

## Density Functional Theory (DFT) Study of O<sub>2</sub>, N<sub>2</sub> Adsorptions on H-Capped (4,4) Single-Walled Carbon Nanotube

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**Abstract:** CNTs are one of the most significant achievements of nano-technology with important applications in the design of electronic nano-devices. The study of their properties is therefore important. Here the DFT method is utilized to study the adsorption of oxygen and nitrogen molecules on the surface of (4, 4) SWCNT. The electronic structure, dipole moment of nitrogen, oxygen and carbon nuclei's are thoroughly studied. Optimization of primary nanotubes which included the exchange of NMR parameters of carbon which was connected to oxygen and nitrogen molecules was studied. Then, adsorption of oxygen and nitrogen molecules on armchair SWCNTs (4, 4) was investigated. The computational results indicate that rich adsorption patterns may result from the interaction of oxygen and nitrogen with the CNTs. Sometimes, C-O bounds are formed via breaking C-C bonds and sometimes a carbon atom is replaced with an oxygen atom. Sometimes molecular oxygen and nitrogen molecular are attracted by a C-C bound. Finally, the optimized adsorption rates are calculated. This study performed by using DFT and Gaussian 98 softwares.

**Keywords:** Adsorption, CNTs, DFT method, nitrogen, NMR, oxygen

### INTRODUCTION

Carbon Nanotubes (CNTs) were discovered by Iijima (1991) and Iijima and Ichihashi (1993). Carbon nanotubes are hollow tubes made entirely from carbon with diameters in the nanometer range (Pedersen, 2004) and can be both semiconductors and metallic, depending on the diameter and "twist" which they display by highly interesting features (Pedersen, 2005). Carbon nano tubes provide considerable remarkable properties, which demonstrate the potential applications in electronic sensors (Wang *et al.*, 1998) and other vacuum microelectronic devices (Terrones, 2003). In addition a small diameter has an extremely large surface ratio with respect to volume. The hollow structure of CNT makes it a suitable candidate for nano-scale chemical sensing. Since the first CNT-based gas sensor discovered by Kong (Kong *et al.*, 2000), many types of CNT-based chemical sensors have been synthesized. CNT networks (Li *et al.*, 2003), functionalized CNTs (Qi *et al.*, 2003), is used as sensor elements.

Nowadays, studying the gas adsorption on CNTs is the point of interesting experimental and theoretical studies (Jang *et al.*, 2004; Cantalini *et al.*, 2004; Wang *et al.*, 2004b). Moreover, there are many studies on the adsorption of nitrogen (Ashrafi *et al.*, 2010; Ghasemi *et al.*, 2010), oxygen and other gases (Jhi *et al.*, 2000; Babanejad *et al.*, 2010; Shirvani *et al.*, 2011; Peng *et al.*, 2003; Cahill *et al.*, 2004; Tang *et al.*, 2000). Considering that the gas adsorption on carbon nano tubes modifies

sensibly their electronic properties (Wang *et al.*, 2004a; Kong *et al.*, 2000) proposed the use of CNT as gas sensors.

According to the electron-transmission mechanism on the surface of CNTs, the detected gas can be classified in the reducing or oxidizing range of gaseous species. By adsorption reducing gaseous species (such as NH<sub>3</sub> (Hayakawa *et al.*, 2000), CO<sub>2</sub> (Chopra *et al.*, 2003), N<sub>2</sub> (Ong *et al.*, 2002; Varghese *et al.*, 2001; Ashrafi *et al.*, 2010)), the electrical resistance of CNTs was found to increase, whereas by adsorption to oxidizing ones such as O<sub>2</sub> (Zhao *et al.*, 2002) and NO<sub>2</sub> (Chang *et al.*, 2001) the electrical resistance decrease. These show that the electrical conductance of the CNTs can change obviously upon adsorption of O<sub>2</sub>, NO<sub>2</sub>, or NH<sub>3</sub> gases (Collins *et al.*, 2000; Kong *et al.*, 2000; Lantz *et al.*, 2003; Kleinhannes *et al.*, 2003; Li *et al.*, 2003). Even though experimental techniques have advanced, theoretical calculations have preserved their significant role in predicting geometries and energy levels and interpreting spectroscopic data.

Pathways to oxygen and nitrogen chemisorption and physisorption armchair (4, 4) CNTs model were probed by Froudakis (Froudakis *et al.*, 2003). Difficulties in CNTs production and spectroscopic characterization have made computational studies of these systems indispensable.

