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INTERACTION OF AMINO ACIDS WITH SINGLE WALLED CARBON NANOTUBE: A QUANTUM MECHANICAL STUDY

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ABSTRACT

In the present study, the interaction of Aromatic amino acids with zig-zag Single Walled Carbon Nanotube CNT(12,0) is investigated using density of functional theory. It is found that among the four aromatic amino acid such as histidine, phenylalanine, tyrosine, tryptophan considered for the study, tryptophan has the strongest binding energy in the interior position of SWCNT than in the exterior position. The HOMO-LUMO energy gap of the complex molecular structure has been explored by B3LYP/6-31G* method before and after interaction. This work revealed that the HUMO-LUMO energy gap of the complex molecular structure with B3LYP/6-31G* method are in good agreement with the other theoretical studies. Our results are expected to serve useful insight to comprehend the binding affinity of the aromatic amino acid with zig zag CNT.

Keywords **–** DFT,Aromatic amino acids, single walled carbon nanotube, noncovalent interaction, CNT based biosensors.

1. INTRODUCTION

Carbon nanostructures (CNSs) such as graphene and carbon nanotube are one of the most important materials in the field of recent research in nano sensors. The carbon nano-structures such as graphene and carbon nanotube have emerged as the promising nanomaterials for biomedical and environmental applications due to unique physical and chemical properties such as a tunable band gap, room temperature Hall effect, high mechanical strength (200 times greater than steel), and high elasticity , thermal conductivity and high entangle network structure. The exceptional electrical properties of graphene (such as, high charge mobility and capacity, highly tunable conductance) makes it as an ideal for sensing applications.[1,2,3] Carbon nanostructures (CNSs) exhibit the non-covalent interaction such as cation-π, π-π and CH-π towards the small molecules, metal ions and bio molecules as amino acid, nucleic acids. The noncovalent interaction of amino acids with various substrates and their proton affinity values have been studied.[4,5] The importance of aromatic amino acid for the interaction between a peptide and a single walled carbon nanotube has also been studied through experiment.[6] A recent experimental study revealed that π-π noncovalent interactions between CNTs and the aromatic residue (Trp, Phe, Tyr) of the proteins were found to play a significant role in determining the strength of the CNT-protein interaction.[7]Subramanium et al. have brought out new insight to study the interaction of CNT and peptides.[8,9,10,11] The interaction between these can be seen in figure1. The study of noncovalent carbonaceous materials play a vital role in understanding various carbon nanostructures, such as diagnosis of life threatening diseases (sensors), cancers therapy (drug delivery system), DNA sequencing (personalized medicines).[12,13,14] Developing sensors based on CNT-biomolecule composites for amplified detection methods is an area of recent interest, and such sensors can be

