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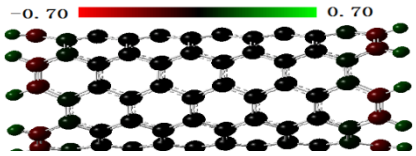
NH_2-functionalized open-ended armchair single-wall carbon nanotubes (SWCNT) studied by density functional theory

Hao Li, Aiping Fu*, Wenbo Huai, Fengna Guo, Zonghua Wang

Collaborative Innovation Center for Marine Biomass Fiber, Laboratory of New Fiber Materials and Modern Textile, the Growing Base for State Key Laboratory, College of Chemistry and Chemical Engineering, Qingdao University, Qingdao 266071, China

Abstract: **We study the effects of covalent functionalization of single wall carbon nanotubes on their geometric and electronic properties. The studies are based on the first principles calculationsin the framework of density functional theory. The structures of ideal (5,5) single wall carbon nanotubes (SWCNTs) with 1-5 amino groups at the end of nanotube were fully optimized at the B97D /6-31G* level. We have determined the energies of reaction and the charge distributions of the functionalized SWCNTs with the -NH_2 radical.**



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*Corresponding Author: Aiping Fu, apfu@qdu.edu.cn

1. Introduction

Carbon nanotubes (CNTs), since discovered in 1991, have quickly developed as the working horse of nanotechnology, mostly owing to their superior electronic, mechanical and thermal properties [1-2]. Especially, single wall carbon nanotubes (SWCNTs) have potential applications in different fields, ranging from electronics to drug delivery systems, owing to their nanoscale dimensions and quantum properties [3-5]. However, the fact that they do not disperse in polar solvents such as water and have tendencies to create bundles limits their wider applications. Therefore, the practical application of the SWCNTs usually demands an enhancement or turning of the SWCNTs' properties to obtain the desired physical and chemical characteristics. The common remedy of these problems is the functionalization of the SWCNTs. One solution to this problem is the covalent functionalization with simple organic groups (such as –OH, -COOH and -NH_2) [6-7]. The functionalization of the single wall carbon nanotubes emerged as an alternative to make them dispersible in water and get many attractive qualities. As a consequence, SWCNTs functionalized at their ends by different groups are formed for various utilizations. Therefore, it is very important to investigate the effects of covalent functionalization of single wall carbon nanotubes on their geometric and electronic properties [8-9].

In this paper, we have reported the calculated results of the structures for armchair (5,5) SWCNTs at 13.61Å in length. The end-functionalized structures were optimized at the level of B97D/6-31G*. From one to five NH_2 groups added at one end of the nanotubes were calculated. Based on the calculations, we tried to address the following questions: (i) how the functionalization procedure changes the equilibrium geometry of the functionalized systems, (ii) the energy of reaction (E_b) between NH_2 groups and the SWCNT, (iii) how the functionalization procedure changes the charge distribution of the functionalized systems. The paper would provide insights into the NH_2 functionalization of armchair single-wall carbon nanotubes, and indicates the possibility of functionalizing one end of the tube with 1-5 NH_2 substituents.

2. Computational methods

All calculations were performed using the Gaussian 09 programs. Density-functional computations have been performed using the B97D as exchange-correlation functional, which has been widely used and proved to be accurate enough for extensive systems including nanostructured materials. The standard basis set of 6-31G* was used throughout. Full structure optimization of unsubstituted open-ended (with dangling bonds on carbon saturated with hydrogen atoms), and NH_2-modified SWCNTs were performed.

In order to characterize how these systems interact, binding energy (Eb) between NH_2 groups and the SWCNT was quantified through eqn (1)

$$E_b=-[E_{total}\text{-ESWCNT-n}(ENH_3)+nH_2]/n \quad (1)$$

where E_{total}l [ESWCNT] is the total energy of the system [pristine SWCNT] and ENH_3 is the energy of an isolated amino molecules n times, where n is the number of amino groups considered. The studied systems have fully relaxed atomic positions. In addition, for all calculations the spin polarization was considered.

3. Results and discussion

3.1. Structural analysis

In Figure 1, selected ideal armchair SWCNTs with length of 13.61 Å are shown, with a diameter of 6.98 Å. The free dangling bonds on carbon atoms are saturated

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with hydrogen atoms. The calculated values are in good agreement with the literature and experimental values. The structures of armchair SWCNTs differ from those of zigzag ones. In addition, the rims of SWCNTs show different shapes.