The aim of this study is investigating adsorption properties of H-Capped (4, 4) Single-Walled Carbon Nanotube as a gas sensor and optimized adsorption rates by using DFT calculations.

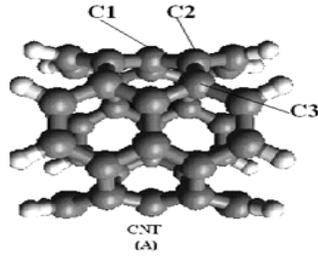


Fig. 1: (4, 4) SWCNT (A)

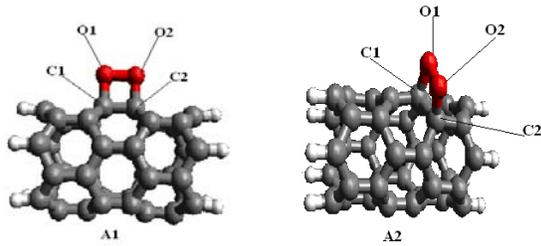


Fig. 2: (A<sub>1</sub>) and (A<sub>2</sub>) adsorption configurations of oxygen molecules

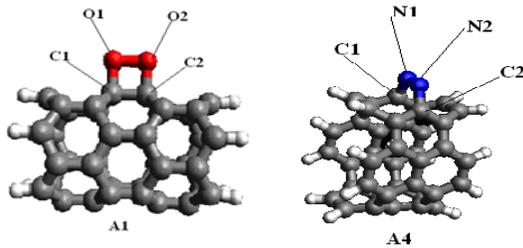


Fig. 3: (A<sub>3</sub>) and (A<sub>4</sub>) adsorption configurations of nitrogen molecule

## MATERIALS AND METHODS

This study was performed in Payame Noor University, Sari, Iran, as a research project of PhD thesis (National University of Tajikistan), over carbon nanotubes adsorption properties in 2009 to 2011.

Our representative H-doped model of armchair CNTs in the present study (Fig. 1) is a 4.88 nm long (4, 4)

single-walled CNT consisting of 40 C atom. Adsorption configurations of Oxygen and nitrogen molecules are shown in Fig. 2 and 3, respectively. The calculations are performed by hybrid functional B3LYP and DFT based method and 6-311G\* standard basis set by GAUSSIAN 98 package program (Frisch *et al.*, 1998). Geometrical parameters, bond length, binding energies, moment dipole are summarized in Table 1.

The calculated CS tensors in Principal Axes System (PAS) are converted to measurable NMR parameters, chemical shielding isotropic and chemical shielding anisotropic using CNT (A, A<sub>1</sub>, A<sub>2</sub>, A<sub>3</sub> and A<sub>4</sub>) are shown in Table 2, respectively.

London (London, 1937) initially suggested local gauge origins to define the vector potential of the external magnetic field in the study of molecular diamagnetism. The idea was then adapted by Ditchfield (1974) in the Gauge Independent Atomic Orbitals (GIAO) method for magnetic shielding calculations. We have performed experiments on single-wall carbon nano tube SWCNT networks and compared with DFT calculations to identify the microscopic origin of the observed sensitivity of the network conductivity to physisorbed O<sub>2</sub> and N<sub>2</sub>.

First DFT calculations of the transmission function for isolated previous SWCNTs have found that the physisorbed molecules have a little influence on their conductivity. However, by calculating we show that, physisorbed O<sub>2</sub> and N<sub>2</sub> affect the junction's conductance. This may be understood as an increase in tunneling probability due to hopping via molecular orbitals. We find the effect is substantially larger for O<sub>2</sub> than for N<sub>2</sub> SWCNTs junctions, in agreement with experiment (Mowbray *et al.*, 2009).

Components of CS tensor are defined by following relation (Duer, 2002):

$$\sigma_{ij} = \left( \frac{\partial^2 E}{\partial B_i \partial \mu_j} \right) \mu_j B_i \quad (1)$$

where,  $E$  is energy of system and  $\mu_j$  and  $B_i$  are components of magnetic moment and external magnetic field, respectively.