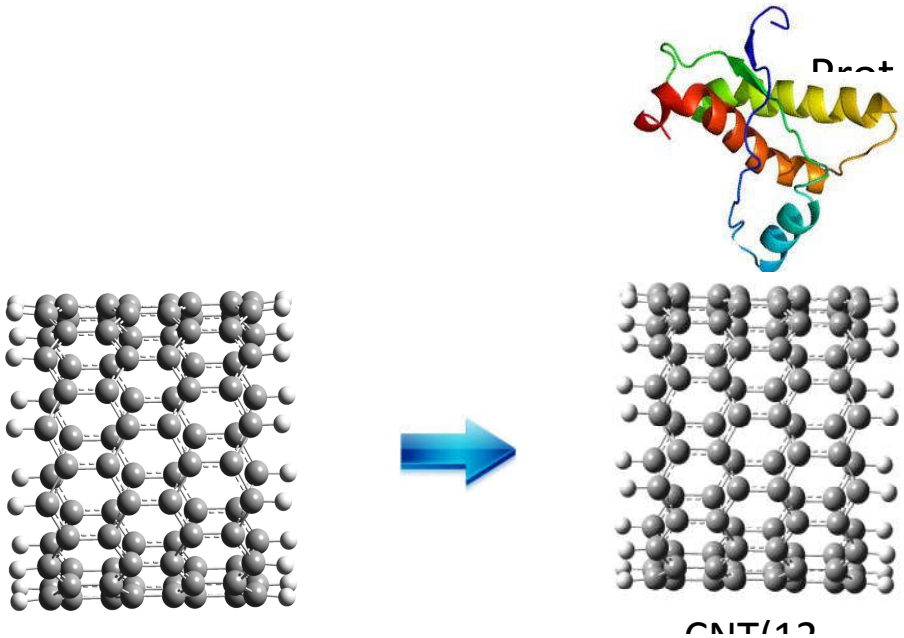
efficiently used for the detection of various carbon nanostructures as well as different biomaterials such as DNA, protein, and so on**.**[15]Umadevi et al. investigated the adsorption of biological molecules such as amino acids, enzymes, antibodies and nucleic acids, metal ions as Na^{+}, Ka^{+}, Ca^{+2}, Mg^{+2}, Be^{+2} and small molecules as CO_2, H_2O, CO, NH_3, H_2O, CH_4 on the surface of graphene/CNTs along with thesignificant changes in the energy as well as sensitivity and specificity of biosensor.[16-20] Wang et al.[21] carried out a study to understand the affinity of the specific peptides to CNTs and delineate contribution of the constituents of amino acids to the binding strength of the peptides with CNTs. Further the studies on the structure-function-affinity of the peptides with the CNT have shown that phenylalanine has an important role to play in enhancement of the adsorption of peptides on the CNTs**.**[22] Li et al. demonstrated that polytryptophan peptides bind more strongly through their aromatic rings with the CNTs compared to the polylysine**.**[23] However, the role of interaction of these bio molecules with the CNTs and the extent to which the nanotube can be used is not understood much for these biological systems. Other studies on the adsorption of polynuclear aromatic compounds to CNTs, suggest that the π-π interactions play a critical role in the binding strength towards the nanotubes.[24,25] Dai and co-workers have investigated the potential of carbon nanotube to be used as gas sensors for detection of molecules such as NO_2 and NH_3**.**[26]Schedin et al. reported their experimental observation that graphene – based sensors could detect even the adsorption of individual gas molecules**.**[27] Carbon nanostructures can absorb a number of species such as gas molecule, metal ions, polymers, organic molecules, and bio molecules such as proteins, nucleobases and DNA on their surfaceand these adsorption properties provide opportunities for potential industrial applications**.**[28-29] Several studies have been carried out on the immobilisation of proteins and nucleic acid on nanotube.[30,31,32] However recent studies elaborate on the appreciable changes in nanotube conductivity as bio molecules which are immobilised, directly or indirectly, on the CNT sidewalls.[33,34,35] Roman et al used DFT method to investigate the adsorption of any few amino acids on (3, 3) CNT.[36] In the present work detailed theoretical calculations has been done for interaction between aromatic amino acids and single walled carbon nanotube (CNT(12, 0)) using DFT method.

2. COMPUTATIONAL DETAILS

The calculations of the interaction between CNT and phenylalanine complex system was carried out using the density functional theory. The geometry of all the structures was optimized using B3LYP/6-31G* method for isolated individual structures as well as complex structures. In this study we calculated the binding energy of the complex system using the following equation (1).

$$\text{Binding Energy} = E_{CNT\_A} - E_{CNT} - E_{A} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

The binding energy is defined as the difference between the total energy of the isolated individual structures (E_{CNT} and E_{A}, CNT = carbon nanotube and A = amino acids) and the total energy of the CNT-Amino acid complex (E_{CNT_A}). All calculations were done using Gaussian 09 program suit. [37] The complex structures thus generated by placing amino acid parallel to the surface of SWCNT at a distance of 3Å. These complex structures was optimized using B3LYP method and 6-31G* basis set. We also calculated the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for the results thus obtained.



