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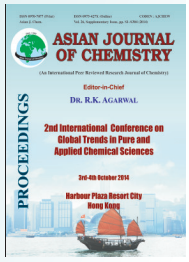

Small Gas Molecules on Functionalized Single-Walled Carbon Nanotubes: Gas Sensor Application

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The quantum mechanical calculations with own N-layered Integrated molecular orbital and molecule mechanics (ONIOM) method have been conducted to investigate the interactions between the small gases (*i.e.*, hydrogen and oxygen) and the functionalized (8,8) single-walled carbon nanotubes (SWCNTs). The role of tip functionalizations of single walled carbon nanotube (SWCNTs) on gas adsorption has been determined. As the results, the hydrogen molecule can be well adsorbed by the SWCNT with positive charge functionalization, while the oxygen molecule prefers to adsorb on the non-functionalized SWCNT. Moreover, it appears that H_2 molecule binding with positive charged carbon nanotube (CNT^+) in the vertical direction is the most favorable because the average binding energy is equal to -18.5 ± 4.4 kcal/mol. Although, the average binding energy between H_2 molecule with negative charged carbon nanotube (CNT^-) in the vertical is -19.9 ± 7.0 kcal/mol, its standard deviation is greater than the standard deviation of H_2 molecule binding with CNT^+ in the vertical direction. In addition, O_2 molecule binding with carbon nanotube in the vertical direction is the most favorable because the average binding energy is equal to -48.3 ± 6.4 kcal/mol. This theoretical investigation provides information which will be very useful for development of gas sensors.

Keywords: Gas sensor, Adsorption, Surface, Quantum calculations.

INTRODUCTION

Carbon nanotubes (CNTs) have been proposed by Iijima[1] in 1991 and have became extremely popular. They have been promising materials developed for many applications *e.g.*, water desalination, semiconductor and nanosensors, *etc*. Their structures are like the rolled up graphene sheets. The chirality of carbon nanotube is presented by a pair of integer (n, m). If n-m = 3j; (j ≠ 0), the carbon nanotubes are metallic, otherwise, they are semiconducting. Among many carbon nanotube applications, gas sensors have been interested since they are very useful in *e.g.*, biomedicine and environmental gas detection applications. The carbon nanotube gas sensing systems have been experimentally and theoretically studied for many years[2,3]. The adsorption of NO_2 on single-walled carbon nanotubes (SWCNTs) has been generally determined by density functional theory (DFT)[4,5]. Yim *et al.*[4] have examined the chemisorptions of NO_2 on SWCNTs by using plane wave/pseudo potential-based density functional theory. They showed that the chemisorptions of NO_2 increases the conductivity of (8,0) carbon nanotube and indicated that carbon nanotube is more reactive than graphene sheet to NO_2 gas. It is due to the curvature of the tube. Zhao *et al.*[6] have investigated the adsorption of small gases on SWCNT using density functional theory with either localized basis (DMol) or plane wave basis (CASTEP). It was indicated that these gas molecules can be identified as physisorption. Although, the results agree well with the experiments[7,8], however, it is still no clear explanation for the adsorption on the size and the chirality of tube. In addition, the theoretical investigation of other small gas molecules *e.g.*, NH_3, N_2, O_2, H_2 and CH_4, are also needed for gas sensor development.

The present study aims to investigate the behaviorof gases *i.e.*, O_2 and H_2 molecules on a pristine (6,6) SWCNT and modified SWCNT at microscopic level. The quantum chemical calculations with ONIOM (our own N-layered Integrated molecular orbital and molecule mechanics) method has been applied[9].

CALCULATIONS DETAILS

The (6,6) SWCNT was selected and constructed with the length of about 7 Å and the diameter of 8 Å. The tips of

SWCNT were terminated by hydrogen atoms, NH_3^+ and COO- for uncharged, positive charged (CNT^+) and negative charged (CNT^-) carbon nanotube, respectively. The positions of gas molecule were located at 5 different points shown in Fig. 1. The geometry optimizations were conducted to find the optimum structure at each position. The possible orientations of each gas, shown in Fig. 2, were placed as a starting structure for each geometry optimizations.

