Comparison of NQR of O2, N2 and CO on Surface of Single-walled Carbon Nanotubes and Chemisorption of Oxygen-doped on the Surface of Single-walled Carbon Nanotubes: A DFT and Computational NMR Study

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1. Introduction

The discovery of carbon nanotubes produced by graphite, first reported by Iijima in 1991(S. Iijima & T. Ichihasi 1993), ushered in a new and very amazing research field in compacting gases by physisorption methods. The changes in electrical resistance, by adsorption of certain gas molecules are considerable, for example by adsorption of O_2, N_2, NH_3 and H_2 (H. Chang et al. 2001). Figure 1 depicts a $C_{72}H_{16}$ tube modeling an armchair (4, 4) SWCNTs which demonstrates the stated effect on the electronic structure of single-walled carbon nanotubes (SWCNTs).

Comparing the adsorption of gases on the surface, using computational methods substantially reduces costs and thus NQR were used in related investigations. Even at low concentration, due to the charge transfer between gases and tube, gas physisorption can change the conductivity of CNTs. Electronic properties of SWCNT have been studied in a number of theoretical works (H. van C. Houten et al., 1992; H. Aijki & T. Ando, 1993; J. W. G. Wildoer et al., 1998; A. Bezryadin, 1998) and optimized forms of nanotube can be designed by a precise positioning of various gases on considered carbon atoms. Theoretical studies have found that this single-walled carbon nanotube has novel electronic properties, which can be semiconducting, depending on their radius or chiralities (T. Hertel et al., 1998; J. W. Mintmire et al., 1992; N. Hamada et al., 1992; R. Saito et al., 1992; M. Rao et al., 1997; H. Kataura et al., 1999). According to the electron-transmission mechanism on the surface of CNTs, the detected gas can be classified into reducing and oxidizing gaseous species. The electrical resistance of CNTs was found to increase when exposed to reduce gaseous species as N_2 (J. Zhao et al., 2002), whereas being exposed to oxidizing ones as O_2 (P. G. Collins et al., 2000) decreased. A new SWCNT gas sensor would be fulfilled by utilizing such electrical

characteristics. In this study, N_2, O_2, and CO adsorption mechanism on carbon nanotubes was investigated by the surface CNT gas sensor. The physisorption of N_2, O_2, and CO at the open ended single-walled carbon nanotube (SWCNT) has been investigated. It was found that N_2, O_2, and CO can be physisorbed at the surface site of armchair SWCNT that makes the N–N, O-O, and C-O bonds active. This can be attributed to the decisive effect of the local end carbon atoms arrangement of the open-ended SWCNT surface. In addition, comparison of the adsorption amount on CNTs forcefully increases this viewpoint that present theoretical study on open-ended SWCNTs shows larger adsorption capacity. In this paper, a computational study of the adsorption of N_2, O_2, and CO on the surface the open-ended SWCNT is reported. The isosteric adsorption and the binding energy were compared with adsorption predicted on surface SWCNT. Nuclear experimental techniques such as nuclear quadrupolar resonance (NQR) (G. K. Semin et al., 1975) are widely used to study the geometry and electronic structure of molecules. For non-magnetic dielectrics, this response gives information about coordination and geometry around each nucleus with spin I> 0. It is known that when nuclei with spin>1/2 are put in an electric field gradient (EFG) (A. R. Kessel & V. L. Ermakov 1999.; A.K. Khitrin et al., 2001), decayed spin energy levels are created. NQR methods are applied to produce high external magnetic fields and some kind of internal interaction in order to form a non decayed energy spectrum. However, the field has recently started to produce good products and an increasing amount of experimental and theoretical data is becoming available. There are two naturally occurring isotopes for nitrogen-14 with natural abundance of 99.635% and nuclear spin I=1and N-15 with natural abundance of 0.365% and I=1/2. Despite its rich natural plentifulness, present N-14 applied an electric quadrupole moment (NQR) in our study. Dependence of these parameters on length and diameter of CNTs are also considered. The NQR measurable parameters are quadrupole coupling constant (C_Q) and asymmetry parameter (η_Q) which both are also reproduced by quantum chemical calculations of the electric field gradient (EFG) tensors. Nuclei with spin angular momentum I > 1/2 have the nuclear electric quadrupole moment, which interacts with the electric field gradient (EFG) tensor originated at the site of quadrupole nuclei. For O-17, N-14, and C-13 spin angular momentums are $\frac{5}{2}$, $\frac{3}{2}$ and $\frac{1}{2}$, respectively. Therefore O-17 and N-14 are very sensitive to the electronic density at the sites of nuclei and feel changes by any disturbance. 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 metodes continue to play a substantial role which is, moreover, likely to grow in the future (C. R. A. Catlow, et al., 2010). Carbon nano-tubes (CNT) are nano structures derived from rolled grapheme planes (fig. 2) (S. Iijima & T. Ichihasi, 1993) whose electronic properties can be controlled. Zhao et al., (J. Zhao, 2002) studied the adsorption of various gas molecules (NO_2, O_2, NH_3, N_2, CO_2, CH_4, H_2O, H_2, 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) (T. Schimizu & M. Tsukada, 1993; M. Lynch & P. A. Hu, 2000; N. D. McClenaghan et al., 2000; C. Noguera, 2001). Jhi et al., (S.H. Jhi, 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 (E.B. Barros et al., 2007; A.G. Souza Filho et al., 2006). Depending on their diameter and felicity it was predicted that they can be semiconductors or metals (R. Saito et al., 1992; J. W. Mintmire et al., 1992). They can also sustain large current densities (Ph. Avouris, 2000), and their electrical properties

can be modified by doping (R.S. Lee, 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 (N.D. Lang, 2000 & 1998). Ulbricht et al (H. Ulbricht et al., 2002) concluded that no evidence for a more strongly bound chemisorbed species or for dissociative oxygen adsorption 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 (S. A. Babanejad et al., 2010; F. 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) zigzag 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 (tables 3 and 4). The study of electronic and structural properties of oxygen-doped single wall nano-tubes have been performed (M. Mirzaei & N. L. Hadipour, 2006). The calculation of NMR (M. J. 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 (A_1, A_2, A_3 and A_4) 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 high-level quantum chemical calculations (F. Ashrafi et al., 2010; G. Wu, 2002). In this computational evaluation, the influence of oxygen-doping on the electrostatic properties of zigzag (5, 0) and arm chair (4, 4) CNTs are studied via the tensors calculations at the sites of ^{17}O nuclei in two case representative O-doped models (A. S. Ghasemi et al., 2010). The length of 7.1 Å and 4.8 Å were obtained for (5,0) and (4,4) single-wall nanotube including oxygen-doped (O-doped), respectively. The forms indicated in figures 2 and 3 are considered in calculations (tables 2 to5).