Table 1: Calculated structural parameters and adsorption energies of N<sub>2</sub> and O<sub>2</sub> adsorbed on the (4, 4) SWCNT<sup>a</sup>

Model (configuration)	r <sub>C-C</sub>	r <sub>C-O</sub>	r <sub>O-O</sub>	r <sub>C-N</sub>	r <sub>N-N</sub>	ΔE <sub>ad</sub>	Dipole moment
CNT(A)	(C-C) <sub>1</sub> = 1.422 (C-C) <sub>2</sub> = 1.452	-	-	-	-	-	0.0010
CNT(4,4)-O <sub>2</sub> (A <sub>1</sub> )	(C-C) <sub>1</sub> = 1.47 (C-C) <sub>2</sub> = 1.47	(C-O) <sub>2</sub> = 1.228 (C-O) <sub>2</sub> = 1.228	2.63	-	-	1112.2774	7.2966
CNT(4,4)-O <sub>2</sub> (A <sub>2</sub> )	(C-N) <sub>2</sub> = 1.447 (C-C) <sub>2</sub> = 1.52	(C-O) <sub>2</sub> = 1.468 (C-O) <sub>2</sub> = 1.473	1.498	-	-	1110.0383	3.4863
CNT(4,4)-N <sub>2</sub> (A <sub>3</sub> )	(C-C) <sub>1</sub> = 1.39 (C-C) <sub>2</sub> = 1.39	-	-	(C-N) <sub>1</sub> = 1.447 (C-N) <sub>2</sub> = 1.447	1.240	1.17	2.7093
CNT(4, 4)-N <sub>2</sub> (A <sub>4</sub> )	(C-C) <sub>1</sub> = 1.51 (C-C) <sub>2</sub> = 1.52	-	-	(C-N) <sub>2</sub> = 1.521 (C-N) <sub>2</sub> = 1.528	1.256	0.981	3.4022

<sup>a</sup>: All calculated distances in Å; All calculated binding energies in electron volt (eV); All calculated in dipole moment Debye

Table 2: Calculated <sup>13</sup>C NMR parameters for CNT, N<sub>2</sub>-CNT, O<sub>2</sub>-CNT systems<sup>a</sup>

Model	Atoms	σ <sub>11</sub>	σ <sub>22</sub>	σ <sub>33</sub>	σ <sub>iso</sub>	Δσ	η <sub>σ</sub>
CNT(A)	C <sub>3</sub>	-35.3100	13.8404	175.9600	51.4968	186.694	0.3949
	C <sub>2</sub>	-35.9811	13.5591	176.0667	51.2149	8187.2777	0.3968
	C <sub>1</sub>	0.02520	0.02520	163.8800	53.8495	165.0308	0.0000
CNT(4,4)-O <sub>2</sub> (A <sub>1</sub> )	C <sub>1</sub>	-80.4572	10.7847	102.7393	11.0223	137.575	0.9948
	C <sub>2</sub>	-80.8301	10.9026	102.4569	10.8431	5137.4207	1.0013
CNT(4,4)-O <sub>2</sub> (A <sub>2</sub> )	C <sub>1</sub>	40.2230	40.2230	141.8900	96.4600	68.1450	0.0000
	C <sub>2</sub>	64.9425	91.1836	133.1339	96.4200	55.0709	0.7147
CNT(4,4)-N <sub>2</sub> (A <sub>3</sub> )	C <sub>1</sub>	-88.7059	38.8741	95.38720	15.1851	120.3032	1.5907
	C <sub>2</sub>	-88.7419	38.8274	95.39100	15.1588	120.3483	00
CNT(4,4)-N <sub>2</sub> (A <sub>4</sub> )	C <sub>1</sub>	62.8717	62.8717	120.5500	97.2760	34.9100	0.0000
	C <sub>2</sub>	64.1611	64.1611	125.8100	499.3120	39.7400	0.0000

<sup>a</sup>: Calculated σ<sub>ii</sub>, σ<sub>iso</sub>, Δσ values in ppm

CS tensor in the Principal Axes System (PAS) (σ<sub>33</sub>>σ<sub>22</sub>>σ<sub>11</sub>) are diagonal and thus principal values for specifications of shielding are defined by this coordinate system as following:

$$\sigma_{iso} = \frac{(\sigma_{11} + \sigma_{22} + \sigma_{33})}{3} \quad (2)$$

$$\Delta\sigma = \frac{3}{2}(\sigma_{33} - \sigma_{iso}) \quad (3)$$

$$\eta_{\sigma} = \frac{3}{2} \left( \frac{\sigma_{22} - \sigma_{11}}{\Delta\sigma} \right) \quad (4)$$

where, σ<sub>iso</sub>, Δσ and η<sub>σ</sub> are isotropic, anisotropic and asymmetric parts of CS tensor, respectively and in certain cases vanishes.

