600	163.8700	51.2149	165.0308	0.0000
	C ₃	-0.7300	-0.7300	163.7900	53.8495	164.5215	0.0000
	C ₄	-0.7500	-0.7500	163.7400	54.0800	164.4900	0.0000
CNT(4,4)- (A ₂)	C ₁	-0.7100	-0.7100	163.8700	54.1157	164.4815	0.0000
	C ₂	-40.9778	52.7796	159.7877	153.8868	153.8868	2.4588
	C ₃	-35.3100	13.8404	175.9600	186.6948	186.6948	1.4317
	C ₄	-1.1700	-1.1700	163.8500	165.0219	165.0219	0.0000
O ₁	C ₁	-66.8441	54.0846	83.9711	23.7372	90.3508	2.0077
	C ₂	-66.4764	54.0373	84.0975	23.9284	90.7075	1.9900
O ₂	C ₁	-66.7714	54.0488	83.9700	23.7491	90.3313	2.0063
	C ₂	-66.3669	54.0373	84.4001	23.9226	90.2623	2.0009
CNT(4,4)-O ₂ (A ₁)	C ₁	-53.8794	39.8243	95.9593	27.3014	102.9869	1.3648
	C ₂	-48.5238	12.7128	100.4479	21.5456	118.3535	0.7761
O ₂	C ₁	-29.8179	7.3599	103.6236	27.0552	114.8526	0.4856
	C ₂	-66.1822	56.8643	97.6708	29.4509	102.3298	1.8037

^a: Calculated σ_{ii} , σ_{iso} and $\Delta\sigma$ values are in ppm; ^b: In each row, the first number is for σ_{11} , the second number is for σ_{22} and the third number is for σ_{33}

et al., 2010; Duer, 2002) parameters using DFT techniques have become a major and powerful tool in the investigation of molecular structure. The calculations showed consistent results with the Computational ones.

The tensors originating at the sites (A₁, A₂, A₃ and A₄) of half-spin magnetic nuclei make available important trends about the electronic properties at the sites of these nuclei. The tensors were computed in the optimized structures by

Table 2: Calculated ¹⁷O NMR parameters for CNT, O₂-CNT (5, 0) systems^a

Model ¹⁷ O (configuration)	Atoms	σ_{11}	σ_{22}	σ_{33}	σ_{iso}	$\Delta\sigma$	η_n
CNT(5,0) - (A ₁)	C ₁	-118.0860	12.8629	163.8700	53.8495	165.0308	0.0000
	C ₂	-116.9704	13.8079	159.2077	53.8495	165.0308	0.0000
	C ₃	-118.1198	12.8584	159.4017	54.1090	164.5215	0.0000
	C ₄	-116.9332	-0.7500	159.2050	54.0800	164.4900	0.0000
CNT(5,0)- (A ₂)	C ₁	-45.2746	155.1751	325.7105	54.1157	164.4815	0.0000
	C ₂	-118.1198	12.8584	159.4017	57.1965	153.8868	2.4588
	C ₃	-27.4737	155.3875	319.5851	51.4968	186.6948	1.4317
	C ₄	-0.0454	120.0800	120.0800	53.8354	165.0219	0.0000
O ₁	C ₁	-63.2476	63.5826	90.1893	23.7372	90.3508	2.0077
CNT(5,0)-O ₂ (A ₁)	C ₂	-69.3226	65.3214	65.3214	23.9284	90.7075	1.9900
O ₂	C ₁	-31.5986	74.3457	104.6805	23.7491	90.3313	2.0063
O ₁	C ₂	-72.6502	-19.9352	74.9677	23.9226	90.2623	2.0009
CNT(5,0)-O ₂ (A ₂)	C ₁	-48.8614	22.4174	75.9510	27.3014	102.9869	1.3648
	C ₂	-72.6368	16.2112	92.0007	21.5456	118.3535	0.7761
O ₂	C ₁	-48.4295	2.6526	96.4404	27.0552	114.8526	0.4856
	C ₂	-128.7315	13.2045	82.9991	29.4509	102.3298	1.8037

