Structure and Electronic Properties of "DNA-Gold-Nanotube" Systems : A Quantum Chemical Analysis

P. Pannopard[a,b], J. Sirijaraensre[a,b], S. Nokbin[a,b], P. Khongpracha[a,b], J. Limtrakul[a,b*]

[a]Laboratory for Computational & Applied Chemistry, Chemistry Department, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand
[b]Center of Nanotechnology, Kasetsart University Research and Development Institute, Kasetsart University, Bangkok 10900, Thailand
Phone: +66-294-28900 ext. 304, Fax: +66-294-28900 ext. 324 E-mail: fscijrl@ku.ac.th

ABSTRACT

The development of a novel DNA sensor is a crucial issue in the diagnosis of pathogenic and genetic diseases. We use the Density Functional Theory (DFT) to investigate the DNA sensor performance of hybrid structures of a gold atom (Au) deposited on two types of single-walled carbon nanotubes: armchair SWCNT(8,0)/Au and zigzag SWCNT (5,5)/Au and compare these with bare Au. We also choose adenine:thymine(A:T) to represent the base pair in the DNA double helix. The hybrid systems, "SWNCTs/Au", exhibit more stability and sensitivity, this is originated from the co-function of gold, acts as a powerful electron withdrawing group and SWNCTs, act as electron collecting centers. With Mulliken population analysis, it is found that the "SWCNTs/Au" can amplify the electronic signal better than the bare gold atom by at most four times when forming with the A:T complex. Therefore, the "SWCNTs/Au" systems could be the potential candidate for a nanostructure-based DNA sensor.

Keywords: DNA sensor, single-walled carbon nanotube, gold atom, adenine: thymine base pair

1 INTRODUCTION

The idea of chemical sensing based on molecular recognition is considered as one of the most promising concepts for single-molecule detection, even though it still remains in an early developmental stage. The approach requires probes which hold a specific recognition of desired chemical species and a transduction ability of that recognition incident into a quantitative response signal. Due to those indispensable functions, this concept is very versatile for the fabrication of a chemical sensing probe that integrates both recognition and transduction moieties into a single molecular assembly. The scheme has been examined in various disciplines, especially for a nature imitated detection of specific DNA sequences[1-2]. The exclusive properties of gold nanoparticles (Au NPs) are high sensitivity, electrical conductivity, size-dependent optical capability and affinity to the biomolecules [3-6]. The recent experimental and theoretical studies reported that adenine base has the highest affinity with gold particles [7] and it preferentially binds to a nitrogen atom at the N7 position [8]. Furthermore, there is considerable interest in applying carbon nanotubes (CNTs) [9-10] that possess fascinating structural, chemical, mechanical and electrical manners as charge-transport centers for electronic transducers [11-18]. Hence, several experimental researches had focused on the deposition of Au NPs onto CNTs [19-21] and there is more and more attraction to exploit a compatible assembly of them as the nanoscale building-blocks of DNA detection [22]. Nevertheless, there is a lack of theoretical study on the entire system, which is the combination of Au NPs, CNTs and DNA molecules.

Accordingly, it is the objective of this current work, to investigate the modulation of adenine-thymine (A:T) hybridization under the interaction with the hybrid structure of a neutral gold atom acting as the reactive sites for anchoring of the DNA bases and both types of single-walled carbon nanotubes (SWCNTs), zigzag (8,0) and armchair (5,5), to be electron transfer supports. Finally, the system's electronic responses are observed.

2 COMPUTATIONAL METHOD

All the calculations were performed at the density functional theory with the Perdew, Burke and Ernzerhof (PBE) non-local generalized gradient functional [23]. Two different Dunning's correlation consistent polarized valence basis sets were employed, cc-pVDZ for SWCNTs and cc-pVTZ, for the A:T base pair moiety. For the Au atom, core electrons were represented by a relativistic corrected effective core potential (ECP), whereas 19 valence electrons were treated explicitly by (7s6p5d)/[6s3p2d] contraction. All fully relaxed optimization processes were done using the Turbomole 5.7 code [24]. With the intention of reducing the computational time without sacrificing accuracy, the coulomb interactions were efficiently treated by resolution of the identity (RI) technique [25].