In order to investigate the chemical functionalization of the CNT by amino groups, we substituted of the hydrogen atoms at one end of the SWCNT with 1-5 amino groups led to stable NH_2- functionalized structures. In Figure 2, several structures are shown. The stability of the functionalized SWCNTs and the change of geometry caused by the functionalization have been studied. According to our calculations, these structures can exist steadily. Furthermore, the electrochemical properties of SWCNTs were analyzed. The functionalization changes the parameters characterizing the backbone of the functionalized SWCNTs.

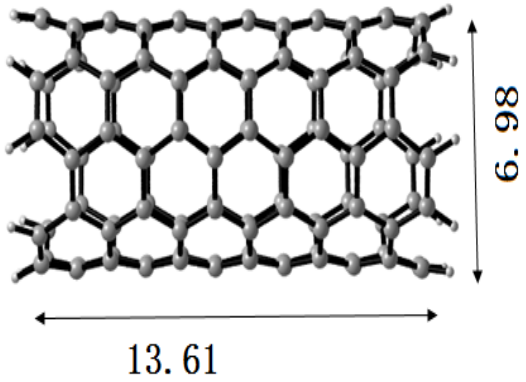

Figure 1. Schematic structures and dimensions (in Å) of B97D/6-31G* optimized ideal armchair (5,5) SWCNTs with five strings of attached hexagon rings.

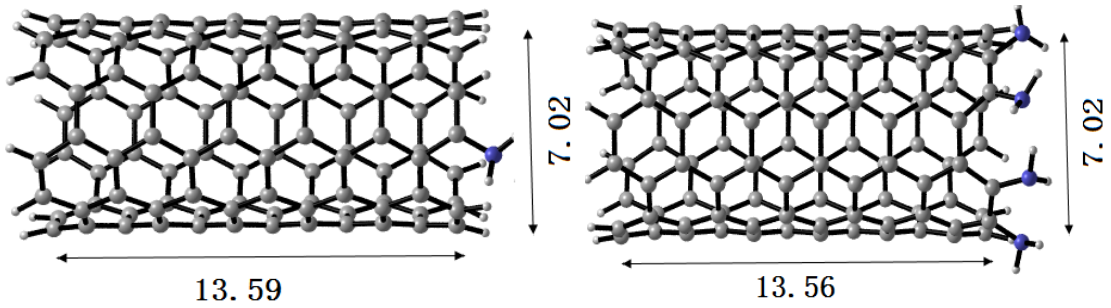

Figure 2. Schematic structures and dimensions (in Å) of B97D/6-31G* optimized ideal armchair (5,5) SWCNTs with attached 1 and 4 NH_2.

3.2. Binding energy and dipole

Binding energy is the energy required to disassemble a whole system into separate parts. The research of binding energy plays an important role in understanding the stability of the system. In order to characterize how these systems interact, the binding energy (E_b) between NH_2 groups and the SWCNT was calculated. The binding energy (per NH_2 group) and dipole for all considered functionalizing SWCNTs are shown in Figure 3.

As we can see in Figure 3, generally, the binding energy per amino groups has a relatively small change with increasing number of attached groups. The binding energy per groups gets less positive (indicating that the bonding weakens) with increasing number of attached fragments. From the figure, we can find that dipole is always increase with the increase of the number of modified groups.

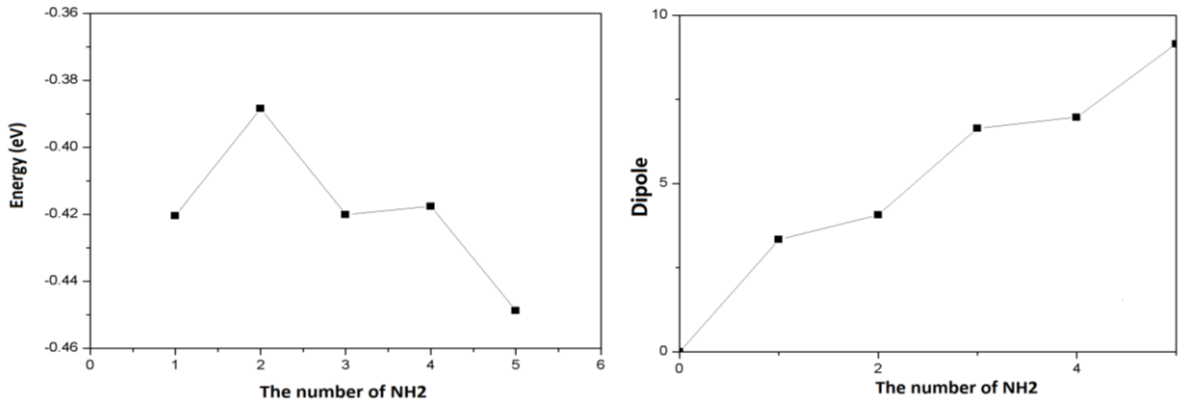

Figure 3. The binding energy and dipole of armchair (5,5) SWCNT and the SWCNT with attached 1-5 NH_2.