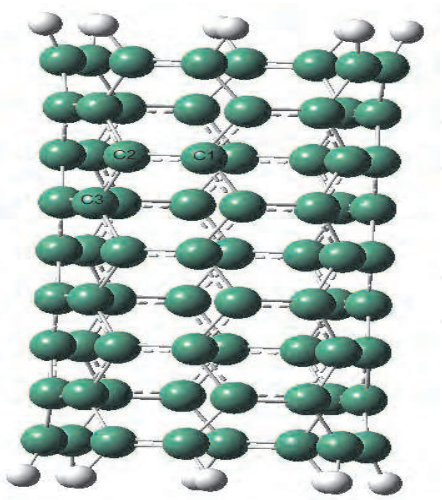


Fig. 1. CNTs(4,4)

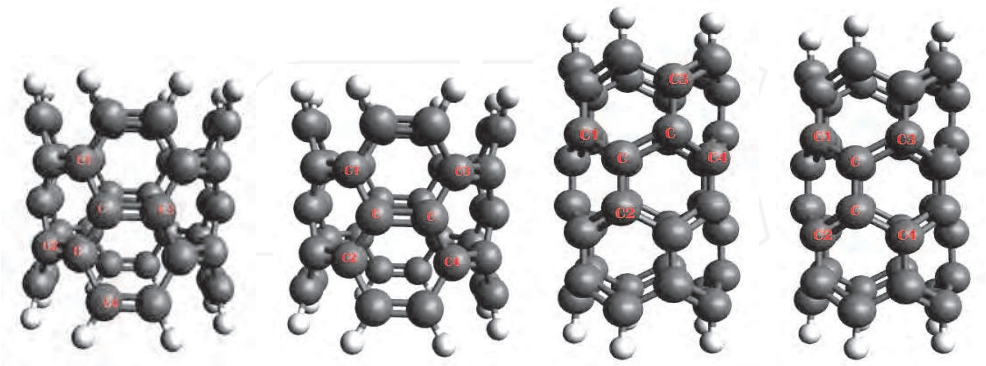
Model (configuration)	R_{C-C} (A˚)	R_{C-X} (A˚) (X=O, N, C)	R_{O-O} (A˚)	R_{C-O} (A˚)	R_{N-N} (A˚)	ΔE_{ab} (ev)	Dipole momentum (Debye)
CNT	$(C-C)_1$=1.424 $(C-C)_2$=1.419 $(C-C)_3$=1.438 $(C-C)_4$=1.405 $(C-C)_5$=1.437 $(C-C)_6$=1.437	-	-	-	-	-	0.4358
N_2-CNTs-A1	$(C-C)_1$=1.48 $(C-C)_2$=1.481 $(C-C)_3$=1.481 $(C-C)_4$=1.481	$(C-N)_1$=1.515 $(C-N)_2$=1.515	-	- -	1.250	-77910.48	3.5448
N_2-CNTs-A2	$(C-C)_1$=1.504 $(C-C)_2$=1.516 $(C-C)_3$=1.517 $(C-C)_4$=1.500	$(C-N)_1$=1.521 $(C-N)_2$=1.525	-		1.255	-77909.73	1.6172
O_2-CNTs-A1	$(C-C)_1$=1.487 $(C-C)_2$=1.487 $(C-C)_3$=1.487 $(C-C)_4$=1.487	$(C-O)_1$=1.465 $(C-O)_2$=1.465	1.485	- -	- -	--79023.84	3.1747
O_2-CNTs-A2	$(C-C)_1$=1.500 $(C-C)_2$=1.507 $(C-C)_3$=1.563 $(C-C)_4$=1.459	$(C-O)_1$=1.436 $(C-O)_2$=1.408	2.66	-	-	-79024.74	3.4475
CO-CNTs-A1	$(C-C)_1$=1.481 $(C-C)_2$=1.48 $(C-C)_3$=1.48 $(C-C)_4$=1.48	$(C-C)_1$=1.584 $(C-O)_2$=1.501	-	1.315	-	-78013.55	3.4764
CO-CNTs-A2	$(C-C)_1$=1.480 $(C-C)_1$=1.480 $(C-C)_1$=1.461 $(C-C)_1$=1.582	$(C-C)_1$=1.477 $(C-O)_2$=1.562	-	1.374		-78012.27	2.6888

Table 1. Calculated adsorption energies E_{ab} (eV), bond energies(A˚) and dipole momentum (Debye) of the O_2 and N_2 and CO adsorbed on surface armchair (n, n), n=4 nanotube.

2. Computational details

In this study O_2 and N_2 molecules adsorption behaviors on the end and surface of single-walled nanotube is taken in to consideration. A (4, 4) CNT containing 72 carbon atoms with length of 9.8A˚ and a diameter of 5.6 A˚ is selected for this purpose. Saturating carbon

dangling bonds with 16 hydrogen atoms is necessary because there is no periodic boundary conditions in molecular calculations and also due to limitation of nanotube length and lack of homogeneity for ending atoms, symmetry breaks down and some changes in geometrical properties are proved for ending atoms during optimization processes. Optimization of a sample system includes relaxation of atoms to lower forces from other constituents on each atom. Calculations were carried out with Gaussian98 suite of programs at all-electron level (M. J. Frisch et al., 1998). It has been established that DFT is able to accurately treat such systems due to incorporation of the exchange-correlation effects (V. Barone et al., 2004; W. L. Yim, & Z. F. Liu, 2004; X. Lu et al., 2005). In quadrupolar spin system, the electric field gradient (EFG) tensor at nitrogen-14 and oxygen-17 nuclear sites has axial symmetry (asymmetry parameter $\eta = 0$). The existence of the zero asymmetry parameter was one of the reasons why this compound is considered to present such interest (S. A. Babanejad et al., 2010; F. Ashrafi et al., 2010; E. A. Hill & , J. P. Yesinowski, 1997; A. Abragam, 1961). Geometry optimizations and EFG calculations were performed using 6-311G* basis set with B3LYP functional (H. S. Kang, 2006; S. Hou, 2004). The interaction between nuclear electric quadrupole moment and EFG at quadrupole nucleus is described with Hamiltonian (A. Abragam, 1961) $\hat{H} = \frac{e^2 Q q_{ZZ}}{4I(2I-1)}[3\hat{I}_Z^2 - \hat{I}^2) + \eta_Q(\hat{I}_X^2 - \hat{I}_Y^2)]$ where eQ is the nuclear electric quadrupole moment, I is the nuclear spin and q_{zz} is the largest component of EFG tensor. The principal components of the EFG tensor, q_{ii}, are computed in atomic unit (1 au = 9.717365 × 10^{21} V m^{-2}), with $|q_{xx}| \le |q_{yy}| \le |q_{zz}|$ and $q_{xx} + q_{yy} + q_{zz} = 0$. These diagonal elements are related by a symmetry parameter $\eta_Q = \left|(q_{yy} - q_{xx})/q_{zz}\right|$ and $0 \le \eta_Q \le 1$, that measures the deviation of EFG tensor from axial symmetry (E. A. C. Lucken, 1992). Cluster model is proved to be valid for nanotubes (G. E. Froudakis et al., 2003; D. C. Sorescu et al., 2001). The computed q_{zz} component of EFG tensor is used to obtain nuclear quadrupole coupling constant from the equation $C_Q = e^2 Q q_{ZZ} / h$ (E. A. C. Lucken, 1992).