Our chemical model systems are divided into four subsystems: a SWCNT, a gold atom (Au) and the two bases (A,T). Each term of binding energy is determined as follows

$$E_b(\text{SWCNT/Au/A} \cdots \text{T}) = E(\text{SWCNT/Au/A:T})$$
$$- E(\text{SWCNT/Au/A}) - E(\text{T}) \quad (1)$$

$$E_b(\text{SWCNT/Au} \cdots \text{A:T}) = E(\text{SWCNT/Au/A:T})$$
$$- E(\text{SWCNT/Au}) - E(\text{A:T}) \quad (2)$$

$$E_b(\text{SWCNT} \cdots \text{Au/A:T}) = E(\text{SWCNT/Au/A:T})$$
$$- E(\text{SWCNT}) - E(\text{Au/A:T}) \quad (3)$$

$$E_{tb}(\text{SWCNT} \cdots \text{Au} \cdots \text{A} \cdots \text{T}) = E(\text{SWCNT/Au/A:T})$$
$$- E(\text{SWCNT}) - E(\text{Au})$$
$$- E(\text{A}) - E(\text{T}) \quad (4)$$

E_b is defined as the binding energy between two subsystems in a complex separated by dot-line in the parentheses.

E_{tb} is defined as the total binding energy of all subsystems.

E is defined as the total energy of each subsystem or complexe.

3 RESULTS AND DISCUSSION

3.1 Structures

For revealing the effects of the gold atom on the A:T base pair, Figure 1 shows optimized geometrical parameters in the double hydrogen bonds region of A:T base pair complexes. It is noted that the gold atom causes a weaker N3-H3$\cdots$N1 hydrogen bond, and is even much weaker when the gold atom is attached on a sidewall of the SWCNT. The distances between N3 and N1 in the N3-H3$\cdots$N1 hydrogen bond are 2.82, 2.84, 2.86 and 2.85 Å for A:T, Au/A:T, SWCNT(8,0)/Au/A:T and SWCNT(5,5)/Au/A:T systems, respectively. However, the findings in the O4-H6′$\cdots$N6 hydrogen bond are in an opposite way to that in the N3-H3$\cdots$N1 one. The O4$\cdots$N6 distance is shortened from 2.88 Å to 2.87, 2.83 and 2.84 Å via interactions of the base pair with Au, SWCNT(8,0)/Au and SWCNT(5,5)/Au, respectively. Surprisingly, in all complexes, the A:T base pairs always arrange in a perpendicular direction to the SWCNTs alignments even though the Cs symmetry constraint was not applied (cf. Figure 2). Moreover, the adenine base remained connected to the gold atom deposited on SWCNT via the interaction at the N7 anchor point, asserting the most favorable binding site [26].

Figure 2 shows intermolecular distances, binding energies and Mulliken charges for all complexes in this study. It should undoubtedly be observed that the most sensitive geometrical parameters due to an assembling of the base pair, gold atom and SWCNT are Au10-N7 and Au10-C11 bonds. The Au10-N7 bonds are obviously contracted from 2.26 Å in Au/A to 2.14 Å in both SWCNT(8,0)/Au/A and SWCNT(5,5)/Au/A complexes. The interactions of thymine with adenine do not alter the Au10-N7 bond in all cases. Similar results are found for the Au10-C11 bond, the interactions of A or A:T cause the Au10-C11 bond to shorten from 2.18 Å to around 2.12 Å in both SWCNT(8,0)/Au and SWCNT(5,5)/Au systems. These findings refer to an effectiveness of the integration between SWCNTs and gold particles for being a steady probe because it enhances an immobilization of the recognition layer via a cooperative effect of SWCNTs, gold particles and DNA base compartments.

3.2 Energetics

The comparisons of binding and total binding energies are shown in Figure 2. It is found that most of the binding energies exhibited correspond with the bond length modulations. The interactions of A:T base pairs are weakened from 16.4 kcal/mol to 15.8, 15.5 and 16.0 kcal/mol for Au/A:T, SWCNT(8,0)/Au/A:T and SWCNT(5,5)/Au/A:T complexes, respectively. The minute destabilization of the base pair can be justified by a counter balance between a weakening of N3-H3$\cdots$N1 bond and a strengthening of O4-H6′$\cdots$N6 bond in the A:T base pair.

It should be noted that both types of SWCNTs improve the strength of the interaction between the gold atom and the base pair. In comparison to the Au/A:T complex, the binding energies between the gold atom and the base pair are increased by 4.9 kcal/mol in the SWCNT(8,0)/Au/A:T complex and by 8.6 kcal/mol in the SWCNT(5,5)/Au/A:T complex. Likewise, the interaction between the gold atom and the SWCNT is increased after interacting with the base pair, the magnitude of $E_b(\text{SWCNT} \cdots \text{Au/A:T})$ is increased by 4.9 and 8.6 kcal/mol as in SWCNT(8,0)/Au/A:T and SWCNT(5,5)/Au/A:T complexes respectively, when compared with the SWCNT/Au system. Overall, for binding energy analysis, it could be mentioned that the energy characteristics of SWCNT(8,0)/Au/A:T complexes quite resemble the SWCNT(5,5)/Au/ A:T complex.