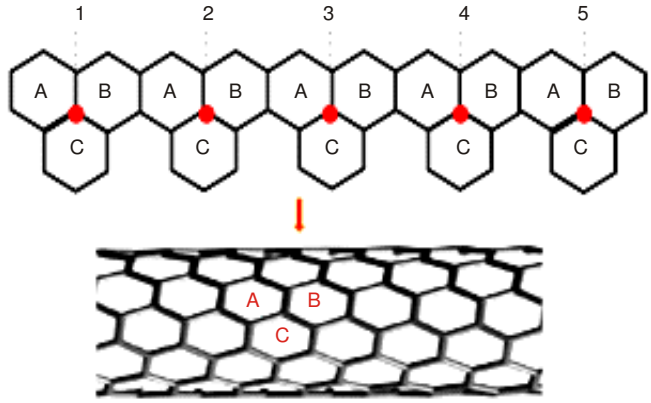

Fig. 1. Illustration of five different points of all kinds of carbon nanotubes for gas interactions

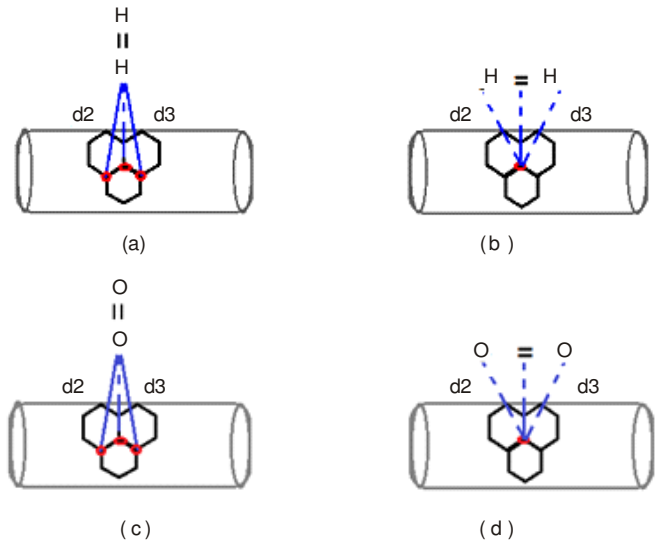

Fig. 2. Possible orientations of H_2 (2a &2b) and O_2 (2c & 2d). The d1, d2 and d3 are distances between gas molecule and carbon nanotube

The geometry optimizations and the energy calculations have been carried out using the ONIOM(M06/6-31G(d):HF/3-21G) calculations with basis set superposition error (BSSE) correction. ONIOM method is proposed to save the computational effort for large systems and has been successfully used in many molecular systems[10-12]. An important small region is treated by the high level of calculation, so-called "model part" and a larger region is treated by the lower accurate calculation, so-called "real part" (Fig. 3). The ONIOM energy (ΔE_{ONIOM}) can be estimated from eqn. 2, which contains three energy terms.

$$\Delta E_{ONIOM} = \Delta E_{(real, low)} + \Delta E_{(model, high)} - \Delta E_{(model, low)} \quad (1)$$

where $\Delta E_{(real, low)}$ is the total energy for the "real part" using the low level of calculation. $\Delta E_{(model,high)}$ and $\Delta E_{(model, low)}$ are the total energies of the "model part" obtained from the high and low level methods, respectively.

The M06/6-31G(d) (called high level) and the HF/3-21G (called low level) methods were applied for "real" and "model" parts in eqn. 1. The GAUSSIAN09 package[13] has been used for all calculations. The binding energies were then calculated as eqn. 2:

$$\Delta E_{bind} = \Delta E_{gas\text{-}CNT} - \Delta E_{CNT} - \Delta E_{gas} \quad (2)$$

where ΔE_{bind} is the binding energy, $\Delta E_{gas\text{-}CNT}$ is the gas-CNT complex energy, ΔE_{gas} the gas energy and ΔE_{CNT} is the carbon nanotube energy.

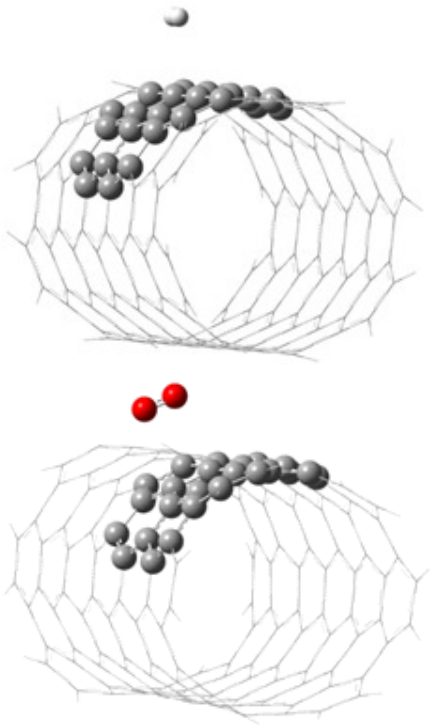

Fig. 3. Model part (only atoms shown in ball-and-stick) and the real part (all atoms) for CNT-H_2 (a) and CNT-O_2 (b) complexes which were used in ONIOM calculations