CNT(4,4)(A_1) CNT(4,4)(A_2) CNT(5,0)(A_1) CNT(5,0)(A_2)

Fig. 2. (A_1 & A_2) The (5, 0) and (4, 4) SWCNT

In the present study, the effects of oxygen (O_2) 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 O_2 molecules, the computations were fully implemented by Gaussian 98 Software package (E.B. Barros et al., 2007; A.G. Souza Filho et al., 2006; M. J. Frisch et al., 1998). Geometry optimizations were performed using 6-31G* basis set with DFT/B3LYP functional (R. G. Parr & W. Yang, 1994; A. D. Becke, 1993). NMR ^{17}O and ^{13}C chemical shielding calculations were computed at B3LYP/6-311G* level of theory using gauge including atomic orbitals (GIAO) approach (K. Wolinski et al., 1990). The undoped models (4, 4) and(5, 0) consisted of 40 C atom with length of 4.8 Å 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 (M. J. Duer, 2002). This shows a second-order change in the molecular energy.

Model	r_{C-C}	r_{C-O}	R_{O-O}	ΔE_{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 $(C-O)_3$=1.334 $(C-O)_4$=1.333	2.563	-43762.03
CNT(4,4)-O_2(A_4)	-	$(C-O)_1$=1.378 $(C-O)_2$=1.395 $(C-O)_3$=1.386 $(C-O)_4$=1.384	2.547	-43763.24

[a] All calculated distances are in Å. All calculated binding energies are in electron volt (eV).

Table 2. Calculated structural parameters and binding energies of O_2 Chemisorption on the (4 , 4) SWCNT [a].

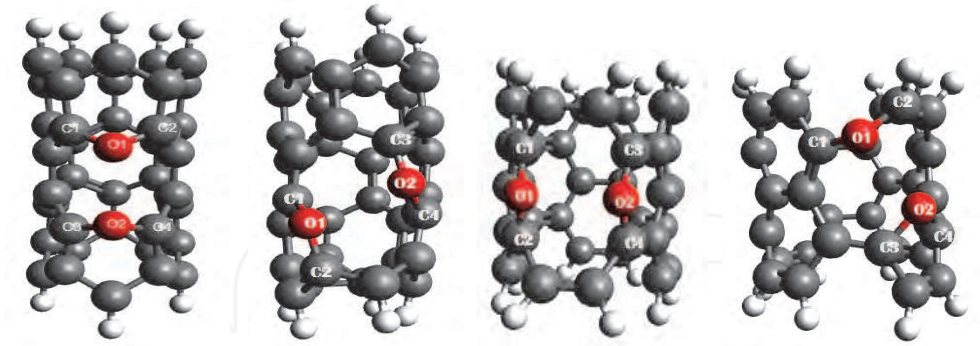
$$E = E_0 + B_0 \chi B_0 + \sum_{i=1}^{N} \mu_i \sigma B_0 + \cdots \tag{1}$$

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.

Model	r_{C-C}	r_{C-O}	r_{O-O}	ΔE_{ads} - 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 $(C-C)_3$=1.408 $(C-C)_4$=1.437	-	-	-
CNT(5,0)-O_2(A_3)	-	$(C-O)_1$=1.408 $(C-O)_2$=1.408 $(C-O)_3$=1.408 $(C-O)_4$=1.409	2.421	-43652.95
CNT(5,0)-O_2(A_4)	-	$(C-O)_1$=1.375 $(C-O)_2$=1.373 $(C-O)_3$=1.335 $(C-O)_4$=1.399	2.563	-43653.63

[a] All calculated distances are in Å. All calculated binding energies are in electron volt (eV).

Table 3. Calculated structural parameters and Chemisorption energies of O_2 adsorbed on the (5, 0) SWCNT [a].



CNT(4,4)-O_2(A_3) CNT(4,4)-O_2(A_4) CNT(5,0)-O_2(A_3) CNT(5,0)-O_2(A_4)

Fig. 3. Chemisorption configurations of an O_2 molecule (The sites A3, A4 of (4, 4) and(5, 0) SWCNT-O_2, respectively)

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

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 (C.M. Marian, & M. Gastreich, 2001).

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

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

3. Results and discussion

Geometries, binding energies and NQR (4, 4) SWCNT interacted with O_2 ,N_2 and CO molecule species have studied in this work. The calculated geometry parameters and binding energies, dipole momentum and EFG tensors have shown in tables 1 and 5 in the following sections, molecular geometries and binding energies, E_{ab}, C_Q, EFG tensors and the data obtained from O_2, N_2, and CO molecules adsorptions are discussed, separately.
In the present work, two models of zigzag (5,0)and armchair (4, 4) SWCNTs with specefied tube lengths are studied using quantum chemical calculations (figs. 2 and 3). 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 ^{17}O and ^{13}C chemical shielding tensors are presented in tables 2 to 5. The molecular geometries and binding energies and NMR chemical shielding tensors resulted from oxygen molecular chemisorptions are discussed in following sections, sepa.