3.3 Electronic Responses

The Mulliken population analysis is shown in Figure 2. It also demonstrates the directions of electron flow within the SWCNTs/Au/A:T complexes. The interaction of Au and SWCNT with the A:T base pair causes the electron loss in the adenine molecule (more positive charge) consequently, it retards the electron transfer from the adenine to thymine molecule (less negative charge). This phenomenon can be explained by intrinsic electron withdrawing properties of the gold atom as well as outstanding charge transport characteristics of SWCNTs. These manners are emphasized by negative charges of the gold atom and SWCNT after binding with the adenine base. Especially for the Au atom, it not only performs as a good linker but also enhances the electron transfer from the adenine base to SWCNT, which leads to an electron loss on Au and Adenine by 0.12 a.u. and 0.27 a.u., respectively and an electron gaining on SWCNT by -0.39 a.u. in both types of the SWCNTs/Au/A complexes.
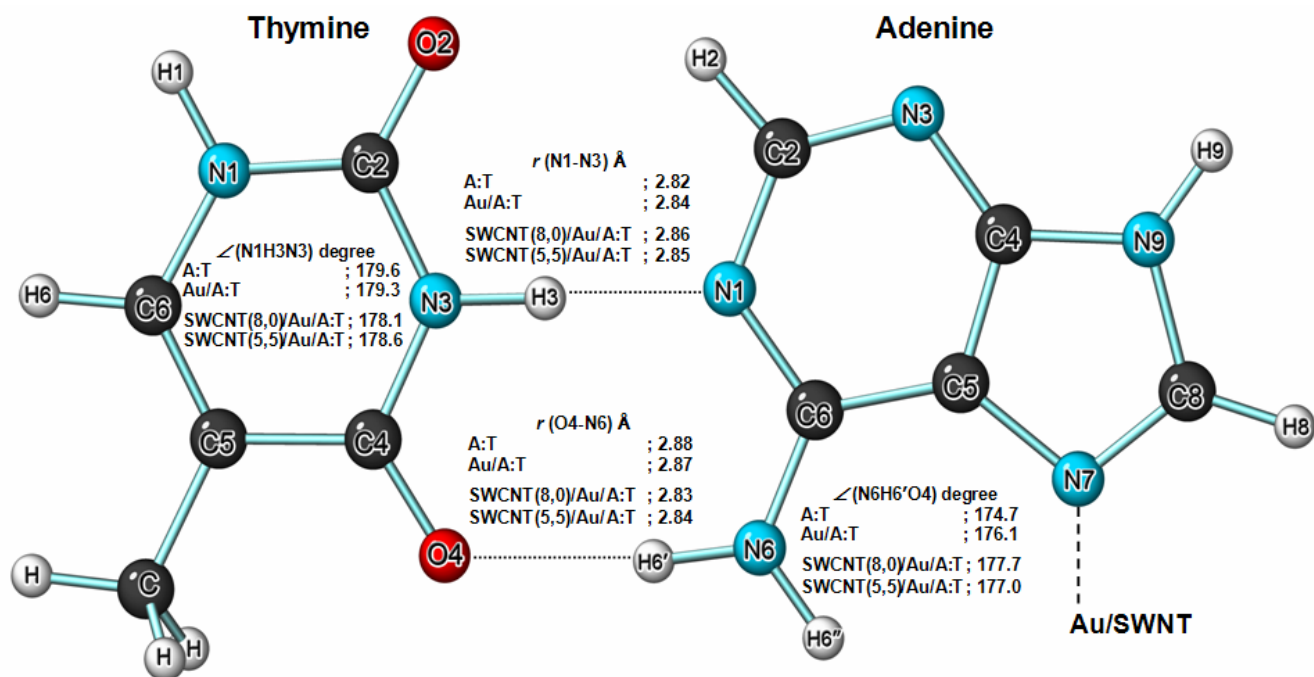
Figure 1

