# The formation mechanism of chiral carbon nanotubes

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## ARTICLE INFO

## ABSTRACT

The nuclei and the formation mechanism of chiral carbon nanotubes, namely, single-, double-, and triple-walled carbon nanotubes are simulated by the first principle density functional theory. The formation mechanism from nuclei to corresponding infinitely long carbon nanotubes occurs spirally and via absorbing carbon atoms layer by layer. Carbon atoms at the open end are metastable state compared with ones in the tube wall or the closed end, which indicate the growth point of chiral carbon nanotubes is located at the open end. Growth of outer layer tubular clusters takes precedence over the inner layer in the process of forming multi-walled nuclear structures. Because of the ratio of carbon atoms at the open end to all carbon atoms decreases, the stability of the tubular clusters increases with their length. The infinitely long carbon nanotubes are obtained by executing periodic boundary conditions depend on corresponding nuclear structures.

## 1. Introduction

Owing to the advent of multi-walled carbon nanotubes (MWCNTs) [1], this kinds of nanomaterial have attracted considerable attention of engineers and scientists in the field of related nanotechnology. The potential value of these structures have been widely application in electronic devices [2,3], biological engineering [4], chemical sensors [5], medical carrier [6], hydrogen storage [7,8], carbon nanotube field effect transistor [9] and carbon nanotube composite materials [10,11].

Carbon nanotube (CNT) can be seen as a curled graphene sheet [12]. Synthetic techniques of CNTs mainly include arc discharge vaporization [13], laser evaporation synthesis [14], chemical vapor deposition (CVD) [15,16] and the template method [17]. Those methods are different from each other and have their own strengths. However, the achievement of high purity, high productivity and good controllable structure is slightly inadequate, researchers compensate deficiencies by combining these synthetic methods. Yang F et al. obtain (12, 6) and (16, 0) single-walled carbon nanotubes (SWCNTs) using CVD under the action of a specific catalyst, the purity is 92% and 80% respectively [18–20]. They point out that specific catalysts are capable of obtaining specific nuclei (also known as seeds) of SWCNTs, and the nuclei can also grow to the corresponding SWCNTs under certain conditions. Thus, the key to the production of high purity CNTs is to prepare a catalyst that matches the nucleus of CNTs.

In theory, investigations of CNTs nuclear growth are rarely reported. Ching H K [21] proposes that carbon rings or carbon cages can act as nuclei for CNTs growth; Yao Y [17] proposes that the smallest repeating units of CNTs can act as nuclei for cloning growth; Yu X [22] proposes that nuclei of CNTs can be obtained by intercepting a portion of $C_{60}$.

Besides, the most controversial question is to determine whether the growth of these CNTs was open or closed [23,24]. Moreover, it is worth to discuss whether the outer layer or inner layer grows first in MWCNTs [25,26].

Discussing the nuclear structures can provide a useful reference for preparing corresponding catalysts, thereby achieving high purity preparation of CNTs. The growth process of CNTs cannot be directly observed because of the limitation in detection and analysis. Therefore, the simulation of the formation process can provide theoretical guidance for understanding the formation mechanism of CNTs on the nanometer scale.

The first part of this paper presents the detail calculation method. The first-principles density functional theory (DFT) is applied to optimize the chiral SWCNTs and MWCNTs. The second part of this paper presents the formation mechanism from the nuclei to the corresponding chiral SWCNTs and MWCNTs. Then, the stability and thermodynamics of these structures are discussed. The last part of this paper presents the conclusion of this research.

## 2. Calculation method and detail

The structural parameters of large diameter SWCNTs have very little

difference from graphene, such as bond angle and bond length, but the geometric features of small diameter SWCNTs with the strong curl effect have a larger difference from graphene. In this paper, the chiral single- and multi-walled nuclear structures, carbon tubular clusters, and the corresponding infinitely long CNTs are optimized by DFT performed in the Gaussian 03 package [27]. The exchange-correlation potential is described by the hybrid Becke's 3-parameter and the Lee-Yang-Parr (B3LYP) function [28,29]. To better describe the structural characteristics of chiral CNTs, the 3-21G [30,31] as basis set is chosen.

In order to obtain the stable tubular clusters, the structural optimization is performed firstly, and then their frequencies are analyzed. Structures with no virtual frequency are chose as stable clusters. Besides, the thermodynamic properties, e.g. the constant volume heat capacity ($C_V$), entropy ($S$) and internal energy ($U$), are also used to discuss the stability of tubular clusters. The corresponding infinitely long chiral SWCNTs and MWCNTs are obtained by executing periodic boundary conditions (PBC) [32] on the smallest repeating units of CNTs.