3.1 Geometries properties and adsorption and binding energies

In this study, the use of electronic properties of nano tubes has been established to appear field of spin-electronics, a field that influences the electron's spin degree of freedom for transfer and storage of information and communication. The optimized geometries of calculated configurations of O_2, N_2, and CO molecules adsorbed on (4, 4) SWCNT are schematically displayed in fig. 4. Geometrical parameters, adsorption energies and dipole moment are summarized in table1. The nature of stationary points are confirmed by vibrational frequency calculations at the B3LYP/6-311G* level. For nitrogen, oxygen and CO molecules we have considered distinct adsorption sites, marked as CNT, CNT–O_2, CNT–N_2 and CNT–CO adsorption energies, ΔE_{ab}, (Table1) are calculated using:

$$E_{ad} = E_{tot}(\text{molecule}O_2 + \text{CNT}_S) - E_{tot}(\text{CNT}_S) - E_{tot}(\text{molecule}O_2) \tag{4}$$

$$E_{ad} = E_{tot}(\text{molecule}N_2 + \text{CNT}_S) - E_{tot}(\text{CNT}_S) - E_{tot}(\text{molecule}N_2) \tag{5}$$

$$E_{ad} = E_{tot}(\text{molecule}CO + \text{CNT}_S) - E_{tot}(\text{CNT}_S) - E_{tot}(\text{molecule}CO) \tag{6}$$

Where, E_{tot}(CNT), E_{tot} (O_2), E_{tot} (CNT+O_2), E_{tot} (N2), E_{tot} (CNT+N_2), E_{tot} (CO) and E_{tot} (CNT+CO) are the energies of the optimized tubes, which are adsorption systems, respectively**.** By this explanation, $E_{ad} < 0$ corresponds to exothermic adsorption which leads to local minima stable for adsorption of gas molecules on the surface of nanotube. Armchair (4, 4) nanotube has two different C–C bonds ((C1–C2) =1.405A˚ and (C2–C3) =1.438A˚) thus suggests two distinct adsorption sites. A diagrammatic view of this form is showed in fig. 4.

CNT, N2-CNT-A1&2, O2-CNT-A1&2 and CO2-CNT-A1&2. Such a structure has also been observed for other SWCNTs (S. Dag et al., 2003; H. He et al., 1998; S. P. Walch, 2003). For the molecular O_2–CNTs, N_2-CNTs, and CO–CNTs systems, O2, N2 and CO seemed to place parallel to the outer surface of the tube. Geometry calculations of distortion caused by the oxygen and nitrogen and carbon monoxide molecules on the (C1–C2) bond are changed partly. Placing the oxygen molecule in CNT-A1, CNT-A2 sites doesn't change the bridge distance of (C2–C3) considerably. Two different types of adsorbed O_2, N_2 and CO molecules were recognized (Fig. 4. CNT, N_2 -CNT-A1, N_2,- CNT-A2, O_2 -CNT-A1, O_2,- CNT-A2, CO-CNT-A1 and CO-CNT-A2). The calculated adsorption energies were predicted to be -77910.48 and -77909.73 eV for N_2 and -79023.84 and -79024.74 eV for O_2 and -78013.55 and -78012.27 eV for CO, respectively. The length of nanotube have selected with regard to the length of unit cell of nanotube. Such adsorptions of O_2 molecule are known as cycloaddition which is very similar to those found for larger diameter tubes (M. J. Duer, 2002; Y. F. Zhang & Z.F. Liu, (2004). Nitrogen molecules adsorbed with a comparatively lower rate and almost never formed a chemical binding with the carbon nanotube. The geometry of (4, 4) tube is considerably modified when such oxidation occurs and physisorbed product is formed. The electron configuration of O_2 is KK $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2pz})^2 (\pi_{2px})^2 (\pi_{2py})^2 (\pi_{2px}^*)^1 (\pi_{2py}^*)^1$. The electron configuration of N_2 is KK $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2px})^2 (\pi_{2py})^2 (\pi_{2pz})^2$, and the transferred electron is placed in the half-filled anti-bonding orbital of O_2, thus weakens the O–O bond. The electron can't enter into N_2 molecule binding orbital because the binding orbital is filled. This arrives to either sp^3 hybridization for two carbon atoms or breaking of one C–C bond. Two different types of adsorbed O_2, N_2, and CO species were identified (Fig. 4. and Table 1). Also, the dipole moments were calculated by Gaussian software and have shown in table1. Obtained values demonstrate that as the dipole moment becomes bigger, the absolute value of bond energy increases. We can explain this reality as following: the big dipole moment relies to the large distance between electron clouds, then, as the distance becomes bigger the absolute value of bond energy will become higher. By comparing the obtained results with Jordan's one (D. C. Sorescu et al., 2001). It is well known that the tendency for sp^2–sp^3 re hybridization upon O_2 adsorption is strong for thin nanotubes, because highly bent sp^2 bonding of thin nanotubes is favored for the transition to sp^3 bonding. According to adsorption energy and dipole moment parameters in table1, O_2 molecule shows the highest adsorption rate.

This is a general reason for the binding performed studies, which shows that nitrogen molecules energy values of adsorption on armchair model with determined diameter and length have about twice differences in grandeur. Based on performed calculations, we approach that the adsorption accomplishes over open ends of nanotubes has more advantages. In addition, all these energies are positive which demonstrate the reaction is improbable. Based on these results, we can conclude that the physical adsorption over the surface area of nanotube occurs very hard and so this is an appropriate case.

Also, 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 zigzag (5, 0)and armchair (4, 4) SWCNTs were calculated as shown in Figures (2) and (3). The results at the level of the B3LYP DFT method and the 6-311G* standard basis set are summarized in tables 1 and 2. Upon chemisorption of a O_2 molecule on the C-C bond at the surface, the molecule O_2 dissociates toward the O-O bond lengths. Chemisorption on nanotube increases from 1.21 Å 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 A_1, A_2, A_3 and A_4 (table 1 and 2). CNT and CNT–O_2 binding energies, E_{ad}, are calculated using, $E_{ad} = E_{tot}(\text{molecule}O_2 + CNT_S) - E_{tot}(CNT_S) - E_{tot}(\text{molecule } O_2)$ Where, E_{tot} (CNT), E_{tot} (O_2) and E_{tot} (CNT+O_2) are the energies of the optimized tubes, that are chemisorption and tube–adsorb ate systems, respectively. Armchair (4, 4) and zigzag (5, 0) tube has different C–C bonds thus offers two distinct chemisorption sites (table 1and 2) before and after the doping of O atoms, the bond length of in SWNT-A_1(4, 4) from.
$(C\text{-}C)_{1,3}$=1.421 A˚ and $(C\text{-}C)_{2,4}$=1.422 A˚ decreased to 1.333A˚-1334 A˚ and bond length of in SWNT-A_2(4, 4)) from $(C\text{-}C)_1$=1.451A˚ , $(C\text{-}C)_2$=1.419A˚ , $(C\text{-}C)_3$=1.422A˚ and $(C\text{-}C)_4$=1.452A˚ decreased to 1.378 -1.395 before and after the doping of O atoms, the bond length of in SWNT-A_3(5,0) from $(C\text{-}C)_{1,3}$=1.437A˚ and $(C\text{-}C)_{2,4}$=1.451A˚ decreased to 1.335 A˚ - 1.399 A˚ bond length of in SWNT-A_4(5, 0)) from $(C\text{-}C)_1$=1.426 A˚, $(C\text{-}C)_2$=1.451A˚ , $(C\text{-}C)_3$=1.408A˚ and $(C\text{-}C)_4$=1.437A˚ 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 28668ce95cc(T. Kamimura et al., 2005).