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3.3. Charge distribution

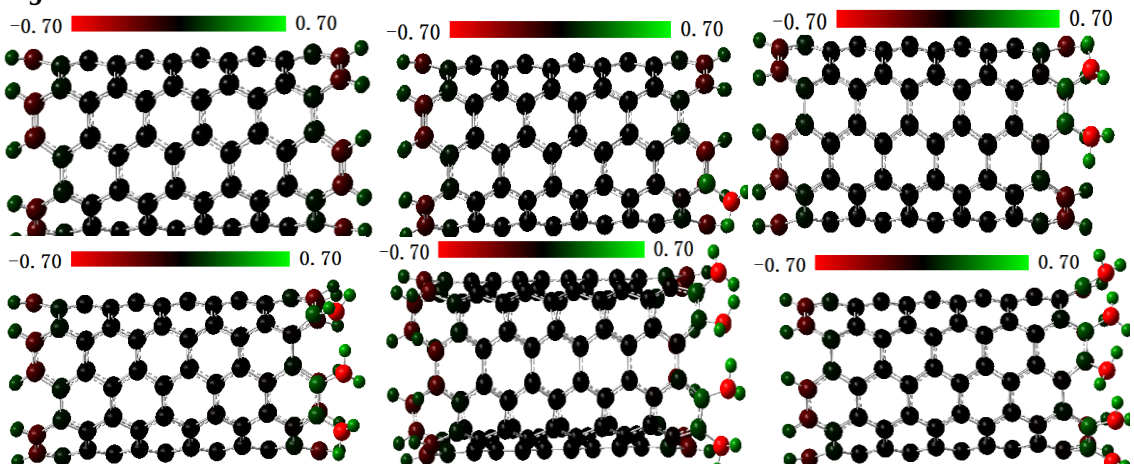

Figure 4. The charge distribution of pure armchair (5,5) SWCNT and the SWCNT with attached 1-5 NH_2.

In order to better understand the influence of the functional groups on the electronic properties of single wall carbon nanotubes, we studied the charge distribution and presented them in Figure 4. As shown in the figure, marginal carbon with attached hydrogen atoms is electronegative for pure SWCNT. However, carbon atoms attached with nitrogen atoms are significantly positively charged. We think it is due to the strong electron withdrawing ability for the nitrogen atom. It is noteworthy that the positively charged carbon atom is the active site of many electrochemical reactions. Therefore, the modification of single carbon nanotubes with amino groups has great application potential.

4. Conclusions

The present density functional theory studies using B97D/6-31G* calculations indicate that it is possible to -NH_2 functionalize one end of an armchair SWCNT with 1-5 substituents. The functionalizing fragments not only induce change charge distribution in the neighborhood of the attachment, but also changes the parameters characterizing the backbone of the functionalized SWCNTs. And, the binding energy per amino groups has a relatively small change with increasing number of attached groups. In addition, the introduction of amino groups produced positive carbon active sites, which have great application potential in the field of electrochemistry.

References

[1] S. Iijima, T. Ichihashi, Nature, 363(1993):603-605.
[2] S. Osswald, E. Flahaut, Y. Gogotsi Y Chemical Materials, 18(2006):1525-1533.
[3] S. Iijima, Nature, 354(1991):56–58.
[4] T. Kar, B. Akdim, X. Duan, R. Pachter, Chemical Physics Letters, 423(2006):126-130
[5] Z. Zhou, M. Steigerwald, M. Hybertsen, L. Brus, RA Friesner, Journal of the American Chemical Society, 126(2004):3597-3607.
[6] H. Kuzmany, A. Kukovecz, F. Simon, M. Holzweber, C. Kramberger, T. Pichler, Synthetic Metals, 114(2004):113-12.
[7] T. Kar, S. Scheiner, AK Roy, Chemical Physics Letters, 460(2008):225-229.
[8] CG Salzmann, SA Llewellyn, G. Tobias, MAH Ward, Y. Huh, MLH Green, Advanced Materials, 19(2007):883-887.
[9] J. Zhao, JP Lu, J. Han, CK Yang, Applied Physics Letters, 82(2003):3746-375.

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