## RESULTS AND DISCUSSION

In this study, geometries, binding energies and <sup>13</sup>C NMR chemical shielding tensors of H-capped (4, 4) SWCNT interacted with molecule O<sub>2</sub> and N<sub>2</sub> species, have studied. The calculated geometry parameters and binding energies, <sup>13</sup>C chemical shielding tensors have shown in Table 1 and 2. In the following sections, molecular geometries and binding energies, NMR chemical shielding tensors, the data obtained from O<sub>2</sub> and N<sub>2</sub> molecules adsorptions are discussed, separately.

**Molecular geometries and binding energy:** The optimized geometries of calculated configurations of O<sub>2</sub> and N<sub>2</sub> molecules adsorbed on (4, 4) SWCNT are schematically shown in Fig. 1. In this model, the end of nano-tube is saturated by H atoms. The fitness of considered tube length and atomic numbers has been examined earlier (Kang, 2006). Geometrical parameters, binding energies, moment dipole are summarized in Table 1. The nature of stationary points are confirmed by vibrational frequency calculations at the B3LYP/6-311G\* level. For molecular oxygen and nitrogen we have

considered two distinct adsorption sites, marked as CNT (A, A<sub>1</sub>, A<sub>2</sub>, A<sub>3</sub> and A<sub>4</sub>), (Table 1). CNT, CNT-O<sub>2</sub>, CNT-N<sub>2</sub> binding energies, ΔE<sub>ad</sub>, are calculated using:

$$E_{ad} = E_{tot}(\text{mol O}_2 + \text{CNT}_s) - E_{tot}(\text{CNT}_s) - E_{tot}(\text{mol O}_2) \quad (5)$$

$$E_{ad} = E_{tot}(\text{mol N}_2 + \text{CNT}_s) - E_{tot}(\text{CNT}_s) - E_{tot}(\text{mol N}_2) \quad (6)$$

where, E<sub>tot</sub>(CNT), E<sub>tot</sub>(O<sub>2</sub>), E<sub>tot</sub>(N<sub>2</sub>) and E<sub>tot</sub>(CNT+O<sub>2</sub>), E<sub>tot</sub>(CNT+N<sub>2</sub>) are the energy of the optimized tubes, adsorbate and tube-adsorbate system, respectively.

Armchair (4, 4) nano-tube has two different C-C bonds ((C-C)<sub>1</sub> = 1.422 Å and (C-C)<sub>2</sub> = 1.452 Å) thus offers two distinct adsorption sites. A schematic view of site form is shown in Fig. 1 CNT (A, A<sub>1</sub>, A<sub>2</sub>, A<sub>3</sub> and A<sub>4</sub>). Such a structure has also been observed for other SWCNTs (Sorescu *et al.*, 2001; Dag *et al.*, 2003; He *et al.*, 1998; Walch *et al.*, 2003; Zhang and Liu, 2004). Using DFT-GCA method, for the molecular O<sub>2</sub>-CNT system reached to following deduction; O<sub>2</sub> seemed to lie parallel to the outer surface of the tube. Geometry calculations of distortion caused by the oxygen and nitrogen molecules at the middle of the (C-C)<sub>1</sub> bond is very different. Placing the oxygen molecule in sites A<sub>1</sub>, A<sub>2</sub> do not change considerably the bridge distance of (C<sub>1</sub>-C<sub>2</sub>). The C-C distance increases from 1.422 to 1.47 Å and the calculated C-O distance is 1.228 Å, which is very similar to literature (Sorescu *et al.*, 2001; Dag *et al.*, 2003; He *et al.*, 1998; Walch *et al.*, 2003; Zhang and Liu, 2004). In both sites, we have the addition of one C-O bond to each of two neighboring sp<sub>2</sub> hybridized carbon atoms. This leads to either sp<sup>3</sup> hybridization for two carbon atoms or breaking of one C-C bond. Two different types of adsorbed O<sub>2</sub> species were identified (Fig. 1, A<sub>1</sub> and A<sub>2</sub>). The calculated binding energies were predicted to be -1112.2774 and -1110.0383 eV, respectively. We observe that greater dipole moments are associated with higher absolute values of energy. This seems reasonable because greater dipole moments lead larger shifts in the probability distribution of electrons and hence a larger change in energy levels.