3.2 The N_2, O_2 and CO NQR parameters and ^{17}O NMR parameters (4, 4) and (5,0)

Semiconducting SWCNTs are ballistic conductors with two and one spin degenerate conducting channel(s), respectively (A. Bachtold et al., 2000; V. Krstić et al., 2000). The channels belong to the first π and π^*-band of the delocalized π-electron system. The N-14, O-17, C-13 NQR parameters (C_Q and η) in the geometrically optimized SWCNTs model armchair (4, 4) were estimated by EFG tensors calculations at the B3LYP level of the DFT method and the 6-311G* standard basis set.
Tables 6 shows the calculated NQR and EFG tensors for SWCNTs η parameter of O_2, N_2 and CO adsorption on the CNTs surface has a remarkable effect on EFG tensors. A glimpse to η values presented in table 2 reveals that the for N-14 and O-17 changes in EFG tensor for molecular adsorptions are quite significant which is in complete agreement with calculations. The B3LYP/6-311G* calculations indicate that all three principal components of the EFG tensor(q_{ii}) and associated asymmetry parameter are affected due to adsorption of oxygen, nitrogen and CO molecules. For the (O_2–CNT) and (N_2–CNT) systems, the EFG tensors of CNT (4, 4)- O_2(A2) and CNT(4, 4)-N_2(A1) are more significantly affected compared to CNT(4, 4)- O_2 (A1) and CNT(4,4)-N_2(A2), respectively. As previously mentioned, oxygen molecules adsorption at the CNT (4, 4)-O_2(A2) leads to the O_1–O_2 bond cleavage and N_2 molecules adsorption at the CNT(4, 4)-N_2(A1) breaks C1-C2 bond. Therefore, a noticeable change in the field gradient, especially at the C_1 and C2 is detected. O_2 adsorptions produce more EFG change at CNT (4, 4)- O_2(A2 which can be attributed to their hybridization effect (from sp^2 to sp^3). This is consistent with the bond angle distortion from 120 to 109, induced by oxygen and nitrogen adsorption. The principle components of EFG tensor change significantly after CO adsorption at C1 and C2 atoms in CNT(4, 4)-CO (A2).
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 3and 4). 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 (H.J. Liu, 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

Model	^{17}O	atoms	σ_{ii} (σ_{11}, σ_{22}, σ_{33})[b]	σ_{too}	$\Delta\sigma$	η_σ
CNT(4, 4) (A_1)	-	C_1 C_2 C_3 C_4	(-1.16; -1.16; 163.87) (-1.16; -1.16; 163.87) (-0. 73; -0. 73; 163.79) (-0. 75; -0. 75; 163.74)	53.8495 53.8495 54.1090 54.0800	165.0308 165.0308 164.5215 164.4900	0.0000 0.0000 0.0000 0.0000
CNT(4, 4) (A_2)	-	C_1 C_2 C_3 C_4	(-0.71; -0.71; 163.77) (-40.9778; 52.7796; 159.7877) (-35.3100; 13.8404; 175.9600) (-1.17; -1.17; 163.85)	54.1157 57.1965 51.4968 53.8354	164.4815 153.8868 186.6948 165.0219	0.0000 2.4588 1.4317 0.0000
CNT(4, 4)-O_2 (A_3)	O_1	C_1 C_2	(-66.8441; 54.0846; 83.9711) (-66.4764; 53.8616; 84.4001)	23.7372 23.9284	90.3508 90.7075	2.0077 1.9900
	O_2	C_3 C_4	(-66.7714; 54.0488; 83.9700) (-66.3669; 54.0373; 84.0975)	23.7491 23.9226	90.3313 90.2623	2.0063 2.0009
CNT(4, 4)-O_2 (A_4)	O_1	C_1 C_2	(-53.8794; 39.8243; 95.9593) (-48.5238; 12.7128; 100.4479)	27.3014 21.5456	102.9869 118.3535	1.3648 0.7761
	O_2	C_3 C_4	(-29.8179; 7.3599; 103.6236) (-66.1822; 56.8643; 97.6708)	27.0552 29.4509	114.8526 102.3298	0.4856 1.8037

[a] Calculated σ_{ii}, σ_{iso} and $\Delta\sigma$ values are in ppm
[b] In each raw, the first number is for σ_{11}, the second number is for σ_{22} and the third number is for σ_{33}.

Table 4. Calculated ^{17}O NMR parameters for CNT, O_2–CNT (4, 4) systems [a]

Model	^{17}O	atoms	σ_{ii} (σ_{11}, σ_{22}, σ_{33})[b]	σ_{iso}	$\Delta\sigma$	η_σ
CNT(5, 0) (A_1)	-	C_1 C_2 C_3 C_4	(-118.0860; 12.8629; 163.87) (-116.9704; 13.8079; 159.2077) (-118.1198; 12.8584; 159.4017) (-116.9332; 13.8073; 159.2050)	18.0597 18.6817 18.0467 18.6930	212.0138 210.7890 212.0325 210.7680	10.8763 10.5005 10.8866 10.4911
CNT(5, 0) (A_2)	-	C_1 C_2 C_3 C_4	(-45.2746; 155.1751; 325.7105) (-118.1198; 12.8584; 159.4017) (-27.4737; 155.3875; 319.5851) (-0.0454; 120.08; 120.08)	145.2037 18.0467 149.1663 78.5398	270.7602 212.0325 255.6282 62.3103	2.0707 10.8866 1.8388 0.0000
CNT(5, 0)-O_2 (A_3)	O_1	C_1 C_2	(-63.2476; 63.5826; 90.1893) (-69.3226; 65.3214 - 8.8003i; 65.3214 + 8.8003i)	30.1748 20.4401	90.0217 67.3219 +13.2005i	6.3048 9.8809 - 0.6458i
	O_2	C_3 C_4	(-31.5986; 74.3457; 104.6805) (-72.6502; 74.9677 -19.9352i; 74.9677 +19.9352i)	49.1425 25.7617	83.3070 73.8090 +29.9028i	3.2338 8.5952 - 1.1607i
CNT(5, 0)-O_2 (A_4)	O_1	C_1 C_2	(-48.8614; 22.4174; 75.9510) (-72.6368; 16.2112; 92.0007)	16.5023 11.8584	89.1730 120.2134	1.1990 1.1086
	O_2	C_3 C_4	(-48.4295; 2.6526; 96.4404) (-128.7315; 13.2045; 82.9991)	16.8878 -10.8427	119.3289 140.7627	0.6421 1.5125

[a] Calculated σ_{ii}, σ_{iso} and $\Delta\sigma$ values are in ppm
[b] In each raw, the first number is for σ_{11}, the second number is for σ_{22} and the third number is for σ_{33}.