^a: Calculated σ_{ii} , σ_{iso} and $\Delta\sigma$ values are in ppm; ^b: In each row, the first number is for σ_{11} , the second number is for σ_{22} and the third number is for σ_{33}

Table 3: Calculated structural parameters and binding energies of O₂ Chemisorption on the (4, 4) SWCNT^a

Mode (configuration)	r_{C-C}	r_{C-O}	r_{O-O}	$\Delta E_{abs-DFT}$
CNT (4, 4) (A ₁)	(C-C) ₁ = 1.421	-	--	
	(C-C) ₂ = 1.422			
	(C-C) ₃ = 1.421			
	(C-C) ₄ = 1.422			
CNT (4, 4) (A ₂)	(C-C) ₁ = 1.451	-	-	-
	(C-C) ₂ = 1.419			
	(C-C) ₃ = 1.422			
	(C-C) ₄ = 1.452			
CNT (4, 4)-O ₂ (A ₃)		(C-O) ₁ = 1.333	-	
		(C-O) ₂ = 1.334		2.563-43762.03
		(C-O) ₃ = 1.334		
		(C-O) ₄ = 1.333		
CNT (4, 4)-O ₂ (A ₄)		(C-O) ₁ = 1.378	-	
		(C-O) ₂ = 1.395		2.547-43763.24
		(C-O) ₃ = 1.386		
		(C-O) ₄ = 1.384		

^a: All calculated distances are in Å; All calculated binding energies are in electron volt (eV)

Table 4: Calculated structural parameters and binding energies of O₂ adsorbed on the (5, 0) SWCNT^a

Model (configuration)	r_{C-C}	r_{C-O}	r_{O-O}	$\Delta E_{abs-DFT}$
CNT (5, 0) (A ₁)	(C-C) ₁ = 1.437	-	--	
	(C-C) ₂ = 1.451			
	(C-C) ₃ = 1.437			
	(C-C) ₄ = 1.451			
CNT (5, 0) (A ₂)	(C-C) ₁ = 1.426	-	-	-
	(C-C) ₂ = 1.451			
	(C-C) ₃ = 1.403			
	(C-C) ₄ = 1.437			
CNT (5, 0)-O ₂ (A ₃)		(C-O) ₁ = 1.408	-	
		(C-O) ₂ = 1.408		2.563-43762.03
		(C-O) ₃ = 1.408		
		(C-O) ₄ = 1.408		
CNT (5, 0)-O ₂ (A ₄)		(C-O) ₁ = 1.375	-	
		(C-O) ₂ = 1.373		2.547-43763.24
		(C-O) ₃ = 1.335		
		(C-O) ₄ = 1.399		

^a: All calculated distances are in Å; All calculated binding energies are in electron volt (eV)

high-level quantum chemical calculations (Wu *et al.*, 2002). In this computational evaluation, the influence of oxygen-doping on the electrostatic properties of zig-zag (5, 0) and arm chair (4, 4) CNTs are studied via the tensors calculations at the sites of ¹⁷O nuclei in two case representative O-doped models (Ghasemi *et al.*, 2010). The length of 7.1 and 4.8 Å were obtained for (5, 0) and

(4, 4) single-wall nano-tube including Oxygen-doped (O-doped), respectively. The forms indicated in Fig. 1 and 2 are considered in calculations (Table 1 to 4). The aim of this study is investigating chemisorption properties of oxygen-doped (4, 4) and (5, 0) on the surface of single-walled carbon nanotubes as gas sensors and optimizing absorption rates by using DFT calculations.

MATERIALS AND METHODS

This study was performed in Payame Noor University, Sari Center, Iran, as a research project over carbon nanotubes absorption properly in 2010 and 2011. The calculations are performed by a GAUSSIAN 98 program package (Chang *et al.*, 2006).

