RESEARCH ARTICLE OPEN ACCESS

Studying and Comparing Sensing Capability of Single Walled Carbon Nanotubes for Adsorption of O_2 and N_2 Gases Using DFT

Fereydoun Ashrafi*
*(Department of Chemistry, Payame Noor University, P. O. Box 19395-3697, Tehran, Iran)

ABSTRACT
In this study sensing capability of single walled carbon nanotubes (SWCNTs), of both zigzag (5, 0) and armchair (4, 4) models were investigated for adsorption of O_2 and N_2 molecules were investigated using density functional theory (DFT) method. Using this computational method, it is possible to obtain much more data to apply in medical science and industrial technologies. Geometrical optimization have carried out using standard set and B3LYP/6-311G* basis set of Gaussian 98 program. Those parts of SWCNT which have demonstrated more contribution in adsorption energy, ΔE_{ads} (eV) were studied and compared. Electronic configurations were discussed and the results were interpreted.
Keywords **-** Adsorption energy, DFT method, Gaussian program, sensing capability, SWCNTs

I. INTRODUCTION

Nano sensors such as electronic devices have the ability to specify very weak physical exciters in nano scales [1-3]. In recent years, gas adsorption over outer surface of carbon nanotubes was arguably a very interesting theoretical study [2]. Electrical resistance of semiconductor nanotubes significantly changes by adsorption of certain gas molecules such as O2, N2, NH3 and H2 [3- 5]. Gas adsorption on surface and open end of SWCNT was studied widely by theoretical calculations [6]. Nuclear magnetic resonance (NMR) spectroscopy parameters and chemisorption energies ΔEads were studied to investigate the electronic structure properties [7, 8]. The electronic structures, NMR spectrum, dipole moment of nitrogen, oxygen and carbon nuclei's were thoroughly studied. Also, DFT method was used to study the adsorption of oxygen and nitrogen molecules on the surface of (5, 0) and (4, 4) SWCNT [9, 10]. So that, DFT calculations were performed to calculate ^{14}N and ^{17}O nuclear magnetic resonance (NMR) spectroscopy parameters in the representative considered models of zigzag and armchair SWNTs [11]. Density functional theory (DFT) and hartree-fock (HF) methods were used to investigate the adsorption of oxygen and nitrogen molecules on the surface of (5, 0) and (4, 4) carbon nanotubes. Electronic structure and dipole moment of both oxygen and carbon nuclei were accurately studied [12, 13].

Computation results of O^2 and N^2 molecules which have bonded to the surface and open end of SWCNTs using DFT and based on B3LYP/6-311G* basis set and Gaussian atomic orbital method [14] show that O^2 and N^2 adsorption cause vast changes in electrical resistance of SWCNTs which may be a suitable method for gas identification [15]. The amount of adsorbed energy may be calculated by following equations [4, 5, 16-18]:

$$E_{ads} = E_{tot}(molec.O_2 + CNTs) - E(CNTs) - E(molec.O_2) \quad (1)$$

$$E_{ads} = E_{tot}(molec.N_2 + CNTs) - E(CNTs) - E(molec.N_2) \quad (2)$$

Where E_{ads} is energy adsorbed throughout the process.

In this work, firstly, investigation by DFT method was performed to study adsorption of oxygen and nitrogen molecules on the surface of (5, 0) and (4, 4) models of CNTs. Then, those parts of SWCNT which have demonstrated more contribution in adsorption energy ΔEads(eV), were compared. Finally, electronic configurations were used for discussion and interpretation of obtained results.

II. COMPUTATIONAL METHODS

Calculation was performed using density functional theory. Physical and chemical adsorption of nitrogen and oxygen molecules on the surface of SWCNTs armchair (4, 4) and zigzag (5, 5) models were studied and compared using Gaussian 98 software based on standard set and B3LYP/6-311G* basis set. Comparison of adsorption of oxygen and nitrogen gases on the surface of carbon nanotubes was carried out on the diagrams.

III. RESULTS AND DISCUSSION

Two models of SWCNTs, zigzag (5, 0) and armchair (4, 4), which their length and diameter have been optimized by quantum chemistry computations were studied. The calculations for zigzag model (5, 0) with length of 7.10 A and diameter of 2.26 A, and armchair model (4, 4) with length of 4.18 A and diameter of 5.67 A were performed. The length of nanotubes has selected considering the length of nanotube unit cell.

The manners of adsorption of nitrogen and oxygen gases on the surface of carbon nanotube were shown in tables 1 to 4 and also in figures 1 and 2, and may be discussed and interpreted as follows. Obtained results show that interaction of oxygen molecule with the surface of two models of carbon nanotubes, (5, 0) and (4, 4), is exothermic. Changing the location of the oxygen molecule on the surface of carbon nanotubes does not change the amount of released energy in 3 cases (tables 1 and 2 and figure 1).