Table 5. Calculated ^{17}O NMR parameters for CNT, O_2–CNT (5, 0) systems [a].

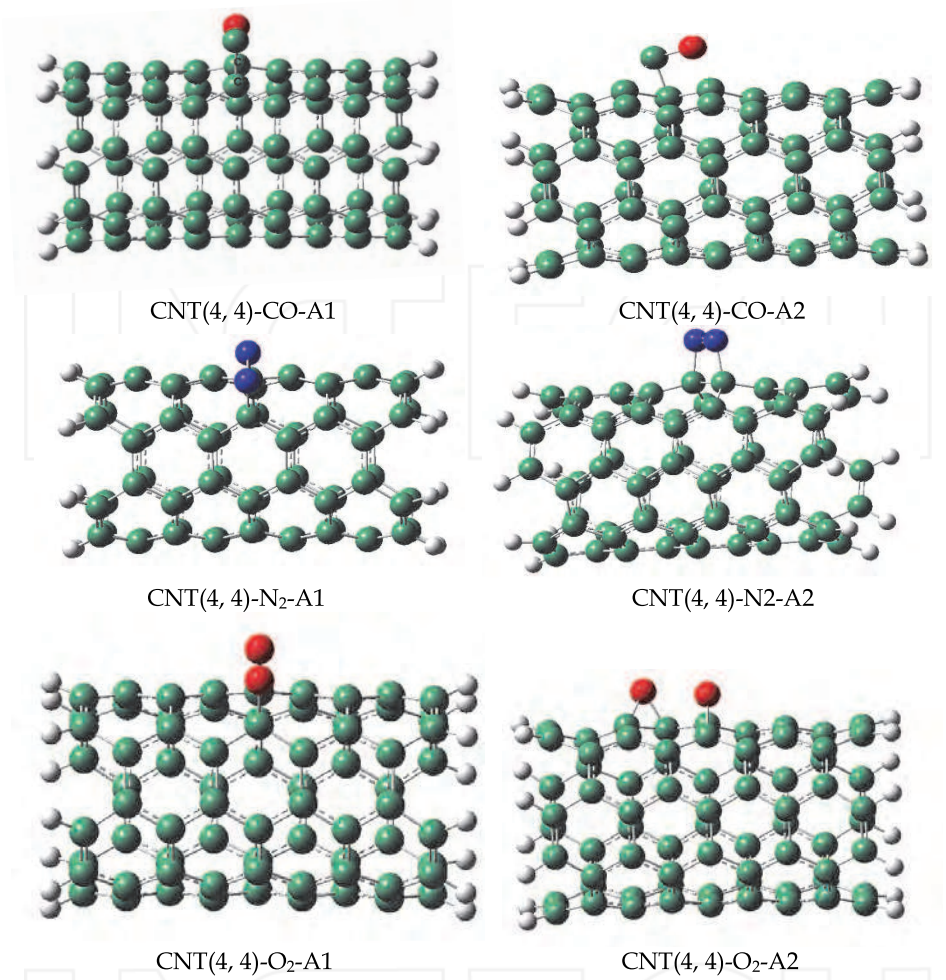


Fig. 4. (A1) and (A2) adsorption configurations of an Oxygen. Nitrogen and Carbon monoxide molecule.

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 (A. Rubio et al., 1994; X. Balase, 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 ppm, 54.1090ppm and 78.5398 ppm, 149.1663 ppm, respectively (table 3and 4). 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 (E.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 (Y. Liu, & H. Guo, 2004; Y. 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, $\sigma_{22,}$ 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 (V. 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

Model	Atom	q_{xx}	q_{yy}	η_Q	q_{zz}
CNT(4, 4)	C1 C2 C3	0.095540 0.115713 0.115853	0.137945 0.118493 0.118548	-0.233485 -0.234206 -0.234401	0.18 0.01 0.01
CNT(4, 4)-O2 (A1)	C1 C2	0.114913 0.115191	0.217092 0.217377	-0.332005 -0.332568	0.30 0.30
CNT(4, 4)-O2(A2)	C1 C2	0.056708 0.134179	0.235503 0.172331	-0.292211 -0.306510	0.61 0.12
CNT(4, 4)-CO (A1)	C1 C2	0.131771 0.026205	0.279074 0.139259	-0.410845 -0.165464	0.36 0.68
CNT(4, 4)-CO (A2)	C1 C2	0.002444 0.201458	0.226654 0.223643	-0.229098 -0.425101	0.98 0.05
CNT(4, 4)-N2(A1)	C1 C2	0.062574 0.007669	0.133920 0.136100	-0.196494 -0.143769	0.36 0.89
CNT(4, 4)-N2(A2)	C1 C2	0.046359 0.037639	0.090398 0.158783	-0.136757 -0.196422	0.32 0.62

Table 6. Calculated Carbon-13 EFG parameters for the CNTs, N_2–CNTs and O_2–CNTs systems.

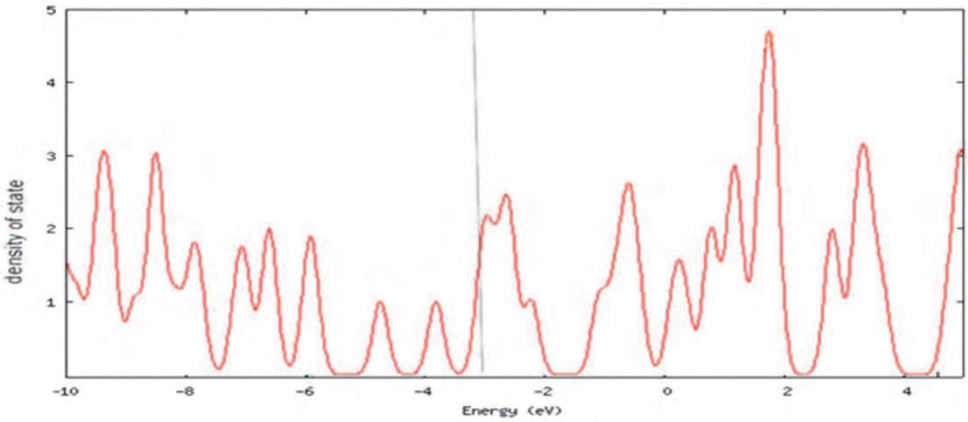
presence, distribution and chemistry of oxygen. Peng and Cho first suggested O_2-CNT for use in gas sensors, due to the ability of oxygen dopants to bind to incoming gas species (S. Peng & K. Cho, 2003). The oxygen in the nanotubes can be seen as regular defects which change the chemical behavior of tubes.