In the present study, the effects of Oxygen (O₂) molecules chemisorption on SWCNTs of models (4, 4) and (5, 0) was investigated. In order to investigate the electronic structure in semiconductor nanotube contacts of O₂ molecules, the computations were fully implemented by Gaussian 98 Software package (Chang *et al.*, 2006; Souza *et al.*, 2007; Souza *et al.*, 2006; Saito *et al.*, 1992). Geometry optimizations were performed using 6-311G* basis set with DFT/B3LYP functional (Parr and Yang, 1994; Becke, 1993). NMR ¹⁷O and ¹³C chemical shielding calculations were computed at B3LYP/6-311G* level of theory using Gauge Including Atomic Orbitals (GIAO) approach (Wolinski *et al.*, 1990). The undoped models (4, 4) and (5, 0) consisted of 40 C atom with length of 4.8 and 7.1 Å are chosen for the purpose, respectively. In absence of periodic boundary conditions in molecular calculations, it is necessary to saturate the carbon dangling bonds with hydrogen atoms. Curvature of small tubes is a crucial feature responsible for intense interaction of atoms in tubes. Quantum chemical calculated tensors at the Principal Axes System (PAS) ($\sigma_{11} \leq \sigma_{22} \leq \sigma_{33}$) is converted to a diagonal matrix with σ_{11} , σ_{22} and σ_{33} components, measurable NMR parameters, chemical shielding isotropic (σ_{iso}), chemical shielding anisotropic ($\Delta\sigma$) and asymmetric (μ_j) are used, respectively (Ghasemi *et al.*, 2010; Marian and Gastreich, 2001). This shows a second-order change in the molecular energy:

$$E = E_0 + B_0 \chi B_0 + \sum_{i=1}^N \mu_i \sigma B_0 + \dots \quad (1)$$

The summation is taken over the O nuclei in the system. We are not interested in the magnetic susceptibility, χ , but only in the bilinear response property:

$$\sigma_{ij} = \left(\frac{\partial^2 E}{\partial B_i \partial \mu_j} \right)_{B_i = \mu_j = 0} \quad (2)$$

where μ_j is the components of magnetic moment and B_i is external magnetic field. The principal components for specification of shielding are defined by this coordinate system as following equation (Marian and Gastreich, 2001; liu *et al.*, 2007):

$$\Delta\sigma = \frac{3}{2}(\sigma_{33} - \sigma_{iso}), \sigma_{iso} = \frac{(\sigma_{11} + \sigma_{22} + \sigma_{33})}{3}, \eta_{\sigma} = \frac{3}{2} \left(\frac{\sigma_{22} - \sigma_{11}}{\Delta\sigma} \right) \quad (3)$$

In which σ_{iso} , $\Delta\sigma$ and are isotropic, anisotropic and asymmetric parts of tensor, respectively and in certain cases vanishes.

RESULTS AND DISCUSSION

In the present study, two models of zig-zag (5, 0) and armchair (4, 4) SWCNTs with specified tube lengths are studied using quantum chemical calculations (Fig.1 and 2). Chemical shielding tensors of H-capped (5, 0) and (4, 4) SWCNTs interacted with oxygen molecules are obtained. The calculated geometry parameters and binding energies and ¹⁷O and ¹³C chemical shielding tensors are presented in Table 1 to 4. The molecular geometries and binding energies and NMR chemical shielding tensors resulted from oxygen molecular chemisorptions are discussed in following sections, separately.