RESULTS AND DISCUSSION

Binding energy between H_2 and all kinds of carbon nanotubes: The possible orientations of the H_2 molecule interacting to all kinds of carbon nanotubes would be two important features that are in horizontal and vertical direction. The results show that uncharged carbon nanotube does not like ($\Delta E > 0$) to bind with the H_2 molecule but the charged carbon nanotubes (CNT^+ and CNT^-) prefer to bind with H_2 molecule. It appears that H_2 molecule binding with CNT^+ in the vertical direction is the most favorable because the average binding energy is equal to -18.5 ± 4.4 kcal/mol. Although, the average binding energy between H_2 molecule with CNT^- in the vertical is -19.9 ± 7.0 kcal/mol, its standard deviation is greater than the standard deviation of H_2 molecule binding with CNT^+ in the vertical direction. While, the H_2 molecule binding with CNT^+ in the horizontal direction (ΔE = -10.8 ± 5.8 kcal/mol) is also better than in the vertical direction (ΔE =

-7.6 ± 5.3 kcal/mol). Therefore, the binding between H_2 and CNT^+ in any direction is the most favorable among other type of carbon nanotube.

The distances and binding energy for each point between H_2 molecule and all carbon nanotubes are shown in Tables 1-6.

TABLE-1
ALL DISTANCES AND BINDING ENERGY FOR EACH POINT BETWEEN H_2 MOLECULE IN HORIZONTAL DIRECTION AND CARBON NANOTUBE

Carbon nanotube interacts H_2 in horizontal direction				
Point	d1	d2	d3	ΔE ONIOM (kcal/mol)
1	2.3	34.03	32.10	20.82
2	2.3	31.13	30.00	17.19
3	2.3	33.10	32.00	33.54
4	2.3	33.2	31.61	22.15
5	2.3	33.00	31.04	15.95

TABLE-2
ALL DISTANCES AND BINDING ENERGY FOR EACH POINT BETWEEN H_2 MOLECULE IN VERTICAL DIRECTION AND CARBON NANOTUBE

Point	d1	d2	d3	ΔE ONIOM (kcal/mol)
1	2.3	33.00	31	5.18
2	2.3	33.12	31	13.00
3	2.3	33.20	32	38.00
4	2.3	32.91	32	37.10
5	2.3	34.10	33	14.68

TABLE-3
ALL DISTANCES AND BINDING ENERGY FOR EACH POINT BETWEEN H_2 MOLECULE IN HORIZONTAL DIRECTION AND CNT^+

CNT^+ interacts H_2 in horizontal direction				
Point	d1	d2	D3	ΔE ONIOM (kcal/mol)
1	2.3	35.0	35.20	-4.03
2	2.3	35.0	33.30	-19.64
3	2.3	35.0	34.61	-10.76
4	2.3	33.2	34.20	-11.99
5	2.3	33.2	33.40	-7.61

TABLE-4
ALL DISTANCES AND BINDING ENERGY FOR EACH POINT BETWEEN H_2 MOLECULE IN VERTICAL DIRECTION AND CNT^+

CNT^+ interacts H_2 in vertical direction				
Point	d1	d2	d3	ΔE ONIOM (kcal/mol)
1	2.3	34.02	33.10	-17.94
2	2.3	32.80	31.00	-22.05
3	2.3	35.31	34.40	-17.37
4	2.3	35.13	34.30	-12.03
5	2.3	36.00	34.33	-22.97

TABLE-5
ALL DISTANCES AND BINDING ENERGY FOR EACH POINT BETWEEN H_2 MOLECULE IN HORIZONTAL DIRECTION AND CNT^-

CNT^- interacts H_2 in horizontal direction				
Point	d1	d2	d3	ΔE ONIOM (kcal/mole)
1	2.3	33.32	34.51	-6.04
2	2.3	33.04	32.41	-14.74
3	2.3	33.64	33.91	-0.38
4	2.3	33.30	33.20	-6.55
5	2.3	34.00	34.00	-10.16

TABLE-6
ALL DISTANCES AND BINDING ENERGY FOR EACH POINT BETWEEN H_2 MOLECULE IN VERTICAL DIRECTION AND CNT^-

CNT^- interacts H_2 in vertical direction				
Point	d1	d2	d3	ΔE ONIOM (kcal/mol)
1	2.3	33.34	33.1	-22.04
2	2.3	32.00	32.0	-29.11
3	2.3	34.10	34.0	-10.67
4	2.3	33.10	32.3	-15.58
5	2.3	33.30	33.2	-22.12

Binding energy between O_2 and all kinds of carbon nanotubes: The possible orientations of the O_2 molecule interacting to all kinds of carbon nanotubes would be two important features that are in horizontal and vertical direction as well as H_2 molecule. The results show that charged carbon nanotubesboth of CNT^+ and CNT^- do not like ($\Delta E > 0$) to bind with the O_2 molecule but the uncharged carbon nanotube prefers to bind with O_2 molecule for both direction. It appears that O_2 molecule binding with carbon nanotube in the vertical direction is the most favorable because the average binding energy is equal to -48.3 ± 6.4 kcal/mol. While, the O_2 molecule binding with carbon nanotube in the horizontal direction has the average binding energy as -44.5 ± 21.7 kcal/mol). Therefore, the binding between H_2 and carbon nanotube in vertical direction is the most favorable among other type of carbon nanotube.