3.3 Electronic properties

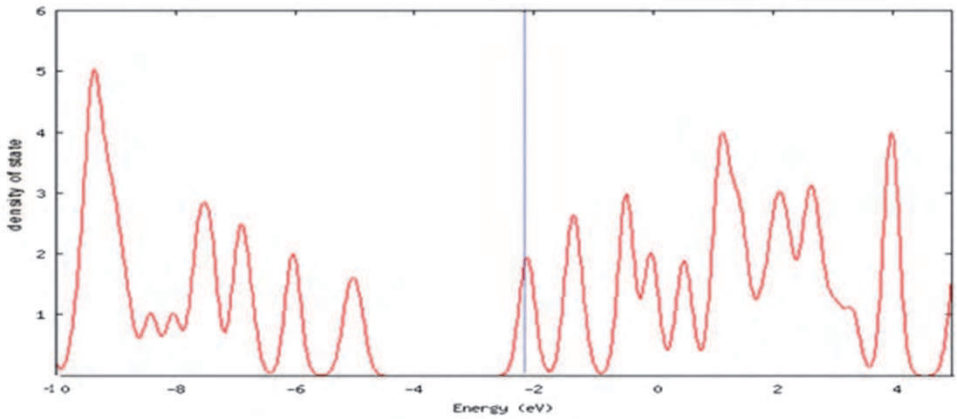
Collins et al., (P. G. Collins et al., 2000) found that oxygen gas has dramatic effects on conductivity, thermoelectric power, and the local density of states of nanotube. Kang et al., (D. Kang wt al., 2005) reported the characteristic behavior of afield effect transistor based on an individual SWCNT 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. 5. We study the efficacy on electronic properties of SWCNT by O_2 chemisorptions. The calculated band gap of nanotube model zigzag (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 (W. L. Yim, & Z. F. Liu, 2004; M. A. Rantner 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 zigzag (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 (V. Derycke, 2002). As shown in Figure3, 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 chemisorption at the seat models are mainly localized within the C-C bonds (Fig. 3). Indeed, Kang et al. (D. Kang et al., 2005) 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 (D. Kang et al., 2005). All of these, suggest that different electronic properties of an open zigzag (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 zigzag (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 zigzag (5, 0) and armchair (4, 4) SWCNT increases the bond gap energy.

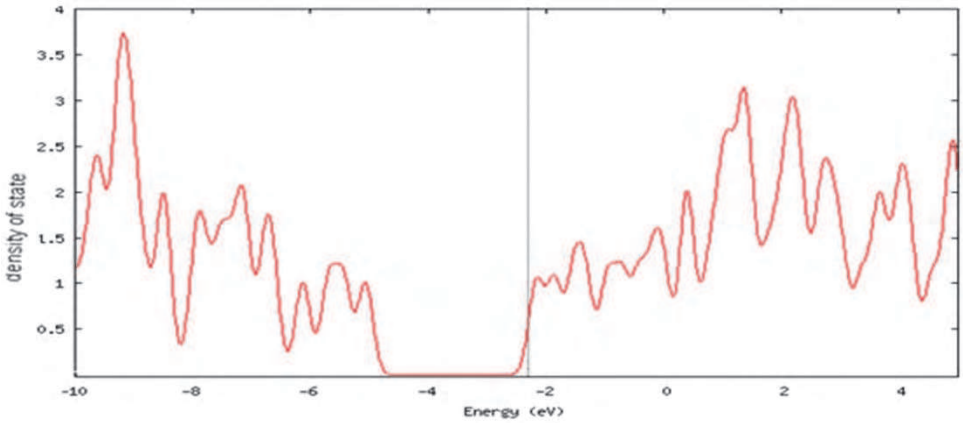
The effect is more obvious for CNT (4, 4)-O_2 (A_4). Also the TDOS plots for the sites (A_1, A2, A3 and A4) are significantly differ from the zigzag (5, 0) and armchair (4, 4) nanotube near an electric filed, which may result in a conductance change of nanotube up to chemisorption of O_2.



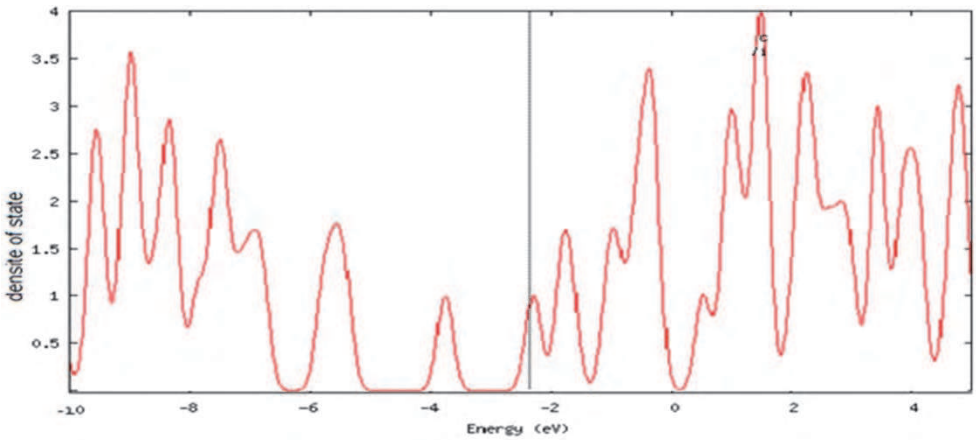
(a) CNTs (5,0) (A_1)



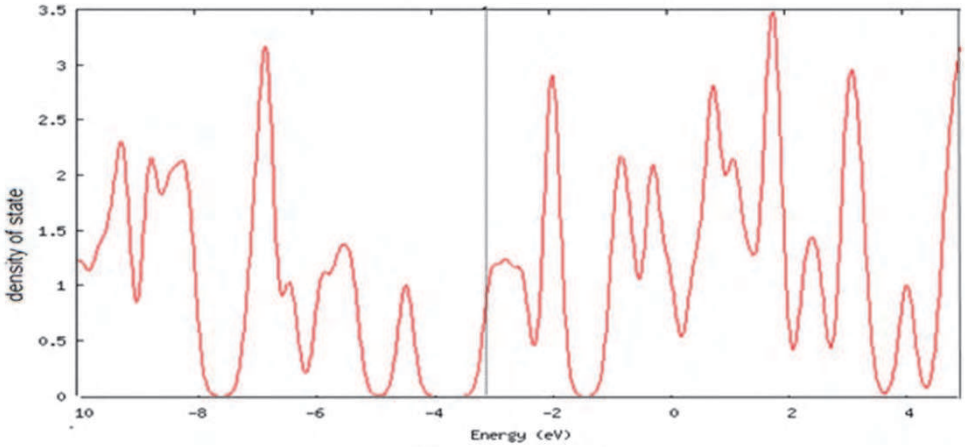
(b) CNTs (4,4) (A_2)



