Research Journal of Applied Sciences, Engineering and Technology 2(6): 547-551, 2010
ISSN: 2040-7467

Submitted Date: June 09, 2010 Accepted Date: July 13, 2010 Published Date: September 10, 2010

Optimization of Carbon Nanotubes for Nitrogen Gas Adsorption

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Abstract: Carbon nanotubes (CNTs) are one of the most significant achievements of nano-technology because of his important applications in the design of electronic nano-devices. The study of their properties is therefore important. In this investigation the Density Functional Theory (DFT) of electron and the Hartree-Fock (HF) method are utilized to study the adsorption of nitrogen molecules on the surface of (4, 4) and (5, 0) carbon nanotubes. The electronic structure, single point and dipole moment of both nitrogen and carbon nuclei are thoroughly studied. The computational results, which includes, indicate that rich adsorption patterns may result from the interaction of nitrogen with the carbon nanotubes. Sometimes C-N bounds are formed via breaking C-C bounds and sometimes a carbon atom in the nanotube is replaced by a nitrogen atom. Sometimes nitrogen atoms are attracted to a C-C bound. In summary, the optimized adsorption rates are calculated. Gaussian 98 software has been used to carry out quantum chemistry calculations.

Key words: Carbon nanotube, density functional theory, gaussian 98 software, hartree-fock

INTRODUCTION

Gas sensors used in many factories and hospitals are important to environmental monitoring. In order to prevent the gas from leaking and endangering human body, it is necessary to do the detection and examination on different gases. Although traditional gas sensors made by using semiconducting oxides, are inexpensive, safe and sensitive, they have been operated at high temperature (Tang *et al*., 1995) to enhance chemical reactivity between the material and the target gas molecule. This major fault leads traditional gas sensor to a limitation for future applications. The search for new materials which performed at ambient temperature, continue always.

Due to the discovery of nanostructure materials, such as carbon nanotubes (CNTs) (Ong *et al*., 2002; Huang *et al*., 2004), nanoparticles (Hong-Ming *et al*., 1997; Hayakawa *et al*., 2000), nanobelts (Zhong, 2003; Comini *et al*., 2002), titanium nanotubes (Dawei *et al*., 2001, Oomman *et al*., 2003) and nanowires (Walter *et al*., 2002; Zhou *et al*., 2003), it has been concluded that the smaller material size and higher specific surface area, improve the sensitivity and response time.

Many much investigations have been performed for studying effect of diameter and deflection of nanotube on its electrical characteristics (White and Mintmire, 2005). The electrical resistance of nanotubes change considerably by adsorption of certain gases, as O_2, N_2, NH_3 and H_2 (Harris, 1999). Small size and electrical characteristics set these materials incomparable for sensor utilities (Chang *et al*., 2001). Because of their biological agreements and high consistency, nanotubes have introduced in biomedicine and pharmacology (Zhao *et al*., 2002; Darkrim *et al*., 1998).

Nitrogen gas adsorption on the surface of semiconductor nanotubes, have a vast effect on its electrical characteristics, but haven't any effect on electrical characteristics of conductor nanotubes. All armchair nanotubes (4, 0) are semiconductors, the zigzag nanotubes (5, 0), also, are semiconductors (Meyyappan; 2005, Alessandra and Charles, 2006).

Impurity addition to semiconductor nanotubes with zigzag form (5, 0), causes energy gap decrease and tend to quasi-metallic state which results in conductivity increase. The presence of nitrogen molecule and addition of pair electrons to CTNs, increase its electrical resistance and the diameter.

The purpose of this research is studying the adsorption of nitrogen molecule on single-walled nanotube with both armchair (4, 4) and zigzag (5, 0) models by means of Hartree-Fock (HF) method and Density Functional Theory (DFT). This approach consists of: a) configuration of adsorption, b) determination of binding energy locate on carbon nucleuses on nanotube which involve in chemical binding with nitrogen molecules, and c) determination of bond length after nitrogen molecule adsorption over nanotube surface which have optimized by calculation methods.

As we observe on Fig. 1, the total number of carbon atoms in a single-walled nanotube is many much, which causes long calculations even for one small wire of nanotube. For resolve this problem we have used based method and standard basis set and adequate calculations.

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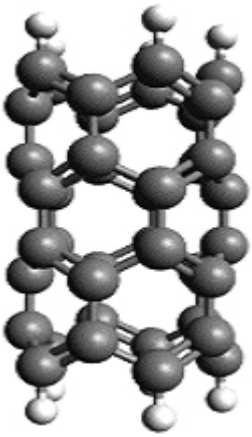

Fig. 1: The structure of carbon nano-tubes, zigzag.