Thymine

H1 — N1 — C2 — O2
H6 — C6 — N3 — H3
C5 — C4
C — H, H, H
O4

r (N1-N3) Å
A:T ; 2.82
Au/A:T ; 2.84
SWCNT(8,0)/Au/A:T ; 2.86
SWCNT(5,5)/Au/A:T ; 2.85

∠(N1H3N3) degree
A:T ; 179.6
Au/A:T ; 179.3
SWCNT(8,0)/Au/A:T ; 178.1
SWCNT(5,5)/Au/A:T ; 178.6

r (O4-N6) Å
A:T ; 2.88
Au/A:T ; 2.87
SWCNT(8,0)/Au/A:T ; 2.83
SWCNT(5,5)/Au/A:T ; 2.84

∠(N6H6'O4) degree
A:T ; 174.7
Au/A:T ; 176.1
SWCNT(8,0)/Au/A:T ; 177.7
SWCNT(5,5)/Au/A:T ; 177.0

Adenine

H2 — C2 — N3
N1 — C4 — N9 — H9
C6 — C5 — C8 — H8
N6 — N7
H6' H6"

Au/SWNT

Figure 1: Geometrical parameters at the Adenine-Thymine base pair in the A:T, Au/A:T, SWCNT(8,0)/Au/A:T and SWCNT(5,5)/Au/A:T complexes.

Figure 2

Thymine   Adenine

r (N7-Au10) Å
Au/A ; 2.26
Au/A:T ; 2.26
SWCNT(8,0)/Au/A ; 2.14
SWCNT(8,0)/Au/A:T ; 2.14
SWCNT(5,5)/Au/A ; 2.14
SWCNT(5,5)/Au/A:T ; 2.14

E_b (SWCNT/Au···A:T) kcal/mol
Au/A ; 14.1
Au/A:T ; 13.4
SWCNT(8,0)/Au/A ; 19.2
SWCNT(8,0)/Au/A:T ; 18.3
SWCNT(5,5)/Au/A ; 22.4
SWCNT(5,5)/Au/A:T ; 22.0

r (Au10-C11) Å
SWCNT(8,0)/Au ; 2.18
SWCNT(8,0)/Au/A ; 2.11
SWCNT(8,0)/Au/A:T ; 2.12
SWCNT(5,5)/Au ; 2.18
SWCNT(5,5)/Au/A ; 2.12
SWCNT(5,5)/Au/A:T ; 2.12

E_b (SWCNT···Au/A:T) kcal/mol
SWCNT(8,0)/Au ; 23.1
SWCNT(8,0)/Au/A ; 28.2
SWCNT(8,0)/Au/A:T ; 28.0
SWCNT(5,5)/Au ; 21.5
SWCNT(5,5)/Au/A ; 29.9
SWCNT(5,5)/Au/A:T ; 30.1

E_b (SWCNT/Au/A···T) kcal/mol
A:T ; 16.4
Au/A:T ; 15.8
SWCNT(8,0)/Au/A:T; 15.5
SWCNT(5,5)/Au/A:T; 16.0

q_M (A & T) a.u.
A:T ; 0.046 & -0.046
Au/A ; 0.170
Au/A:T ; 0.204 & -0.032
SWCNT(8,0)/Au/A ; 0.276
SWCNT(8,0)/Au/A:T; 0.291 & -0.010
SWCNT(5,5)/Au/A ; 0.271
SWCNT(5,5)/Au/A:T; 0.295 & -0.017

E_{tb} (SWCNT···Au···A···T) kcal/mol
SWCNT(8,0)/Au ; 23.1
SWCNT(8,0)/Au/A ; 42.3
SWCNT(8,0)/Au/A:T; 57.8
SWCNT(5,5)/Au ; 21.5
SWCNT(5,5)/Au/A ; 44.0
SWCNT(5,5)/Au/A:T; 60.0

q_M (Au) a.u.
Au/A ; -0.170
Au/A:T ; -0.172
SWCNT(8,0)/Au/A ; 0.123
SWCNT(8,0)/Au/A:T; 0.128
SWCNT(5,5)/Au/A ; 0.122
SWCNT(5,5)/Au/A:T; 0.122