\Fig.1: The geometrical optimization of zigzag single walled carbon nanotube [CNT(12,0)] and representation of interaction of protein carbon nanotube.

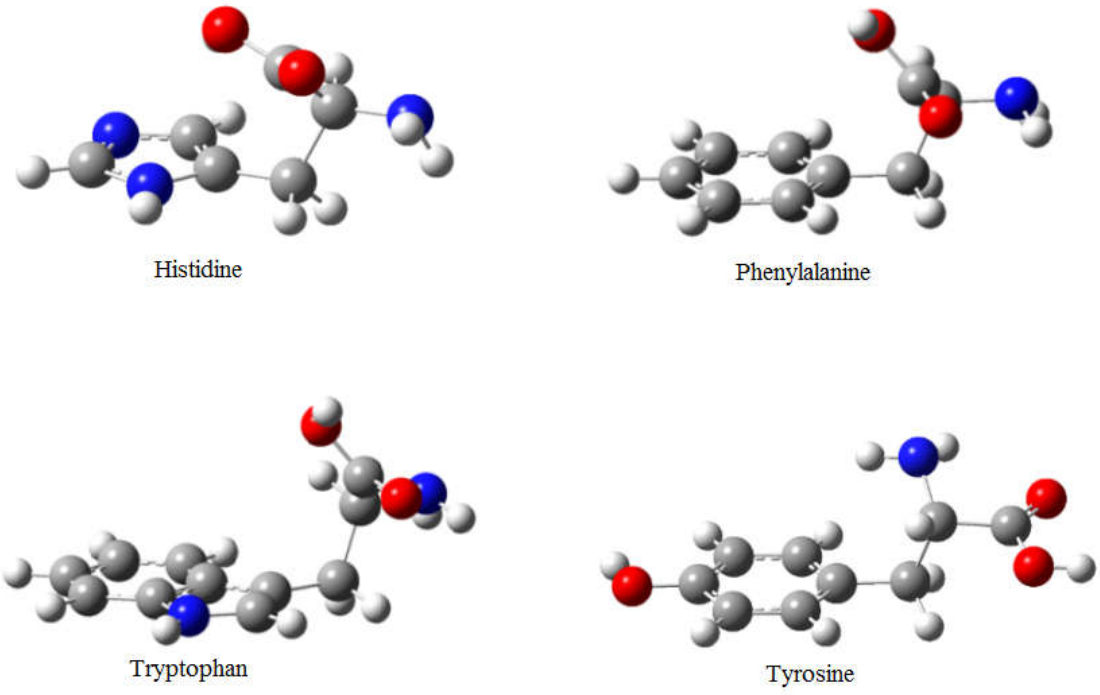


Fig. 2: The geometrical optimized geometry of aromatic amino acids.

3. RESULTS AND DISCUSSION

The optimized structure of aromatic amino acids and single walled carbon nanotube are shown in fig.1 and 2. The initial configurations of all four aromatic amino acid bases were assigned so that their aromatic rings are oriented exactly parallel to the CNT surface. The Fig 3 and Fig 4 shows the aromatic amino acid interaction in exterior and interior position of CNT (12,0). Aromatic amino acid is placed in two different positions i.e. inside the CNT and outside the CNT placed parallel to the surface of CNT at a distance of 3Å to make sure that π-π interaction takes place which plays a crucial role in the non-bonded interaction. The binding strength of all the aromatic amino acid in both the positions (i.e. interior and exterior) is found to bind with different affinity. The calculated binding energy of the aromatic amino acids such as histidine, phenylalanine, tyrosine and tryptophan in the exterior position of carbon nanotube is -7.952, -0.170, -0.649 and -0.791kcal/mole and interior position is -2.891, 4.656, 1.778 and 8.447 kcal/mole respectively. From these results it can observe that the binding strength for tryptophan is greater in interior position than in the exterior position of the CNT (12, 0). It is also observed that the binding energy of the aromatic amino acids is greater in interior position than in the exterior position of the single walled carbon nanotube (CNT (12, 0)).