Molecular geometries and adsorption energies: In this section, stable configurations of oxygen molecule chemisorption at the surface of SWCNT are discussed. After optimized structures were obtained, geometrical parameters and binding energies of the models structure of these oxygen molecule attached to the zig-zag (5, 0) and armchair (4, 4) SWCNTs were calculated as show in Fig. 1 and 2. The results at the level of the B3LYP DFT method and the 6-311G* standard basis set are summarized in Table 3 and 4. Upon chemisorption of a O₂ molecule on the C-C bond at the surface, the molecule O₂ dissociates toward the O-O bond lengths. Chemisorption on nano-tube increases from 1.21 and 2.528 Å to 2.563 Å for (4, 4) and (5, 0) SWCNT, respectively. We have considered two distinct chemisorption sites, marked as A₁, A₂, A₃ and A₄ (Table 3 and 4). CNT and CNT-O₂ binding energies, E_{ad}, are calculated using, E_{ad} = E_{tot} (molecule O₂ + CNT_s) - E_{tot} (CNT_s) - E_{tot} (molecule O₂) Where, E_{tot} (CNT), E_{tot} (O₂) and E_{tot} (CNT+O₂) are the energies of the optimized tubes, that are chemisorption and tube-absorb ate systems, respectively. Armchair (4, 4) and zigzag (5, 0) tube has different C-C bonds thus offers two distinct chemisorption sites (Table 3 and 4) before and after the doping of O atoms, the bond length of in SWNT-A₁(4, 4) from (C-C)_{1,3} = 1.421 Å and (C-C)_{2,4} = 1.422 Å decreased to 1.333-1.334 Å and bond length of in SWNT-A₂(4, 4) from (C-C)₁ = 1.451 Å, (C-C)₂ = 1.419 Å, (C-C)₃ = 1.422 Å and (C-C)₄ = 1.452 Å decreased to 1.378-1.395 before and after the doping of O atoms, the bond length of in SWNT-A₃(5, 0) from (C-C)_{1,3} = 1.437 Å and (C-C)_{2,4} = 1.451 Å decreased to 1.335-1.399 Å bond length of in SWNT-A₄(5, 0) from (C-C)₁ = 1.426 Å, (C-C)₂ = 1.451 Å, (C-C)₃ = 1.408 Å and (C-C)₄ = 1.437 Å increased to 1.454-1.475 Density functional calculations of SWNT, efficient process of charge transfer between the oxygen molecule and the nano-tube is found to substantially reduce the susceptibility of the π-electrons

of the nano-tube to modification by oxygen while maintaining stable doping. Oxygen chemisorption can be achieved with O_2^+ ion implantation (Kamimura *et al.*, 2005).

^{17}O NMR parameters: New data and presentation of results are given here for O-doping computational NMR parameters of oxygen nuclei for two models (4, 4) and (5, 0) of CNTs (Table 1 and 2). Oxygen molecule chemisorptions of SWCNTs have remarkable influence on NMR tensors, which is in complete accordance with the facts mentioned above. Consequently, it has been ^{17}O indicated that for the H-capped SWCNTs, the calculated ^{17}O chemical shielding values at the ends are smaller than in the tube's center if the carbon is directly bound to hydrogen; otherwise it is larger (Liu *et al.*, 2007). It is also depicted that chemical shielding components converge in a way similar to that of the chemical shifts when increasing the tube length albeit not as smoothly as the isotropic shielding.

Chemical shielding tensors and chemical shifts are efficient parameters for characterization of carbon nanotubes. Calculation of these shielding tensors for oxygen nuclei reveals that increasing length and diameter of SWCNTs- A_1 (5, 0) chemical shielding will cause O nuclei converge on nanotube surface. Results are consistent with strong interaction between the tube and O_2 molecule in SWCNTs- A_1 (5, 0). This is consistent with previous results derived from band structure calculations (Rubio *et al.*, 1994; Balase *et al.*, 1994). On the other hand, the calculated ^{17}O chemical shielding values in the middle of the CNT (4, 4) and CNT (5, 0) seem to approach values 53.8495, 54.1090, 78.5398 and 149.1663 ppm, respectively (Table 1 and 2). The NMR chemical shielding of finite SWCNTs were found to converge very slowly, if at all, to the infinite limit, indicating that hydrogen capped tube fragments are not necessarily good models of infinite systems. As the length of the fragment increases, these orbitals do not yield a contribution to the electron density along the tube (except at the ends) and must therefore be regarded as artifacts due to treating the finite-sized systems. More recently, this group indicated that Zurek *et al.* (2008) also, the introduction of oxygen atoms is theoretically predicted to give rise to chiral current flow along the nanotube due to symmetry breaking (Liu and Guo, 2004; Miyamoto, 1996). Due to O_2 chemisorptions the calculated ^{17}O NMR parameters of those interacted carbon atoms are also modified. As understood by comparison of sites (A_1 , A_2 , A_3 and A_4), the carbon atoms included in O_2 chemisorptions become more shielded. Among the four NMR principal components, intermediate shielding component, σ_{22} , shows more change from nanotube to the O_2 -CNT system. The discrepancy between the ^{17}O chemical shielding tensor for the sites (A_1 , A_2 , A_3 and A_4) systems must be attributed to the different nature of the frontier orbital's which will