q_M (SWCNT) a.u.
SWCNT(8,0)/Au ; -0.005
SWCNT(8,0)/Au/A ; -0.399
SWCNT(8,0)/Au/A:T; -0.408
SWCNT(5,5)/Au ; 0.005
SWCNT(5,5)/Au/A ; -0393
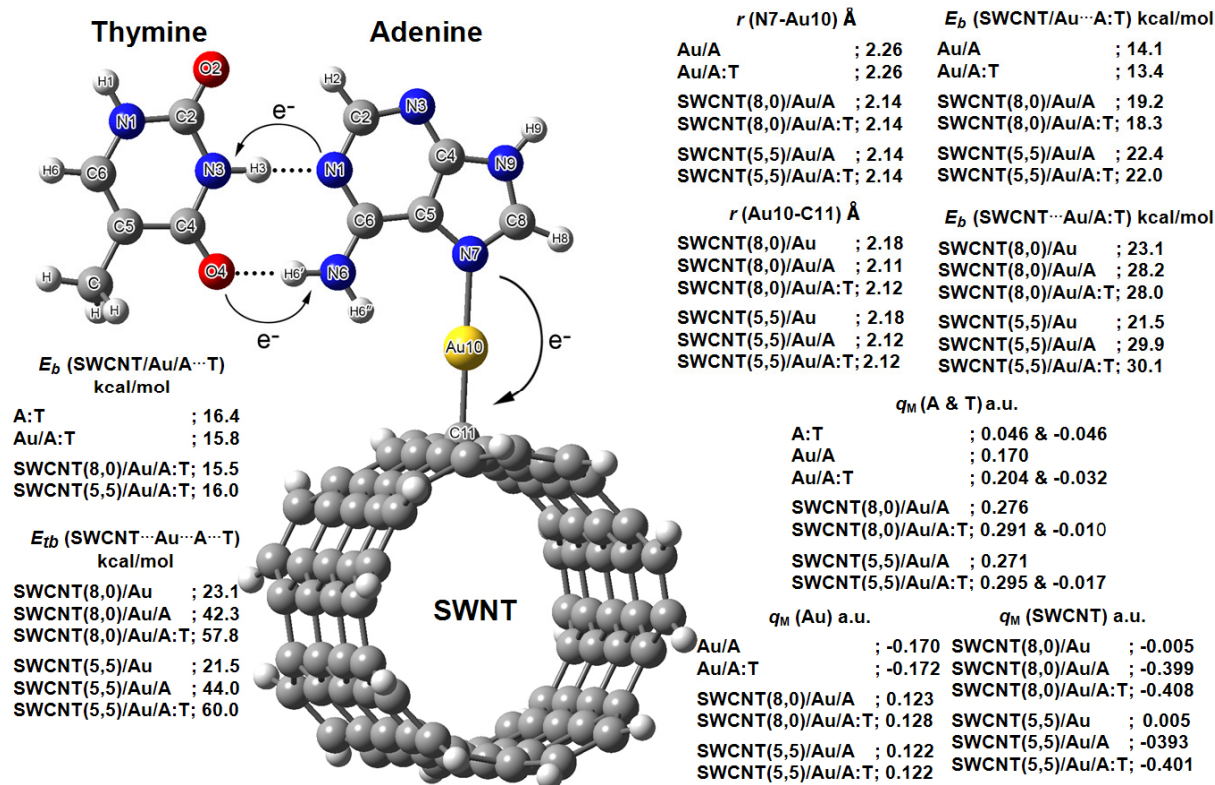SWCNT(5,5)/Au/A:T; -0.401

SWNT

Figure 2: Intermolecular distances, binding energies and Mulliken charges for adenine, thymine, gold atom and carbon nanotubes in the A:T, Au/A:T, SWCNT(8,0)/Au/A:T and SWCNT(5,5)/Au/A;T complex

For the electronic communication aspect, the DNA sensor probes (SWCNT/Au/A) can provide the electronic responses after the hybridization with the thymine molecule which can be elucidated from the modulation of SWCNT/Au charges in SWCNT/Au/A and SWCNT/Au/A:T. The charge alterations which represent the amount of sensor signals are defined as follows

$$\Delta q_{Msensor}(Au) =$$
$$q_M(Au) \text{ in } [Au/A:T] - q_M(Au) \text{ in } [Au/A] \quad (5)$$

$$\Delta q_{Msensor}(SWCNT/Au) =$$
$$q_M(SWCNT/Au) \text{ in } [SWCNT/Au/A]$$
$$- q_M(SWCNT/Au) \text{ in } [SWCNT/Au/A] \quad (6)$$

The $\Delta q_{Msensor}(SWCNT(8,0)/Au)$ and $\Delta q_{Msensor}(SWCNT(5,5)/Au)$ are evaluated to be -0.004 a.u. and -0.008 a.u., respectively while the $\Delta q_{Msensor}(Au)$ is just -0.002 a.u. Therefore, the SWCNT/Au integrated probe has greater efficiency to amplify the electronic signal than the bare gold atom.