Table 1 Structures and Eads of O_2 adsorption on the external surface of zigzag (5, 0) model

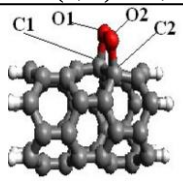
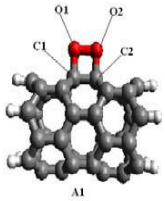
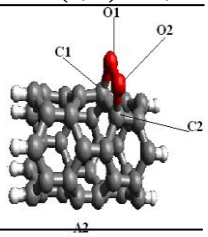
Model	CNT(5, 0)- O2,A1	CNT(5, 0)- O2,A2
Structure		
E_{ads}(eV)	-1111.6171	-1110.7455

Table 2 Structures and Eads of O_2 adsorption on the external surface of armchair (4, 4) model

Model	CNT(4, 4)- O2,A1	CNT(4, 4)- O2,A2
Structure		
E_{ads}(eV)	-1112.2774	-110.0383

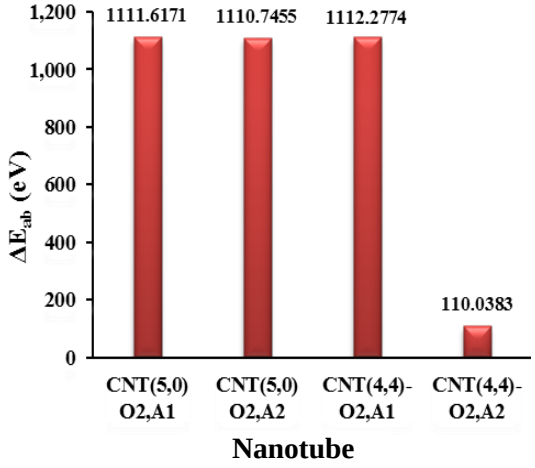


Fig. 1 Diagram of released energy due to O2 adsorption on the surface of carbon nanotubes zigzag (5, 0), and armchair (4, 4) models

In the case of CNT (4, 4) - O2, A2 model the released energy of oxygen adsorption is much more different from 3 precedent cases. This may be the preferably site for oxygen molecule adsorption on the outer surface of carbon nanotube.

Whereas the condition for nitrogen molecule is different. The amount of energy which is required for its absorption is changed by changing its location on the surface of CNT (tables 3 and 4 and figure 2).

Table 3 Structures and Eads of N_2 adsorption on the external surface of zigzag (5, 0) model

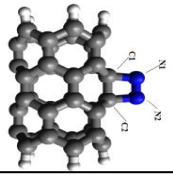
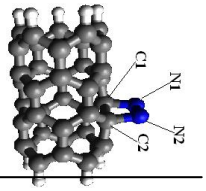
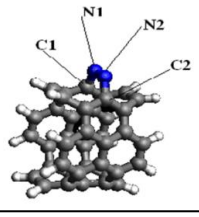
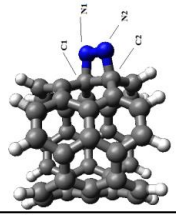
Model	CNT(5,0)-N2,A1	CNT(5,0)- N2,A2
Structure		
E_{ads}(eV)	1.737	2.858

Table 4 Structures and E_{ads} of N_2 adsorption on the external surface of armchair (4, 4) model

Model	CNT(4,4)-N2,A1	CNT(4,4)- N2,A2
Structure		
E_{ads}(eV)	2.170	0.981

The same computations were performed for adsorption of nitrogen molecule on the surface of nanotubes of armchair (4, 4) and zigzag (5, 0) models. Computation results show that adsorption of nitrogen on external surface of nanotubes occur hardly and in low amounts.

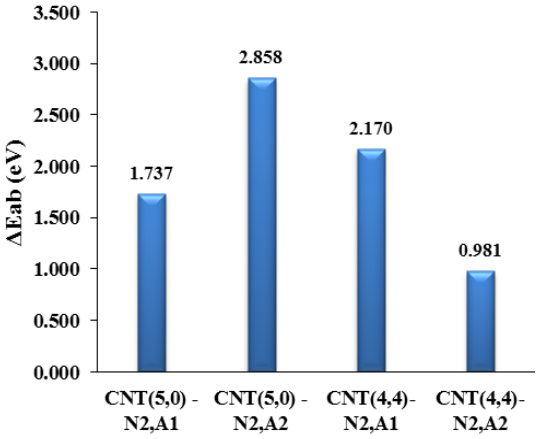


Fig. 2 Diagram of required energy for N_2 adsorption on the surface of carbon nanotubes zigzag (5, 0), and armchair (4, 4) models

Due to the geometry of the armchair (4, 4) and zigzag (5, 0) nanotubes, two different adsorption sites can be consider for oxygen and nitrogen molecules, on the outer surface of the nanotube. The results of computation for this consideration, suggest that a more appropriate model for the oxygen molecule is CNT (4, 4)-O2-A2. The amount of released energy in this case is close to the value previously reported [19].