have an influence on the ^{17}O chemical shielding. However, this theoretical considerations and predictions are undermined by recent experimentally investigations where chiral currents have been observed in undoped single-walled carbon nanotubes (Krstić *et al.*, 2002). The interest in oxygen-doped CNTs in terms of application is the control of the type of charge carriers within the carbon nanotubes. This control is one key-issue for a successful implementation of CNTs in nanotubes and molecular electronics. O_2 -CNTs should show significant advantages over nanotubes for gas sensor applications, due to their reactive tube surfaces and the sensitivity of their transport characteristics to the presence, distribution and chemistry of oxygen. (Peng and Cho, 2003) first suggested O_2 -CNT for use in gas sensors, due to the ability of oxygen dopants to bind to incoming gas species. The oxygen in the nanotubes can be seen as regular defects which change the chemical behavior of tubes.

Electronic properties: Collins *et al.* (2005) found that oxygen gas has dramatic effects on conductivity, thermoelectric power and the local density of states of nanotube (Collins *et al.*, 2005). (Kang *et al.*, 2005b) reported the characteristic behavior of a field effect transistor based on an individual Fig. 3. Electronic density of states for (a) CNT (5, 0) (A_1), CNT (4, 4) (A_2) and SWCNT, (c) CNT (4, 4)- O_2 (A_3), (d) CNT (4, 4)- O_2 (A_4), (e) CNT (5, 0)- O_2 (A_3), (f) CNT (5, 0)- O_2 (A_4) systems. Dashed line denotes the Fermi level. SWCNT upon exposure to O_2 at various pressures and attributed the device behaviors to oxygen induced p-type doping and thus the Fermi level pinning near the top of the valence band. The Total Density of States (TDOS) of these carbon nanotubes quantum structure states in the valence band shown in Fig. 3. We study the efficacy on electronic properties of SWCNT by O_2 chemisorptions. The calculated band gap of nanotube model zig-zag (5, 0) CNT ($A_{1,2}$) is about 0.77eV and of nanotube model armchair (4, 4) CNT ($A_{1,2}$) is about (2.79) eV, which is very close to DFT simulated for the other small diameter nanotubes (Yim and Liu, 2004; Ratner *et al.*, 1998). The existence of this small band gap suggests that the system can be converted into a Narrow-gap semiconductor material. Such a big decrease of the band gap of the zig-zag (5, 0) and armchair (4, 4) nanotubes upon O_2 chemisorption on seat models may originates from the changes of the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) of these systems. The electron conduction mechanism is expected to be tunneling when the Fermi levels of contacts lie within the HOMO-LUMO gap of a short length molecule, as for the case of these SWCNT (Derycke *et al.*, 2002). As shown in Fig. 3, the HOMO and LUMO densities of pure zigzag (5, 0) and armchair (4, 4) SWCNT are mainly positioned at nanotube wall, while those of the open-ended SWCNT with O_2