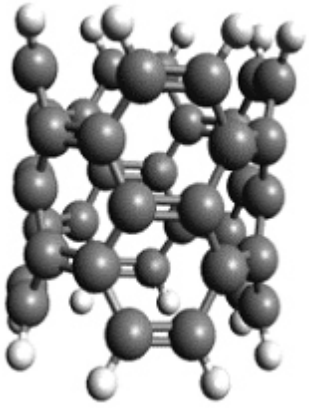

Fig. 2: The structure of carbon nano-tubes, armchair

MATERIALS AND METHODS

This study was performed in Payame Noor University, Sari center, Sari, Iran, as a research project over carbon nanotubes adsorption property in 2009 and 2010.

Computational details: In this approach we use both DFT and HF methods for calculation over armchair (4, 4) and zigzag (5, 0) models. The calculations are performed by hybrid functional B3LYP density functional theory (DFT) based method and 6-311G* standard basis set by GAUSSIAN 98 package of program (Frisch *et al*., 1998).

The choice of adequate model leads us to reasonable results which are comparable with experimental results. Minimum length of nanotube in SWCNTs model is unit cell's representative, which characterizes the comportment of this nanotube adsorption, similar to a real nanotube. It is appointed that, if the length of selected model is $\sqrt{3}/2$ and equal to unit cell, the model is an adequate one for calculation. Determination of the length of this unit cell with respect to its hexagonal rings is simple (White *et al*., 2005).

RESULTS AND DISCUSSION

Zigzag (5, 0) model: Primary structures of zigzag (5, 0) model of nanotubes have optimized in length and diameter by nanotube modeler software. The calculation was performed for a zigzag (5, 0) nanotube of 7.10 Å length and 2.26 Å diameter. The length of nanotube have selected with respect to the length of unit cell of nanotube. Then, after selection a certain length for nanotube, the carbon atoms situated in both ends of this length will have negative charge because of carbon bonds breaking. For carbon bond saturation in two ends of nanowire and create a model approach to a real wire of nanotube, hydrogen atoms was added to the end links of nanotube wire. In the zigzag (5, 0) nanotube, 10 hydrogen atoms were added to basic structure of nanotube wire (Fig. 1). Optimization was performed by GAUSSIAN 98 software, calculation method of B3LYP and 6-311G* basis set (Table 1).

After optimization the basic structure of nano-tube, adsorption energy of nitrogen molecule for two zigzag cases by both DFT and HF methods was determined separately, by studying the structures and the structure variations during nitrogen adsorption (Table 1, the units are in hartry and kcal/mol). The best proposed method for this study is DFT which gives the values approximately approach to real ones. The studies on structural variations during nitrogen adsorption and comparing with studies performed on adsorption of small molecules and atoms on surface areas of nanotubes (Meyyappan, 2005; Dae-Hwang *et al*., 2003), it is approved that this adsorption is most probable one.

Armchair (4, 4) model: Primary structures of armchair (4, 4) model of nanotubes have optimized in length and diameter by nanotube modeler software. The calculation was performed for an armchair (4, 4) model of nanotube of 4.18Å length and 5.67 Å diameter. For carbon bond saturation, 16 hydrogen atoms were added to the end links of nanotube wire in armchair (4, 4) model of nanotubes, for obtaining a model so approach to a real one (Fig. 2).

The length of nanotube has selected with respect to the length of unit cell of nanotube and then was optimized. Optimization was performed by GAUSSIAN 98 software, calculation method of B3LYP and 6-311G* basis set (Table 2, the units are in hartry and kcal/mol).

After optimizing nanotube doped with nitrogen, adsorption energy of armchair molecules has obtained by two calculation method DFT and HF. By comparison with

Table 1: Calculation data obtained of adsorption energy for nitrogen molecule for two zigzag (5, 0) model

Site	Model	Structure	HF Hartry	HF Kcal/mol	Energy difference for comparison HF Kcal/mol	DFT Hartry	DFT Kcal/mol	Energy difference for comparison DFT Kcal/mol
1	CNT5,0-N_2A_1		-1628.9227692	-1022195.89	0.0000	-1639.4593648	-1028776.33	0.0000
2	CNT5,0-N_2A_2		-1628.8793765	-1022137.28	58.6039	-1639.4181595	-1028750.47	25.8563

Table 2: Calculation data obtained of adsorption energy for nitrogen molecule for two armchair (4, 4) model

Site	Model	Structure	HF Hartry	HF Kcal/mol	Energy difference for comparison HF Kcal/mol	DFT Hartry	DFT Kcal/mol	Energy difference for comparison DFT Kcal/mol
1	CNT4,4-N_2A_1		-1632.938866	-1024684.65	0.0000	-1643.5031877	-1031313.86	0.0000
2	CNT4,4-N_2A_2		-1628.8793765	-1022137.28	24.6639	-1643.547032	-1031341.38	26.9627