4 CONCLUSION

By performing the DFT calculation on complexes of SWCNT/Au/A:T with both SWCNT(8,0) and SWCNT(5,5) and their sub systems, the overall outcomes are guiding us to conclude that the SWCNT/Au hybrid structure has a superior sensor performance to the conventional gold probe due to the electron gaining characteristics of the alternative integrated materials. The electron withdrawing property of SWCNT/Au and the Au atom causes a contraction of the N3-H3$\cdots$N1 hydrogen bond and a stretching of O4-H6$'\cdots$N6 one. However, these hydrogen bond alterations are insufficient to cause the A:T base pair destabilization. The present study is intended to provide useful information that can be applied to developing the SWCNT as a novel candidate in a DNA detector)

ACKNOWLEDGMENT

REFERENCES

[1] Z. Junhui, C. Hong and Y. Ruifu, Biotechnol. Adv., 15(1), 43-58, 1997.
[2] W. Vercoutere and M. Akeson, Curr. Opin. Chem. Biol., 6, 816–822, 2002.
[3] C. T. Natalia, and Z. Gao, Nanotoday, 1, 28-37, 2006.
[4] K.K. Jain, Drug Discovery Today, 10, 1435-1442, 2005.
[5] R. Shukla, V. Bansal, M. Chaudhary, A. Basu, R. R. Bhonde and M. Sastry, Langmuir, 21, 10644-10654, 2005.
[6] J. Riu, A. Maroto and F. X. Rius, Talanta 69, 288–301, 2006.
[7] H. Kimura-Suda, D.Y. Petrovykh, M. J. Tarlov and L. J. Whitman, J. Am. Chem. Soc., 125, 9014-9015, 2003.
[8] E.S. Kryachko and F. Remacle, J. Phys. Chem. B, 109(48), 22746-22757, 2005.
[9] C. Warakulwit, S. Bamrungsap, P. Luksirikul, P. Khongpracha and J. Limtrakul, Stud. Surf. Sci. Catal., 156, 823-828, 2005.
[10] S. Namuangruk, P. Khongpracha and J. Limtrakul, J. Mol. Grap. Model., In press.
[11] J. Wang, G. Liu, M. R. Jan and Qiyu Zhu, Electrochem. Commun., 5, 1000–1004, 2003.
[12] H. Cai, X. Cao, Y. Jiang, P. He and Y. Fang, Anal Bioanal Chem, 375, 287–293, 2003.
[13] J. Wang, G. Liu and M. R. Jan, J. Am. Chem. Soc. ,126, 3010-3011, 2004.
[14] H. Gao and Y. Kong, Annu. Rev. Mater. Res. ,34, 123–50, 2004.
[15] A. Merkoc, M. Pumera, X. Llopis, B. Perez, M. D. Valle and S. Alegret, TrAC, Trends Anal. Chem., 24(9), 826-838, 2005.
[16] L. Patolsky and C. M. Lieber, Materialstoday, 20-28, 2005.
[17] M. Valcarcel, B.M. Simonet, S. Cardenas and B.Suarez, Anal Bioanal Chem, 382, 1783–1790. 2005.
[18] C. Song, Y.Xia, M. Zhao, X. Liu, F. Li and B. Huang, Chem. Phys. Lett., 415, 183–187, 2005.
[19] L. Liu, T. Wang, J. Li, Z.X. Guo, L. Dai, D. Zhang and D. Zhu, Chem. Phys. Lett., 367, 747–752, 2003.
[20] L. Jiang and L. Gao, Carbon, 41, 2923–2929, 2003.
[21] X. Maa, X. Li, N. Lunb and S. Wen, Mater. Chem. Phys., 97, 351–356, 2006.
[22] S.H. Lim, J. Wei and J. Lin, Chem. Phys. Lett., 400, 578–582, 2004.
[23] J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 77, 3865–3868, 1996.
[24] R. Ahlrichs, M. Bär, H. Horn and C. Kölmel, Chem. Phys. Lett., 162, 165, 1989.
[25] K. Eichkorn, O. Treutler, H. Öhm, M. Häser and R. Ahlrichs, Chem. Phys. Lett., 242, 652, 1995.
[26] E. Durgun, S. Dag, V. M. K. Bagci, O. Gulseren, T. Yildirim, and S. Ciraci1, Phys. Rev. B, 67, 201401(R), 2003.