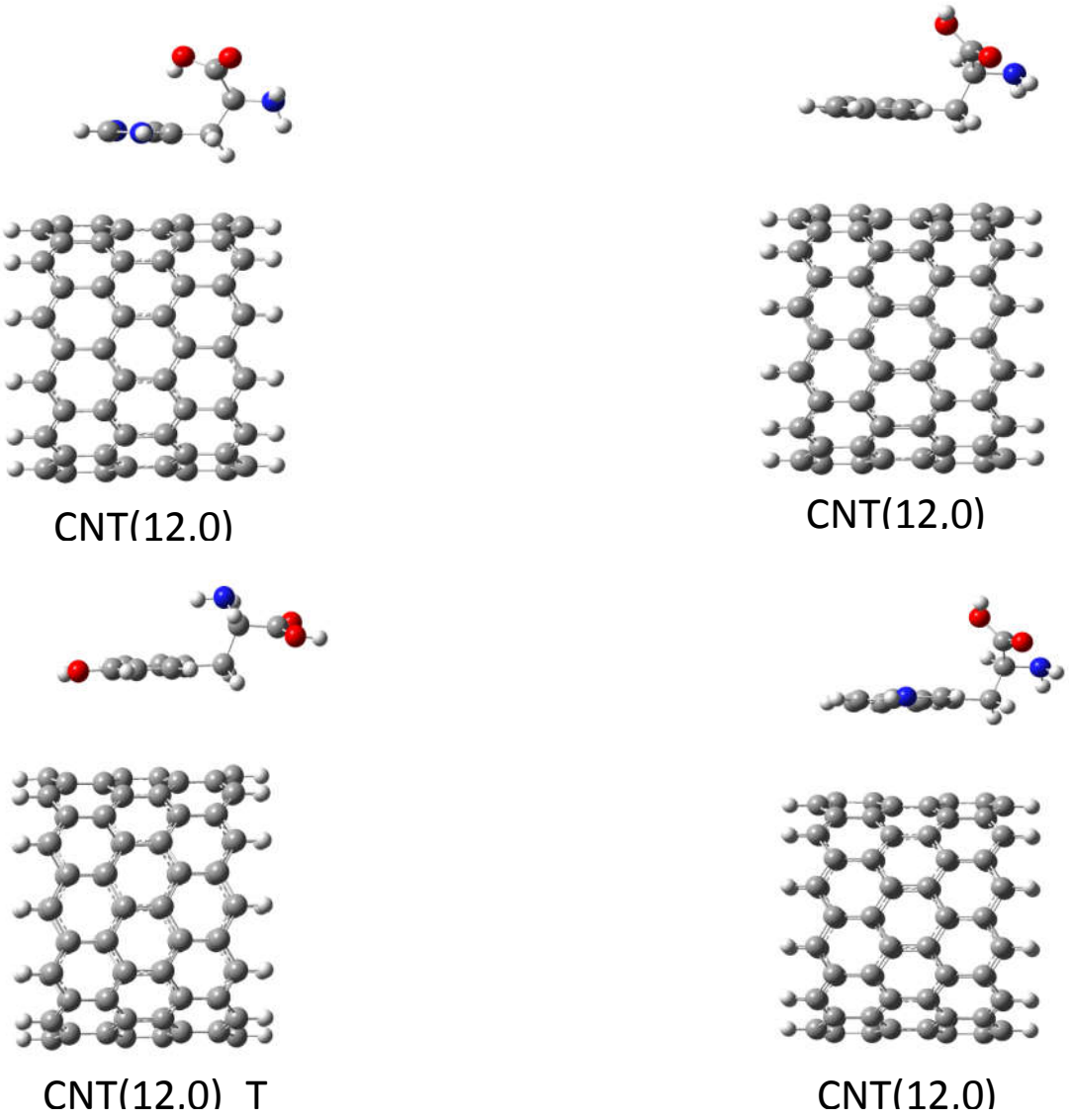


Fig. 3: Optimized geometry of four different adsorption states of aromatic amino acids on the exterior position of single walled carbon nanotube (CNT (12, 0)).