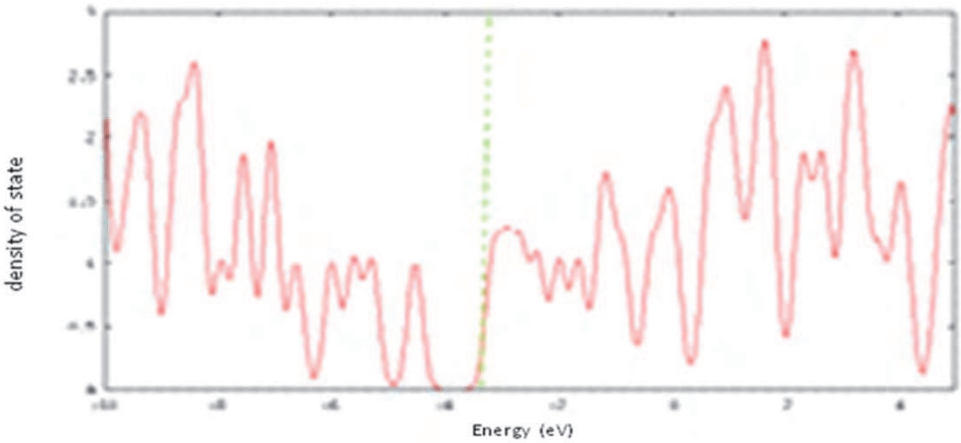
(c) CNT (4,4)-O_2 (A_3)



(d) CNT (4,4)-O_2 (A_4)



(e) CNT (5,0)-O_2 (A_3)



(f) CNT (5,0)-O_2 (A_4)

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

For chemisorptions model CNTs (5, 0) (A_1), 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 O_2 on model CNTs (4, 4) (A_2) appears a peak near electric filed with a band gap about 2.79 eV. The TDOS for (O_2–CNT) system is presented in CNT (4, 4)-O_2 (A_4). For this system significant changes in the DOS are observed near the Fermi level, similar to the O_2 chemisorptions. However, the chemisorption of oxygen molecule is further increases band gap (2.9eV) and reduces the electrical conductance of the zigzag (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) – O_2 (A_3) model, oxygen molecule with a minor change in length of O-O band would be doped on carbon nanotube zigzag model.

4. Conclusion

In summary, our theoretical studies show that CNTs can be used as mechanical sensors. We found the electronic properties of CNTs are sensitive to the adsorptions of oxygen, nitrogen and carbon monoxide gases on the surface. According to DFT theory and hybrid functional B3LYP are applied to study NQR of N_2, O_2 and CO calculations the electronic structure properties of (4, 4) SWCNT.
We calculated Oxygen-17, Nitrogen-14 and Carbon-13 EFG tensors in the various structures of thymine an optimized isolated gas-phase, gas monomer and the target molecule in X-CNTs (X=O_2, N_2 and CO). The calculated results have different effects on the EFG tensor at Oxygen-17, Nitrogen-14 and Carbon-13 nuclei. Theoretical calculations are performed to characterize the behavior of N_2 and O_2 molecules adsorption on external surface and chemisorption on the end of armchair (4, 4), SWCNTs.
The results show that as the diameter of armchair tubes increases, the binding energy of N_2 and O_2 molecules decreases. The equilibrium N_2-CNT and O_2-CNT on the surface distance exhibits considerable sensitivity to the type of tube. The calculated N_2-CNT, O_2-CNT and CO-CNT bond lengths are (1.515-1.525 ˚A, 1.408-1.465 ˚A)and(1.477-1.584 ˚A) on the surface of armchair(4, 4), respectively.
Adsorptions are also dependent upon the nanotube family and radius. Moreover, CQ (Nitrogen-14 and Oxygen-17) of armchair nanotube increases as the diameter of tube decreases while in our study, the diameter of tube increased. The obtained CQ parameters for Nitrogen-14(A1, A2) and Oxygen-17(A1, A2) are(4.148, 4.017)MHZ and(4.466,1.833) MHZ ,respectively. Due to the physisorption, NQR parameters of nitrogen and oxygen molecular are also alerted.
In summary, we studied the influence of substitutional O_2 on the single-walled carbon nanotubes conformation and a quantum-chemical calculation was performed. The calculations show that the combination of hexagons and O_2 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 ^{17}O - 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 O_2 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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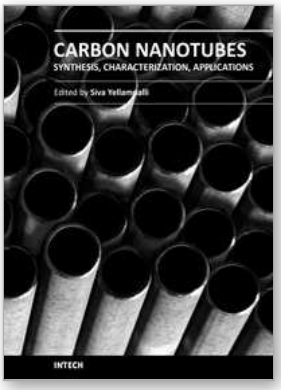

Carbon Nanotubes - Synthesis, Characterization, Applications

Edited by Dr. Siva Yellampalli

ISBN 978-953-307-497-9
Hard cover, 514 pages
Publisher InTech
Published online 20, July, 2011
Published in print edition July, 2011

Carbon nanotubes are one of the most intriguing new materials with extraordinary properties being discovered in the last decade. The unique structure of carbon nanotubes provides nanotubes with extraordinary mechanical and electrical properties. The outstanding properties that these materials possess have opened new interesting researches areas in nanoscience and nanotechnology. Although nanotubes are very promising in a wide variety of fields, application of individual nanotubes for large scale production has been limited. The main roadblocks, which hinder its use, are limited understanding of its synthesis and electrical properties which lead to difficulty in structure control, existence of impurities, and poor processability. This book makes an attempt to provide indepth study and analysis of various synthesis methods, processing techniques and characterization of carbon nanotubes that will lead to the increased applications of carbon nanotubes.

How to reference

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S. A. Babanejad, F. Ashrafi, A. Ghasemi, N. Salarzadeh, M. Rahimova, G. H. Babanejad, G. Babanejad and N. Babanejad (2011). Comparison of NQR of O2, N2 and CO on Surface of Single-Walled Carbon Nanotubes and Chemisorption of Oxygen-Doped on the Surface of Single-Walled Carbon Nanotubes: A DFT and NMR Computational Study, Carbon Nanotubes - Synthesis, Characterization, Applications, Dr. Siva Yellampalli (Ed.), ISBN: 978-953-307-497-9, InTech, Available from: http://www.intechopen.com/books/carbon-nanotubes-synthesis-characterization-applications/comparison-of-nqr-of-o2-n2-and-co-on-surface-of-single-walled-carbon-nanotubes-and-chemisorption-of-

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