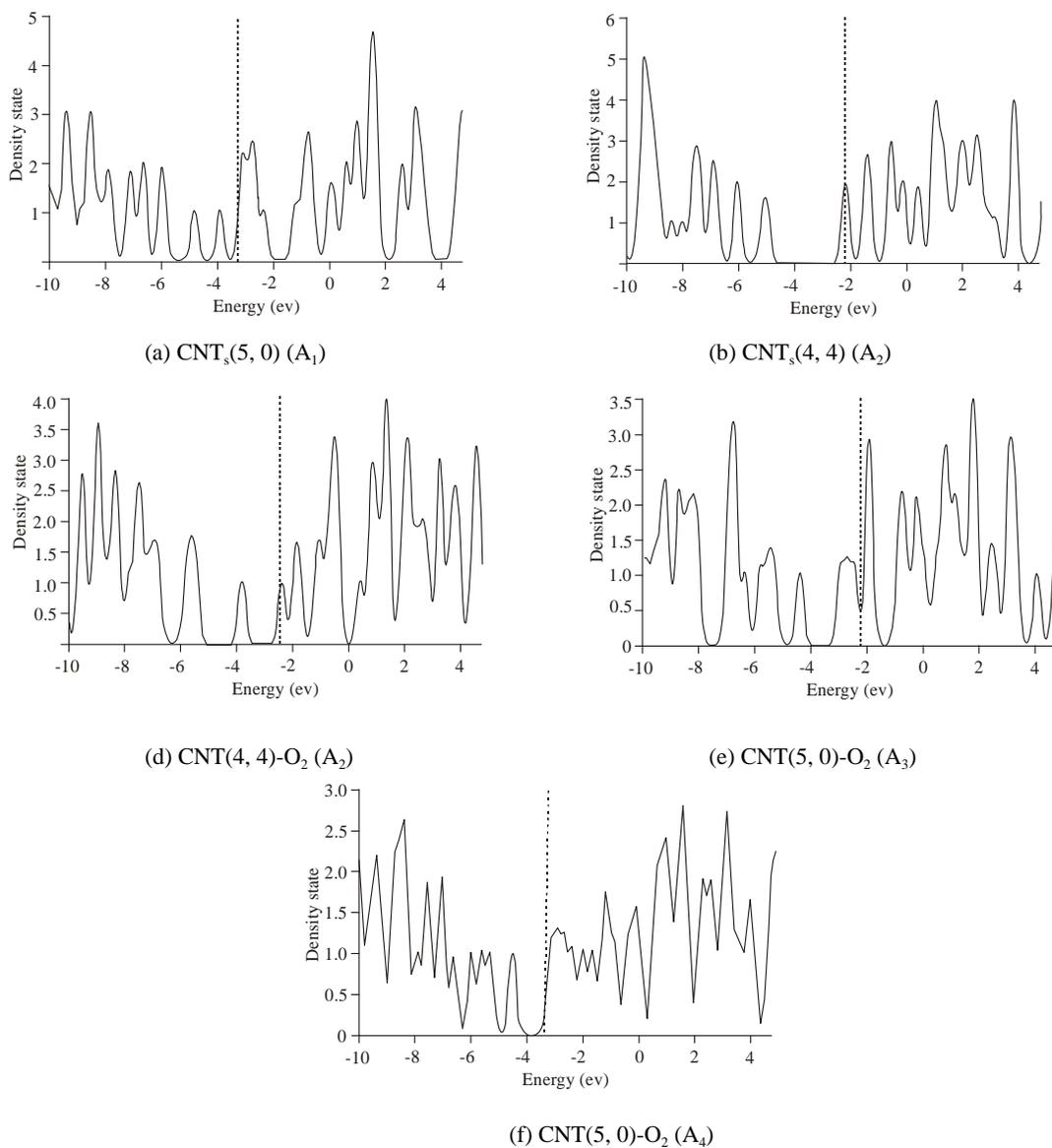


Fig. 3: Electronic density of states for(a) CNT (5,0) (A_1), CNT (4,4) (A_2) and SWCNT, (c) CNT(4,4)- O_2 (A_3), (d) CNT(4,4)- O_2 (A_4), (e) CNT(5,0)- O_2 (A_3), (f) CNT(5,0)- O_2 (A_4) systems. Dashed line denotes the Fermi level