The results of earlier researches indicate that the interaction of N_2 molecule with open end of CNTs is more favorable than the interaction with its surface [20-22].

This phenomenon may be attributed to electronic structure of CNTs. In fact, the electronic structure of CNTs (having free electros) is in such a way that can prevent the easy approaching of nitrogen molecules than oxygen molecules towards its external surface because of their electronic configurations. It seems that this effect is more effective for nitrogen molecules, having a triple bond, than oxygen molecules, having a double bond.

It should be noted that, electronic structure of O_2 is KK $(\sigma^2s)2\ (\sigma^2s^*)^2\ (\sigma^2p_z)2\ (\pi^2p_x)^2\ (\pi^2p_y)^2\ (\pi^2p_x^*)^1(\pi^2 p_y^*)^1$ and the transferred electron, certainly will occupy the half-filled anti-bonding orbitals of O_2, hence will weaken the O–O bond. Electronic structure of N_2 is KK $(\sigma^2s)^2\ (\sigma^2s^*)^2\ (\sigma_2p_z)^2\ (\pi^2p_x)^2\ (\pi^2p_y)^2$ and the binding orbital of N_2 molecule is filled, so that the transferred electron can't enter into this binding orbital. It can be concluded that, these phenomena surely will affect the adsorption of these molecules on the surface of CNTs.

On the other hand, physisorption of NH_3 and NO_2 molecules on the surface of carbon nanotube may be considered as an approval of the effect of electronic configuration on the outer surface adsorption of CNTs [23]. Therefore, electron charge transfer is found to be a major mechanism which determines the conductivity change in CNTs upon exposure to NH_3 and NO_2 molecules [23].

Considering sp2 electronic structure of carbon nanotube, this can be easily understood why adsorption of N_2 molecules on the outer surface of carbon nanotubes is more difficult than O_2 adsorption. In fact, this phenomenon may be attributed mainly to the cloud of free electrons which can prevent the easy adsorption of molecules where they are either filled or half-filled extern orbitals. Considering the obtained results of Eads for O_2 and N_2 physisorption on the outer surface of carbon nanotube, this interpretation seems should be reasonable. Consequently, the results of the comparison of these defined models show that oxygen sensor is more favorable than nitrogen sensor. This phenomenon also may be interpreted by more effective binding of oxygen molecules than nitrogen molecules with CNTs because of its electronic structure (half-filled anti-bonding orbitals of oxygen molecule).

IV. CONCLUSION

Two models of SWCNTs, zigzag (5, 0) and armchair (4, 4), with optimized length and diameter were studied by quantum chemistry computations.

The results obtained from calculations show that interaction of oxygen molecule with the surface of two models of carbon nanotubes, (5, 0) and (4, 4), is exothermic. Whereas, adsorption of nitrogen gas on CNT surface requires heat.

Calculated amounts of adsorption energy of oxygen and nitrogen molecules suggest that adsorption of O_2 may be chemisorption and adsorption of N2 may be physisorption.

On the other hand, because of electronic configuration of O_2 Molecule, the transferred electron is filled in the half-filled anti-bonding orbitals of O_2; thus will weaken the O–O bond. But, the binding orbital of N2 molecule is filled and so the transferred electron can't enter into this binding orbital, consequently, physical binding will form.

In addition, calculated adsorption energies (Eads), may be an approval for adsorption manner of these two molecules.

The results of calculations show that the more suitable model for oxygen molecule, because of its Eads, is CNT (4, 4)-O_2-A2.

REFERENCES

[1] S. Ijima, T. Ichihashi, *Single-shell carbon nanotubes of 1-nm diameter*, Nature, Vol. 363 (1993), 603.

[2] Y.T. Jang, S.I. Moon, J.H. Ahn, Y.H. Lee, B.K. Ju, *A simple approach in fabricating chemical sensor using laterally grown multi-walled carbon nanotubes*, Sens. Actuators, B 99 (2004) 118.

[3] L. Valentini, C. Cantalini, I. Armentano, J.M. Kenny, L. Lozzi, S. Santucci, *Highly Sensitive and Selective Sensors Based on carbon Nanotubes Thin films for Molecular Detection*, Diamond Relat. Mater., Vol. 13 (2004) 130.

[4] A.S. Ghasemi1, F. Aashrafi, *Adsorption 17O, 15N and CO molecules on the surface of SWCNT: A Computational NMR study*, Inter. J. ChemTech Research, Vol.4, No.4 (2012) 1295.