Table 1: B3LYP/6-31G* The binding Energy, HOMO-LUMO Energy Gap of the complex molecular system in the exterior postion.

Complex molecular system	Binding Energy(kcal/mole)	HOMOEnergy(eV)	LUMO Energy(eV)	HOMO-LUMO Gap(eV)
CNT(12,0)_histidine	-7.952	-3.876	-3.478	0.398
CNT(12,0)_phenylalanine	-0.170	-3.849	-3.442	0.407
CNT(12,0)_tyrosine	-0.649	-3.878	-3.474	0.404
CNT(12,0)_tryptophan	-0.791	-3.887	-3.482	0.405

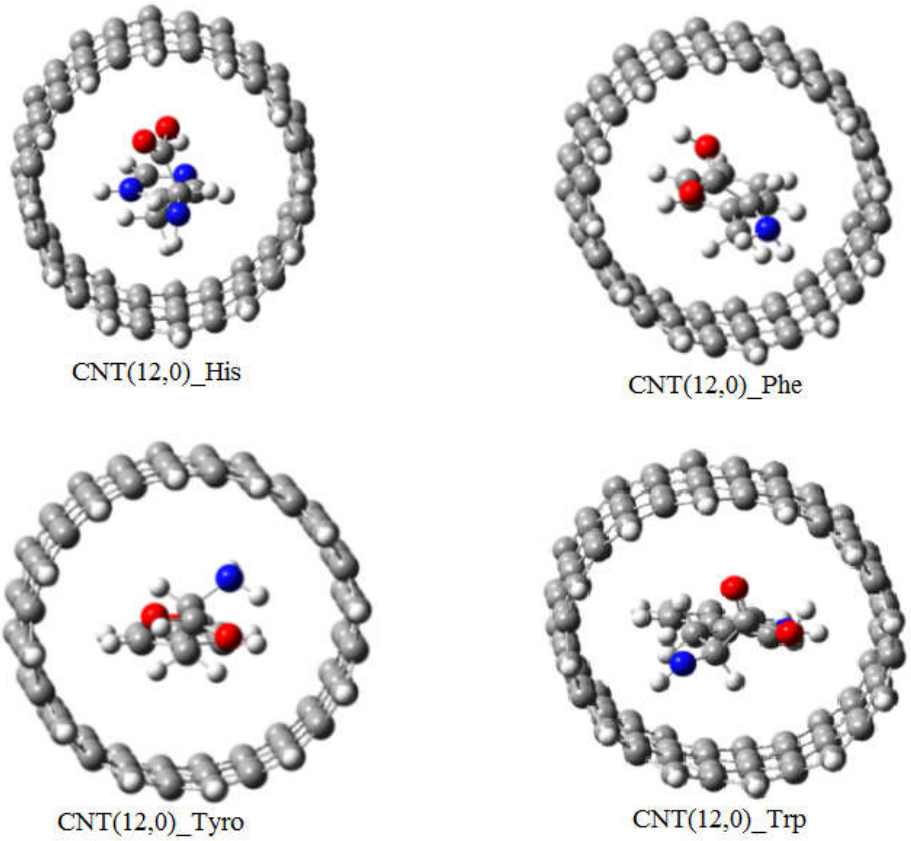


Fig. 4: Optimized geometry of four different adsorption states for aromatic amino acids in the interior position of single walled carbon nanotube (CNT (12, 0)).

Table 2: B3LYP/6-31G* The binding Energy, HOMO-LUMO Energy Gap of the complex molecular system in the interior postion of aromatic amino acid.