Table 3: Bond length comparison of molecular nitrogen adsorption in two cases of both zigzag (5, 0) and armchair (4, 4) models

Site	Model	Dipole moment Debye	R (C-C)$_1$Å	R (C-C)$_2$Å	R (C-N)$_1$Å	R (C-N)$_2$Å
1	CNT 5,0-N_2A_1	2.4530	1.51	1.51	1.511	1.511
2	CNT 5,0-N_2A_2	2.4704	1.50	1.49	1.574	1.553
3	CNT 4,4-N_2A_1	2.7093	1.39	1.39	1.447	1.447
4	CNT 4,4-N_2A_2	3.4022	1.51	1.52	1.521	1.528

these two methods, the values of energy give an acceptable ressults with 4 kcal mol^{-1} of difference. By comparing obtained results for small molecules and atoms adsorption on graphitic and nanotube surfaces (Meyyappan, 2005; Dae-Hwang *et al*., 2003) and present study, it is obvious that the most probable chemical adsorption have done over C-C bond.

The length of C-C bond forming nano-tube, neighbor to C-N bond, was studied in optimized structure. The calculation and determined basis series show that C-C bond parallel to main axe of nano-tube was obtained 1.41 Å and for other bonds 1.39 Å.

Bond length: Observed variations for bond length after nitrogen molecule adsorption on exterior surface of nanotube have shown in Table 3. We can interpret that C-C bond length increasing after nitrogen molecule adsorption over nanotube, is due to the fact that nitrogen is more electronegative than carbon. This property, during formation of C-N bond, cause partial positive charge on both carbon atoms and hence create electrostatic repulsion between this two carbon atoms which results in increasing C-C bond length.

As inter-particular viewpoint of interactions, nitrogen molecule binding to nano-tube results in transmission of non bonded pair electrons of oxygen to two δ^* molecular orbital of C-C bond. This issue causes an increase in electronic population of this anti binding orbital and decrease electronic population of δ binding orbital which result in weakness of C-C bond and increase in its length (Table 3).

As shown in Table 3, the changes in length of bonds are much small. This fact show that physical adsorption of nitrogen molecule over nanotube's surface is very difficult. It may be interpreted that sometimes there is not any adsorption which can leads to apparent changes of length and diameter of nanotube. By this reason, dipole moments were calculated by using GAUSSIAN 98 software as shown in Table 3. We can observe that as dipole moment increase, the absolute value of energy also, increases. This result may be reasonably, because the higher dipole moment demonstrates grater displacement in distribution of electronic clods. There is obvious that as displacement is grater, the absolute value of energy increases.

Table 4: Comparison of nitrogen adsorption energies by DFT and HF methods

	Model	E_{ad} (eV)DFT	E_{ad} (eV)HF
1	CNT 5,0-N_2A_1	1.737	287.0984
2	CNT 5,0-N_2A_2	2.858	289.6398
3	CNT 4,4-N_2A_1	2.170	289.6509
4	CNT 4,4-N_2A_2	0.981	400.11781

Adsorption energy: Performed calculations on the values of nitrogen molecule adsorption energy over zigzag (5, 0) and armchair (4, 4) nanotubes with determined length and diameter, by DFT and HF methods show the difference amounts twice grater (Table 4). In addition, energies are positive. Therefore, these results signify improbability of reaction. Thus, we can say with sureness, physical adsorption of nitrogen molecule over nanotube surface occurs difficultly, and as practical performance is not an adequate alternative. It is advantage to perform nitrogen adsorption over open end of nanotube which gives better results in comparison with performed studies (Dae-Hwang *et al*., 2003).

Then, we can calculate nitrogen adsorption over single walled nanotube by following relation:

$$E_{ad} = E_{tot}(N_2\text{molecule} + \text{CNTs}) - \text{Etot}(N_2\text{ molecule})$$

CONCLUSION

In this study the structures of nitrogen molecule adsorption over single-walled nanotube armchair (4, 4) and zigzag (5, 0) models were studied by using density functional theory (DFT) of electron and Hartree-Fock (HF) methods. It is found that interaction of nitrogen molecule with surface of nano-tube is an exothermic chemical reaction in which the amount of liberated energy varies with adsorption site of nitrogen molecule (Table 1, 2 and 4).

Structural variation include carbon bond increasing which was involved in adsorption. Comparison of bonds length and adsorption energies show that adsorption of nitrogen molecule over surface of nano-tube armchair (4, 4) model is stronger than zigzag (5, 0) model. Because of curvature of nanotube's surface, interactions over surface are major. Moreover, the reducing characteristic of nitrogen molecule and transmission of its non-binding pairs of electrons to neighbor carbon atoms over carbon rings on nanotube surface, cause resistance increasing and also increasing in nanotube diameter.

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