Results in Physics 9 (2018) 656–664

Contents lists available at ScienceDirect

Results in Physics

journal homepage: www.journals.elsevier.com/results-in-physics

Four- and eight-membered rings carbon nanotubes: A new class of carbon nanomaterials

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ARTICLE INFO

Article history:
Received 29 December 2017
Received in revised form 13 March 2018
Accepted 13 March 2018
Available online 17 March 2018

Keywords:
Four- and eight-membered rings
Carbon nanotubes
Stability
Electronic properties

ABSTRACT

A new class of carbon nanomaterials composed of alternating four- and eight-membered rings is studied by density functional theory (DFT), including single-walled carbon nanotubes (SWCNTs) double-walled carbon nanotubes (DWCNTs) and triple-walled CNTs (TWCNTs). The analysis of geometrical structure shows that carbon atoms' hybridization in novel carbon tubular clusters (CTCs) and the corresponding carbon nanotubes (CNTs) are both sp^2 hybridization; The thermal properties exhibit the high stability of these new CTCs. The results of energy band and density of state (DOS) indicate that the electronic properties of CNTs are independent of their diameter, number of walls and chirality, exhibit obvious metal properties.

Introduction

Carbon has unique physical and chemical properties, and its common isomers are diamond, graphene, fullerene (C_{60}) and carbon nanotubes. The C_{60} found by Smalley in 1985 [1] had driven scientists to research other carbon materials. Especially, in 1991 [2] and 1993 [3], Iijima discovered the multi-walled carbon nanotubes (MWCNTs) and SWCNTs which aroused the widespread concern. In recent years, various types of CNTs have been predicted theoretically or prepared experimentally, and due to their excellent chemical and physical properties [4,5], CNTs have been widely used in many fields such as nanotube composites [6], solar battery [7], electrochemical devices [8], hydrogen storage materials [9,10], field emission devices [11], carbon nanotube field effect transistors [12,13], carbon nanotube sensors and probes [14,15], pharmaceutical [16], catalyst carrier [17] and so on, and also have a wide potential application prospects in carbon-based electronics [18–22] and engineering materials [23–26].

It is well known that the electronic properties of the CNTs composed of six-membered rings have a strong dependence on their structures [27–34]. That is, the six-membered rings CNTs with different diameter, number of wall and chirality will exhibit the characteristics of metal or semiconductor. Besides, it is difficult to achieve the macro-preparation and separation of CNTs with certain conductance (metallic or semiconducting) in experiment, although Yang Feng [35–37] prepared two single-walled CNTs (12, 6) and (16, 0) with a special catalyst and their purity could reach to 92% and 79.2% respectively, yet other types of CNTs with high purity have not been reported. Although metal and semiconducting SWCNTs can be separated by agarose gel electrophoresis [38–40], the separation of metal and semiconducting DWCNTs and triple-walled CNTs has not been achieved. Therefore, the preparation of CNTs with uniform structure and electronic properties or the separation of CNTs with certain conductance is great challenges in the experiment, and also provides a rare opportunity to explore the CNTs with uniform electronic properties in theory.

Wang Gang et al. [41] studied a two-dimensional carbon allotrope with tetrarings, called T graphene, and explored its structure and electronic properties. Wang Qian et al. [42] designed a two-dimensional metastable carbon structure entirely composed of pentagons, and the electronic properties of the corresponding armchair pentagon-based SWCNTs were studied. It showed that except for the highly curved (2, 2) penta-tube, the band gap of the CNTs is not related to its diameter, both semiconductor properties. Recently, Professor Zhong et al. [43] have obtained the new graphene-like nanoribbons periodically embedded with four- and eight-membered rings, and have made an indepth study on its electronic properties to realize the regulation of the electronic properties of graphene. Lin et al. [44] designed a new silicene only composed of alternating four- and eight-membered rings and explored the corresponding armchair and zigzag SWSiNTs, the

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https://doi.org/10.1016/j.rinp.2018.03.030
2211-3797/

results of electronic properties showed that the band gap of SWSiNTs increased monotonically with the decreasing of diameter.

At present, thanks to the development of molecular simulation theory and computer technology, molecular simulation has become the third effective and reliable method to explore the structure and properties of materials at the molecular level after the experimental and theoretical methods. The graphene-like nanoribbons with periodically embedded four- and eight-membered rings the has been prepared, therefore, it is natural to expect that the four- and eight-membered rings could replace all six-membered rings, obtaining the graphene only with four- and eight-membered rings, then study the CNTs with four- and eight-membered rings. Consequently, in this research, we simulate and calculate the pure four- and eight-membered rings of CNTs, and study their stability and electronic properties in theory. Analysis of their band structures and DOS indicates that all of stable four- and eight-membered rings CNTs exhibit metal properties, independent of chirality. Our research can provide a new direction for the experimental preparation of CNTs with homogeneous electronic properties, so the uniformity of structure may not be the necessary for experimental preparation, and it is not necessary to develop special techniques to separate the metal and semiconductor CNTs for the second time.