Performed studies, show that the values of energies of nitrogen molecules adsorption on armchair model with

determined diameter and length, have the differences about twice in grandeur. In addition, all these energies are positive which show the reaction is improbable. Based on these results we can conclude that the physical adsorption over the surface area of nano-tube occurs very difficultly and so this is not a suitable case. We approach that, the adsorption carry out over open ends of nano-tubes, based on performed calculations, has more advantages.

**<sup>13</sup>C NMR chemical shielding:** Table 2 shows the calculated <sup>13</sup>C chemical shielding tensors for CNTs. O<sub>2</sub> and N<sub>2</sub> molecules adsorption on the CNT has a remarkable influence on <sup>13</sup>C NMR tensors, which is in complete accordance with the facts mentioned above. It is also explain that, chemical shielding components converge in a way similar to that of the chemical shifts which increasing the tube length however, not as monotonous as the isotropy shielding. On the other hand, the calculated <sup>13</sup>C chemical shielding values in the middle of the (4, 4) CNT seem approach the values 53.8 and 57.3 mg/L.

According to GIAO calculations performed after adsorption of oxygen and nitrogen molecules, the isotropy value of the <sup>13</sup>C NMR shielding tensor is decreased in A<sub>1</sub> and A<sub>3</sub> sites (about 11.0223 and 10.8431 mg/L at C<sub>1</sub> and C<sub>2</sub> of site A<sub>1</sub> and 15.1851 and 15.1588 mg/L at C<sub>1</sub> and C<sub>2</sub> of site A<sub>3</sub>) and increased in A<sub>2</sub> and A<sub>4</sub> sites (about 96.4565 and 96.4200 mg/L at C<sub>1</sub> and C<sub>2</sub> of site A<sub>2</sub> and 99.3120 and 97.2764 mg/L at C<sub>1</sub> and C<sub>2</sub> of site A<sub>4</sub>) (Table 2). The associated anisotropy value decreases for both carbons. However, the effect is more significant for C<sub>1</sub> and C<sub>2</sub> nuclei.

Results reveal that electronic charge distribution around the carbon atoms becomes more symmetric as a result of oxygen adsorption. The anisotropy value of the <sup>13</sup>C NMR shielding tensor is increased approximately about 137.5755 and 137.4207 mg/L, at C<sub>1</sub> and C<sub>2</sub> of site A<sub>1</sub>. In this case, anisotropy values for both carbons decrease by adsorption, while the reduction is more evident for C<sub>1</sub> and C<sub>2</sub>.

Due to O<sub>2</sub> adsorption, the calculated <sup>13</sup>C NMR parameters of those interacted carbon atoms are also modified. As deduced from comparison of sites A<sub>1</sub> and A<sub>2</sub>, the carbon atoms contributed in O<sub>2</sub> adsorption, become more shielded. Among the two NMR principal components, intermediate shielding component, σ<sub>22</sub>, shows more change from nano-tube than O<sub>2</sub>-CNT system, which is in contrast with N<sub>2</sub>-CNT. The results are consistent with fort interaction between nano-tube and O<sub>2</sub> molecule. The discrepancy between <sup>13</sup>C chemical shielding tensor for the site A<sub>1</sub> and A<sub>2</sub> systems and A<sub>3</sub> and A<sub>4</sub> systems must be attributed to the different nature of the frontier orbital.

## CONCLUSION

According to DFT calculations, adsorption of, O<sub>2</sub> and N<sub>2</sub> Molecules extremely influenced geometrical and electronic structure properties of (4, 4) SWCNT. For

oxygen molecule adsorption, the binding energy at the Table 1 is found to be -112.2774 eV, which is more stable than nitrogen molecule adsorption. It is found that <sup>13</sup>C chemical shielding is appropriate parameters to investigate the nature of interactions in (4, 4) SWCNT.

It is found that <sup>13</sup>C chemical shielding is appropriate parameters to investigate the nature of interactions in (4, 4) SWCNT. The <sup>13</sup>C chemical shielding isotropy and anisotropy values vary remarkably from CNT to the CNT-O<sub>2</sub> and CNT-N<sub>2</sub> systems, for adsorption sites.

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