[5] F. Ashrafi, S.A. Babanegad and A.S. Ghasemi, *Comparison of Adsorption of Nitrogen and Oxygen- Molecules on the Open Ended and Surface of Swcnts: A Computational NMR and NQR Study*, Research J. Appl. Sci. Eng. Tech., Vol. 4 (7) (2012) 795.

[6] S.G. Wang, Q. Zhang, D.J. Yang, P.J. Sellin, G.F. Zhong, *Multi-walled carbon nanotube based gas sensors for NH3 detection*, Diamond Relat. Mater.,Vol. 13 (2004) 327.

[7] A. S. Ghasemi, F. Ashrafi, S. A. Babanejad and M. Rahimof, *A Computational NMR Study of Chemisorption of Nitrogen-Dopedon the Surface of Single-Walled Carbon Nanotubes*, Arch. Appl. Sci. Research, Vol. 2 (4) (2010) 262.

[8] A. Ghasemi and F. Ashrafi, *A Computational NMR Study for Chemisorption of oxygen doped on the Surface of Single-Walled Carbon Nanotubes*, Research J. Appl. Sci. Eng. Tech., Vol. 4 (15) (2012) 2529.

[9] F. ASHRAFI, A. S. GASEMI, *Density Functional Theory (DFT) Study of O_2, N_2 Adsorptions on H-Capped (5, 0) Single–Walled Carbon Nanotube (CNT)*, E-Journal of Chemistry, Vol. 9 (4) (2012) 2134.

[10] A.S. Ghsemi and F. Ashrafi, *Density Functional Theory (DFT) Study of O2, N2 Adsorptions on H-Capped (4,4) Single-Walled Carbon Nanotube*, Research J. Appl. Sci. Eng. Tech., Vol. 4 (15) (2012) 2523.

[11] S.A. Babanegad, F. Ashrafi, A.S. Ghasemi, E. Ashrafi, *Influence of hydrogen doping on the 15N and 17O NMR parameters in zigzag and armchair single wall nanotube: A DFT study*, Der Chemica Sinica, Vol. 3 (1) (2012) 124.

[12] S.A. Babanejad, F. Ashrafi, A. Ghasemi, *Optimization of adsorption of oxygen gas on Carbon nanotubes surface*, Arch. Appl. Sci. Research, Vol. 2 (5), (2012) 438.

[13] F. Ashrafi, A.S. Ghasemi, S.A. Babanejad and M. Rahimof, *Optimization of Carbon Nanotubes for Nitrogen Gas Adsorption*, Vol. 2 (6), (2010) 547.

[14] M.J. Frisch et al, *Examination of Gaussian-Type Basis Sets on Alkali Metal Iodides*, GAUSSIAN 98, Gaussian Inc., Pittsburgh, PA, (1998).

[15] G. Zhang, W. Duan, B. Gu, *Effect of substitutional atoms in the tip on field-emission properties of capped carbon nanotubes*, Appl. Phys. Lett., Vol. 80, (2002) 2589.

[16] A.H. Nevidomskyy, G. Csany, M.C. Payne, *Chemically active substitutional nitrogen impurity in carbon nanotubes, Phys. Rev. Letters*, Vol. 91 (2003) 105502.

[17] J.Y. Yi, J. Bernholc, *Atomic structure and doping of microtubules*, Phys. Rev., B 47, (1993) 1708.

[18] C. P. Ewels, M. Glerup, *Nitrogen doping in carbon nanotubes*, J. Nanosci Nanotechnol, Vol. 5 (9), (2005) 1345.

[19] H.J. Liu, J.P. Zhai, C.T. Chan, Z.K. Tang, *Adsorption of O2 on a (4,2) carbon nanotube*, Nanotechnology 18, (2007) 065704.

[20] Z. Jing-xiang, D. Yi-hong, *Theoretical Studies of the Interaction of an Open-Ended Boron Nitride Nanotube (BNNT) with Gas Molecules*, J. Phys. Chem. C, Vol. 112 (51), (2008) 20206.

[21] F. Ashrafi, S.A. Babanegad, A.S. Ghasemi, *Comparison of Adsorption of Nitrogen and Oxygen- Molecules on the Open Ended and Surface of Swcnts: A Computational NMR and NQR Study*, Research J. Appl. Sci. Eng. Tech., Vol. 4 (7), (2012) 795.

[22] S.A. Babanegad, F. Ashrafi, A.S. Ghasemi, N. alarzadeh, *Adsorption of N2 Molecule on the open ended of Single Wall Nanotube: A Computational NMR*, J. nanostructure in chem., Vol. 2 (2), (2012) 94.

[23] Chang, Hyunju; Lee, Jae Do ; Lee, Seung Mi ; Lee, Young Hee, *Adsorption of NH3 and NO2 molecules on carbon nanotubes*, Applied Physics Letters, Vol. 79 (23), (2009), 3863.