Complex Molecular System	Binding Energy (Kcal/mole)	HOMO Energy (eV)	LUMO Energy (eV)	HOMO-LUMO gap (eV)
Cnt(12,0)_Histidine	-2.891	-3.838	-3.481	0.357
CNT(12,0)_Phenylalanine	4.656	-3.895	-3.487	0.408
CNT(12,0)_Tyrosine	1.778	-3.839	-3.436	0.403
CNT(12,0)_Tryptophan	8.447	-3.867	-3.470	0.397

Table 1 and 2 also show the HOMO-LUMO gap of the various aromatic amino acids in exterior and interior position of single walled carbon nanotube. The HOMO-LUMO gap for the interaction of histidine with CNT(12, 0) vary from 0.357 to 0.398eV for the interior and exterior position respectively. The binding energy of histidine increases with decreasing HOMO-LUMO energy gap of CNT (12,0). The binding energy of phenylalanine and tyrosine is greater in interior position than in the exterior position of CNT(12,0) but there is no

significant change of HOMO-LUMO energy gap of CNT(12,0) with increase in binding energy for phenylalanine. On the other hand the binding energy of tryptophan vary from -0.791 to 8.447kcal/mole and the HOMO-LUMO energy gap of CNT(12,0) vary from 0.405 to 0.397eV. The binding energy of tryptophan is increasing with decrease in the HOMO-LUMO energy gap for CNT(12,0) in interior position. Therefore, we also can say that the tryptophan have strongest binding energy in interior position of single walled carbon nanotube.

4. CONCLUSION

The binding of a series of different aromatic amino acids with carbon nanotube has been comprehensively analysed. Our calculations reveal that the binding energy preferences of aromatic amino acids are different in both positions respectively i.e. in exterior and interior positions. The binding energy of aromatic amino acid is greater in interior than the exterior position of single walled carbon nanotube. For the exterior position the preferential order of the interaction for the aromatic amino acids with single walled carbon was histidine < tyrosine < tryptophan < phenylalanine while for the interior position the order is histidine < tyrosine < phenylalanine < tryptophan. The Significant changes occur in the HOMO-LUMO energy gap of the CNT(12,0) on the aromatic amino acids, which are used to design the new nano-bio composite carbonaceous material. This study can also be applied to develop novel bio- sensors, new carbon based drug delivery systems and sensing applications, focusing particularly on the mechanism of binding between biomolecule and carbon nanotube.

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6. REFERENCES

1. Dinadayalane TC and Leszczynski J, Struct. Chem., 2010, 21: 1155–1169.
2. Liang F and Chen B, Curr. Med. Chem., 2010, 17: 10–24.
3. Zhu Y, Murali S, Cai W, Li X, Suk JW, Potts JR and Ruoff RS, Adv. Mater., 2010, 22: 3906–3924.
4. Ready AS, Sastry GN, J. Phys. Chem. A., 2005, 109: 8893-8903.
5. Dinadayalane TC, Sastry GN, Leszczynski J, Int. J. Quantum Chem., 2006, 106: 2920-2933.
6. Zorbas V, Smith AL, Xie H, Ortiz-Acevedo A, Dalton AB, Dieckmann GR, Draper RK, Baughman RH, Musselman IH, J. Am. Chem. Soc., 2005, 127: 12323-12328.
7. Ge C, Du J, Zhao L, Wang L, Li Y, Yang Y, Zhou R, Chai Z, Chen C, Proc. Natl. Acad. Sci. USA, 2011, 108: 16968-16973.
8. Balamurugan K, Gopalakrishnan R, Raman SS, Subramanian V, J. Phys. Chem. B, 2010, 114: 14048-14058.
9. Balamurugan K, Singham E.R.A, Subramanian V, J. Phys. Chem. C, 2011, 115: 8886-8892.
10. Gopalakrishnan R, Balamurugan K, Singham ERA, Sundaraman S, Subramanian V, Phys. Chem. Chem. Phys., 2011, 13: 13046-13057.
11. Balamurugan K, Subramanian V, Biopolymers , 2013, 99: 357-369.
12. Liu Z , Sun X, Nakayama-Ratchford N, Dai H , ACS Nano, 2007, 1: 50-56.
13. Khan MAK, Kerman, Prtryk M, Kraatz H, Anal. Chem., 2008, 80: 2574-2582.
14. Kuang Z, Kim SN, Crookes-Goodson WJ, Farmer BL, Naik RR, ACS Nano 2010, 4: 452-458.
15. Barone PW, Baik S, Heller DA, Strano MS, Nat. Mater., 2005, 4: 86-92.
16. Umadevi D AndSastry GN, J. Phys. Chem. C, 2011, 115: 9656-9667.
17. Umadevi D, Sastry GN, J. Phys. Chem. Lett., 2011, 2: 1572-1576.
18. Umadevi D, Panigrahi S, Sastry GN, Acc. Chem. Res., 2014,47: 2574-2581.
19. Umadevi D and Sastry GN, Curr. Sci., 2014, 106: 1224.