chemisorption at the seat models are mainly localized within the C-C bonds (Fig. 3). Indeed, (Kang *et al.*, 2005a) have used the LUMO of O_2 to allege that this charge trapping transfer should be interpreted as p-type doping regardless of the actual strength of the process. In this study we find much more evidence for both effects. This would occur when electrons accumulate on the nanotube, preventing whole conduction while the Fermi level is pinned at the valence band maximum, creating a barrier to electron introducing. All of these, suggest that different electronic properties of an open zig-zag (5, 0) and armchair (4, 4) SWCNT can be achieved through chemisorption of O_2 on nanotubes by the same

chemisorption on different sites. When molecular oxygen is chemisorbed on the SWCNT, the interaction of them is very strong which cause changes in electronic properties of these nanotubes. Thus, the presence of molecular O_2 increases the bond gap energy of previous zig-zag (5, 0) and armchair (4, 4) SWCNT. With chemisorption of O_2 , the band gap is calculated for model CNT (4, 4)- O_2 (A_3) 1.47 eV, for model CNT (4, 4)- O_2 (A_4) 2.9 eV, for model CNT (5, 0)- O_2 (A_3) 1.44 eV and for model CNT (5, 0)- O_2 (A_4) 1.37eV. The effect of O_2 chemisorption on zig-zag (5, 0) and armchair (4, 4) SWCNT increases the bond gap energy. The effect is more obvious for CNT (4, 4)- O_2 (A_4). Also the TDOS plots for the sites (A_1 , A_2 , A_3 and

A₄) are significantly differ from the zig-zag (5, 0) and armchair (4, 4) nanotube near an electric filed, which may result in a conductance change of nanotube up to chemisorption of O₂. For chemisorptions model CNTs (5, 0) (A₁), we found that band gaps below electric filed become narrow and new local energy levels occur near the Fermi level, which result in the nearly continuous local Density of State (DOS) peaks below electric filed.

Furthermore, bonding the O₂ on model CNTs (4, 4) (A₂) appears a peak near electric filed with a band gap about 2.79 eV. The TDOS for (O₂-CNT) system is presented in CNT (4, 4)-O₂ (A₄). For this system significant changes in the DOS are observed near the Fermi level, similar to the O₂ chemisorptions. However, the chemisorption of oxygen molecule is further increases band gap (2.9eV) and reduces the electrical conductance of the zig-zag (5, 0) and armchair (4, 4) SWCNT. This situation is naturally different from the oxygen molecule chemisorptions on the wall of nanotubes. In CNT (5, 0)-O₂ (A₃) model, oxygen molecule with a minor change in length of O-O band would be doped on carbon nanotube zig-zag model.

CONCLUSION

In summary, we studied the influence of substitutional O₂ on the single-walled carbon nanotubes conformation and a quantum-chemical calculation was performed. The calculations show that the combination of hexagons and O₂ molecule concentration produces kinks that include the regular shaped nanotubes. The GIAO calculations at the B3LYP/6-311G* level using DFT optimized geometries provided isotropic shielding tensors that correlated well with the observed chemical shift data. The calculated values provided the unambiguous definite assignment of the observed ¹⁷O-NMR calculative data and can be used in the prediction of the chemical shifts of known SWCNT molecules. The present calculations can also be used to predict chemical shift data for species the formation of which has not yet been observed. For four O₂ chemisorption model, we found band gaps above Fermi level become narrower and new local energy levels occur near the Fermi level, which result in the nearly continuous DOS peaks below Fermi level. In overall of our studies, it is worthwhile to replace the pure nanotubes by chemically doped nanotubes and exploit the new phenomena.

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