The distances and binding energy for each point between O_2 molecule and all carbon nanotubes are shown in Tables 7-12.

Conclusion

The present study has investigated the optimum orientation of binding between small gases (O_2 and H_2) and all kinds of carbon nanotubes (CNT, CNT^+, CNT^-) using quantum calculations. ONION method was used to calculate the binding energy and optimum structures for all complexes. The results

TABLE-7
ALL DISTANCES AND BINDING ENERGY FOR EACH POINT BETWEEN O_2 MOLECULE IN HORIZONTAL DIRECTION AND CARBON NANOTUBE

Carbon nanotube interacts O_2 in horizontal direction				
Point	d1	d2	d3	ΔE ONIOM (kcal/mol)
1	2.3	32.20	32.00	-10.71
2	2.3	32.00	30.02	-60.62
3	2.3	32.00	34.82	-59.15
4	2.3	30.92	30.63	-57.58
5	2.3	33.20	31.00	-34.28

TABLE-8
ALL DISTANCES AND BINDING ENERGY FOR EACH POINT BETWEEN O_2 MOLECULE IN VERTICAL DIRECTION AND CARBON NANOTUBE

Carbon nanotube interacts O_2 in vertical direction				
Point	d1	d2	d3	ΔE ONIOM (kcal/mol)
1	2.3	33.30	32.00	-46.40
2	2.3	33.30	32.00	-58.53
3	2.3	33.30	32.00	-41.64
4	2.3	32.81	31.52	-45.41
5	2.3	34.21	33.20	-49.54

TABLE-9
ALL DISTANCES AND BINDING ENERGY FOR EACH POINT BETWEEN O_2 MOLECULE IN HORIZONTAL DIRECTION AND CNT^+

CNT^+ interacts O_2 in horizontal direction				
Point	d1	d2	d3	ΔE ONIOM (kcal/mol)
1	2.3	34.00	35.00	34.91
2	2.3	34.14	34.30	33.85
3	2.3	34.00	34.92	30.83
4	2.3	32.63	34.11	32.68
5	2.3	33.61	34.30	30.38

TABLE-10
ALL DISTANCES AND BINDING ENERGY FOR EACH POINT BETWEEN O_2 MOLECULE IN VERTICAL DIRECTION AND CNT^+

CNT^+ interacts O_2 in vertical direction				
Point	d1	d2	d3	ΔE ONIOM (kcal/mol)
1	2.3	33.81	31.80	27.64
2	2.3	33.73	32.40	28.65
3	2.3	35.30	33.52	27.76
4	2.3	32.00	31.00	26.31
5	2.3	34.10	33.00	27.53

TABLE-11
ALL DISTANCES AND BINDING ENERGY FOR EACH POINT BETWEEN O_2 MOLECULE IN HORIZONTAL DIRECTION AND CNT^-

CNT^- interacts O_2 in horizontal direction				
Point	d1	d2	d3	ΔE ONIOM (kcal/mol)
1	2.3	32.64	34.12	87.96
2	2.3	38.10	38.00	103.77
3	2.3	33.43	34.20	93.15
4	2.3	34.00	34.14	105.76
5	2.3	33.30	33.90	82.65

TABLE-12
ALL DISTANCES AND BINDING ENERGY FOR EACH POINT BETWEEN O_2 MOLECULE IN VERTICAL DIRECTION AND CNT^-

CNT^- interacts O_2 in vertical direction				
Point	d1	d2	d3	ΔE ONIOM (kcal/mole)
1	2.3	34.00	33.34	87.98
2	2.3	33.30	33.24	95.06
3	2.3	34.22	34.00	97.3
4	2.3	32.94	34.00	106.15
5	2.3	33.30	33.40	87.23

show that binding between CNT^+ and H_2 molecule is the most favorable among other type of carbon nanotubes. In addition, binding between CNT^+ and H_2 molecule in vertical direction is better than the horizontal direction. For the binding between all type of carbon nanotubes and O_2 molecule, it appears that uncharged carbon nanotube prefers to bind with O_2 molecule rather than the other type of carbon nanotubes. Moreover, this binding likes the vertical direction better than horizontal. Therefore, our study would suggest that O_2 gas sensor can use the uncharged carbon nanotube that will be good enough. While, the H_2 gas sensor needs to use the CNT^+ as the material.

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