Calculation methods and details

In this research, the geometrical structures and electronic properties of CNTs with four- and eight-membered rings are studied using the DFT carried out in the Gassian03 packages. It is well known that the B3LYP [45] method is more suitable for calculating cluster, while the PBEPBE method is preferable to calculate larger system with periodic structure. Studies have shown that the basis set 6-31G have a high accuracy in the theoretical calculation of CNTs, whereas the 3-21G basis set can improve the computational efficiency greatly in the case of high degree of accuracy [32–34,46]. Therefore, under the convergence criterion of 10^{-6} a.u., the geometrical structure and frequency of CTCs with alternating four- and eight-membered rings are optimized and calculated with the 3-21G basis set. At the same time, the structural and electronic property of CNTs are explored by the 6-31G basis set in the PBEPBE. The results are obtained by three steps: firstly, the repeat units cell of the CNTs is constructed through removing the atoms at two ends the stable CTCs (see Fig. 1). Secondly, The energy band structures are calculated with the periodic boundary condition (PBC)[47] and 240 k-points. Finally, the density of state (DOS) of CNTs is calculated, and their discrete peaks are widen with a broadening parameter of 0.3 eV.

The SWCNTs composed of four- and eight-membered rings are studied in this research. Their definitions are the same as the SiNTs [44]. That is, the chiral vector is defined as:

$$C_h = n\vec{a}_1 + m\vec{a}_2 \quad (1)$$

Where $\vec{a}_1$ and $\vec{a}_2$ are the unit basis vector, m and n are integer. When m = 0, the SWCNTs is called zigzag SWCNTs, denoting as (n, 0); When m = n, it is defined as armchair SWCNTs (n, n); When $m \neq n$, it is chiral SWCNTs (n, m). The corresponding single-wall carbon tubular clusters (SWCTCs) are denoted as [n, 0], [n, n] and [n, m], respectively. Whereas, the zigzag, armchair and chiral DWCNTs with four- and eight-membered rings are denoted as (n,0)@(2n, 0), (n, n) @ (2n, 2n) and (n, m) @ (2n − 1, 2 m + 1), and the corresponding double-wall carbon tubular clusters (DWCTCs) are expressed as [n, 0] @ [2n, 0], [n, n] @ [2n, 2n] and [n, m] @ [2n − 1,2m + 1], (m = n-2, n = 3, 4, 5, 6, 7, 8).

Results and discussion

Structure of CTCs

The SWCTCS [n, 0] and [n, n] are an open structure consisting of equal numbers of four membered rings and eight membered rings (see Fig. 1a and b), whereas the SWCTCS [n, n-2], the difference between the four-membered rings and the eight-membered rings is n-1, and the two ends are open structures (see Fig. 1c).

The DWCTCs are obtained by nesting and assembling the corresponding SWCTCs [n, 0], [n, n] and [n, n − 2] selected, whose number of eight-membered rings in the outer wall is twice than that in the inner wall.

Because of the different interface ways of the inner and outer walls of the DWCTCs, different multiple rings are formed at the two seals. For zigzag DWCTCs [n, 0] @ [2n, 0], six-membered ring and ten-membered rings are formed (see Fig. 2a), while for armchair DWCTCs [n, n] @ [2n, 2n], eight-membered rings and fourteen-membered rings are formed (see Fig. 2b). Whereas, for chiral DWCNTs [n, n-2]@[2n-1, 2n-3], due to the different interface ways of the two ends of the inner and outer wall, the connection at one end formed eight-, six- and thirteen-membered rings in order (See Fig. 2c), while the other end formed four-, five-, seven- and thirteen-membered rings in sequence (see Fig. 2d).

The stability of CTCs

Structural stability

The local smooth planar structure shown in Fig. 3 indicates the formation of sp^2 hybridization. Fig. 3 (a) and Table 1 show the sum of the bond angles ($\Sigma\Omega = \Sigma\Omega1 + \Sigma\Omega2 + \Sigma\Omega3$) and the three types of bond lengths (R1, R2, R3) of the single-walled carbon tubular clusters (SWCTCs). Compared with the other two types of SWCTCs, the bond angles of the armchair (n, n) are all between 359° and 360°, closer to the standard sp^2 hybrid. However, with the increase of the diameter, the $\Sigma\Omega$ for the three types of SWCTCs all gradually

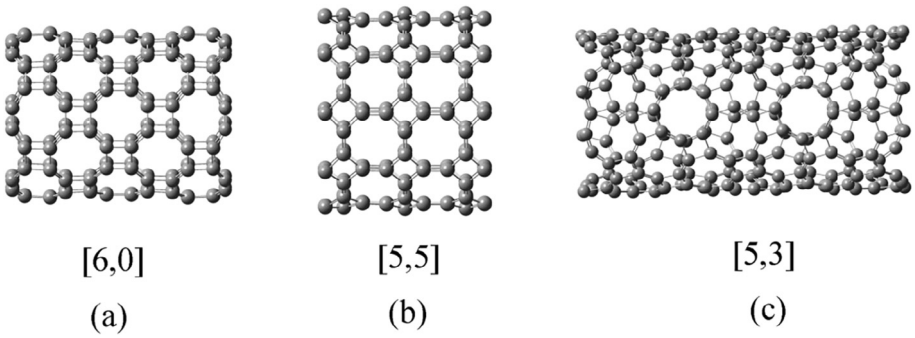

Fig. 1. The structure of the SWCTCs (a) [6,0], (b) [5,5] and (c) [5,3] respectively.