## 3. Results and discussion

First, the chiral carbon tubular clusters are defined as follows: [$n, l$] ($n = 4, 6, 8, 10, 12$) for single-walled carbon tubular clusters; [$n, l$] @ [$n + 4, l + 3$] ($n = 4, 8$) and [$n, l$] @ [$n + 6, l + 5$] ($n = 6, 12$) for double-walled carbon tubular clusters; and [$n, l$] @ [$n + 4, l + 3$] @ [$n + 8, l + 6$] ($n = 4$) and [$n, l$] @ [$n + 6, l + 5$] @ [$n + 12, l + 10$] ($n = 6$) for triple-walled carbon tubular clusters. Where, $n$ is the number of carbon atoms in each layer as determined based on tube diameter, and $l$ is the number of layers as determined based on tube length. The chiral SWCNTs, double-

walled carbon nanotubes (DWCNTs) and triple-walled carbon nanotubes (TWCNTs) corresponding to these carbon tubular clusters are represented as follows: ($n, n/2$) ($n = 4, 6, 8, 10, 12$) for SWCNTs; ($n, n/2$) @ ($n + 4, n/2 + 2$) ($n = 4, 8$) and ($n, n/2$) @ ($n + 6, n/2 + 3$) ($n = 6, 12$) for DWCNTs; ($n, n/2$) @ ($n + 4, n/2 + 2$) @ ($n + 8, n/2 + 4$) ($n = 4$) and ($n, n/2$) @ ($n+ 6, n/2 + 3$) @ ($n + 12, n/2 + 6$) ($n = 6$) for TWCNTs.

### 3.1. Nuclear structures

Similar with the nanoparticles [33–37], the physical and chemical properties of nanotubes depend on the structures, and usually the structures of nanotubes depend on the nuclear morphology. So, the nuclear structures are critical for the nanotubes synthesized controllably. Even synthesis methods of nuclear structures have matured, including coronal nuclear structures [38,39]. But it is still difficult to control the structures of the nuclei in experiments, and usually the nuclear morphology are still unknown. Herein, the nuclear structures of several nanotubes are provided by structural selection and analyzing.

Figs. 1–3 show the nuclear morphology of chiral SWCNTs, DWCNTs, and TWCNTs from different perspectives, respectively. Fig. 1 shows the nuclear structures of (4, 2) (a); (6, 3) (b); (8, 4) (c); (10, 5) (d); (12, 6) (e) chiral SWCNTs. Each nuclear structure comprises six pentagons and a suitable number and distribution of hexagons that perfectly match the cylindrical surface of SWCNTs. The pentagonal distribution determines the helicity of CNTs [40]. Moreover, Euler equation is used to verify the correctness of the coronal nuclei structures, as follows:
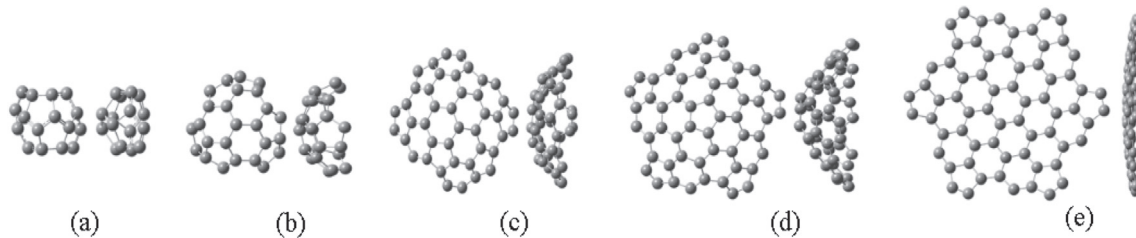
$$F + V - E = 2 \tag{1}$$



**Fig. 1.** Initial configurations, the nuclear structures of chiral SWCNTs (4, 2) (a); (6, 3) (b); (8, 4) (c); (10, 5) (d); (12, 6) (e).
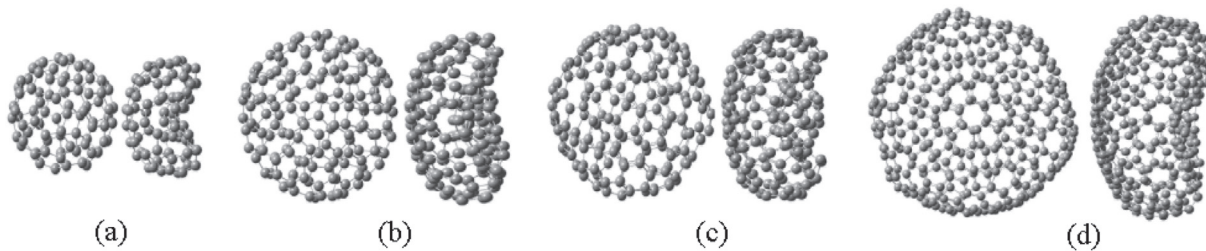


**Fig. 2.** Initial configurations, the nuclear structures of chiral DWCNTs (4,2) @ (8,4) (a); (6,3) @ (12,6) (b); (8,4) @ (12,6) (c) and (12,6) @ (18,9) (d).
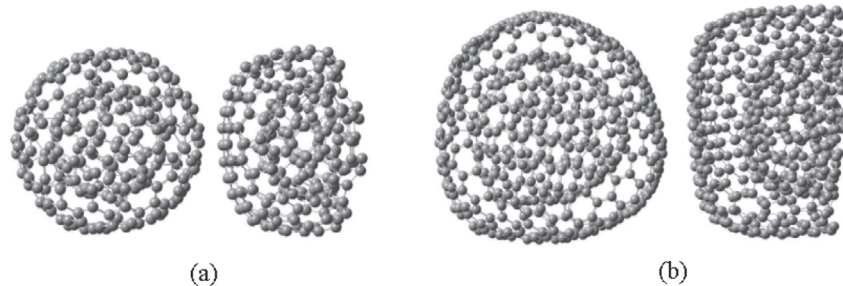


**Fig. 3.** Initial configurations, the nuclear structures of chiral TWCNTs (4,2) @ (8,4) @ (12,6) (a); (6,3) @ (12,6) @ (18,9) (b).