20. Umadevi D and Sastry GN, Chem. Phys. Lett., 2012,549:39-43.

21. Kong J, Franklin NR, Zhou CW, Chapline MG, Peng S, Cho KJ, and Dai H, Science 287, 622_2000_; P. G. Collins, K. Bradley, M. Ishigami, and A. Zettl, ibid.287,1801_2000_; M. Shim, A. Javey, N. Wong Shi Kam, and H.Dai, J. Am. Chem.Soc., 2001, 123:11512.

22. Zorbas V, Smith AL, Xie H, Ortiz-Acevedo A, Dalton AB, Dieckmann GR, Draper RK, Baughman RH, and Musselman IH, J. Am. Chem. Soc., 2005, 127: 12323.

23. Lie X, Chen W, Zhan Q, Sowards L, Pender M, and Naik RR, J. Phys. Chem. B, 2006,110:12621.

24. Chen RJ, Zhan Y, Wang D, and Dai H, J. Am. Chen. Soc., 2001, 123: 3838.

25. Zhan J, Lee JK, Wu Y, and Murray RW, Nano Lett. 2003, 3: 403.

26. Kong J, Franklin N, Zhou C, Chapline M, Peng S, Cho K and Dai H, Science, 2000, 287, 622-625.

27. Schedin F, Geim AK, Morozov SV, Hill EW, Blake P, Katsnelson MI and Novoselove KS, Nature Mater., 2007,6: 652-655.

28. Chen W., Duan L, Zhu D, Environ. Sci. Technol. 2007,41: 8295.

29. Panigrahi S, Bhattacharya S, Banerjee S, Bhattacharyya D, J. Phys. Chem. C,2012, 116: 4374.

30. Balavoine F, Schultz P, Richard C, Mallouh V, Ebbesen T, Mioskowski C, Angew.
Chem. Int. Ed.,1999, 38: 1912.

31. Tsang SC, Davis JJ, Malcolm L, Green H, Allen H, Hill O, Leung YC, Sadler PJ,

32. J. Chem. Soc. Chem.Commun. 1995, 17: 1803.

33. Tsang SC, Guo Z, Chen YK, Green MLH, Allen H, Hill O, Hambley TW, Sadler PJ, Angew. Chem. Int. Ed. Engl.1997, 36: 2197.

34. Chen RJ, Bangsaruntip S, Drouvalakis KA, Kam NWS, Shim M, Li Y, Kim W, Utz P, Dai H, Proc. Natl. Acad. Sci. 2003,100: 4984.

35. Besteman K, Lee J, Wiertz FGM, Heering H, Dekker C, Nano Lett. 2003,3: 727.

36. Star A, Gabriel JCP, Bradley K, Gruner G, Nano Lett. 2003,3:459.

37. Roman T, Dino WA, Nakanishi H, Kasai H, Eur. Phys. J. D.,2006,38: 117.

38. Frisch, MJ et al., Gaussian 09, Revision C. 01, Gaussian Inc., Wallingford, CT, USA,