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The electronic properties of chiral carbon nanotubes

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ABSTRACT

Structural changes in carbon nanotubes (CNTs) alter electronic properties of these structures at the atomic scale. In this work, structure optimization and electronic property of infinitely long chiral CNTs are calculated using the first-principles density functional theory. The infinitely long chiral CNTs, namely, single-, double-, and triple-walled CNTs are obtained by imposing the periodic boundary conditions. Analysis of band structure showed that for chiral SWCNTs, a semiconductor is produced when $n - m \neq 3q$, whereas a conductor is produced when $n - m = 3q$; For chiral DWCNTs we investigated, a semiconductor is produced when $n_1 - m_1 \neq 3q$ @ $n_2 - m_2 = 3q$, whereas a conductor is produced when $n_1 - m_1 \neq 3q$ @ $n_2 - m_2 \neq 3q$ (or $n_1 - m_1 = 3q$ @ $n_2 - m_2 = 3q$); For chiral TWCNTs we investigated, a conductor is produced when $n_1 - m_1 \neq 3q$ @ $n_2 - m_2 \neq 3q$ @ $n_3 - m_3 = 3q$ (or $n_1 - m_1 = 3q$ @ $n_2 - m_2 = 3q$ @ $n_3 - m_3 = 3q$). Energy gaps are caused by the curvature of the tube wall, and they are more remarkable as diameter decreases.

1. Introduction

The discovery of single-walled carbon nanotubes (SWCNTs) [1] and multi-walled carbon nanotubes (MWCNTs) [2] stimulated the inspiration of scientists and engineers in nanotechnology-related fields. The high potential application of these structures in carbon nanotube (CNT) composite materials [3–7], chemical sensors [8,9], biological engineering [10–13], carbon nanotube field effect transistor [14,15], hydrogen storage [16,17], and medical carrier [18] has attracted considerable attention.

The methods [19–26] used in CNT synthesis mainly include laser evaporation synthesis, arc discharge vaporization, chemical vapor deposition, floating catalyst method, low-temperature solid pyrolysis, ion bombardment growth method, electrolytic method, and polymer preparation method. Despite the existence of these methods, one of the urgent problems that remain to be addressed is the implementation of controllable CNT growth [27], which mainly involves control of diameter, conductive properties, chiral selectivity, as well as obtaining local special structure. Theoretical results show that for SWCNTs, a semiconductor is produced when $n - m \neq 3q$, whereas a conductor is produced when $n - m = 3q$ [28]. However, the discussion on electronic properties of double-walled CNTs (DWCNTs) and triple-walled CNTs (TWCNTs) is rarely reported in the references.

The first part of this paper presents the calculation method and detail. We adopt the first-principles density functional theory (DFT) to calculate the electronic properties of chiral SWCNTs and MWCNTs. The second part of this work investigated the structural stability of chiral CNTs in respect of binding energy. The third part of this work investigated electronic properties of chiral CNTs in terms of energy band and density of states (DOS). The last part of this paper presents the conclusion of this research.

2. Calculation method and detail

In this research, structure optimization and electronic property of chiral single- and multi-walled infinitely long CNTs are calculated using DFT, which is implemented using Gaussian 03 package [29]. Gaussian 03 is specially used in molecular orbit ab initio calculation, DFT calculation, and half experience calculation of quantum chemistry, which can predict the properties of polymolecules and their reaction. DFT is used to determine particle density rather than wave function to describe the system. This work aims mainly to solve the Kohn–Sham equation, and the key solution is to select the system involving the exchange-correlation potential energy function. The hybrid Becke's 3-parameter–Lee–Yang–Parr function (B3LYP) [30,31] is applied to solve this problem. We choose 3-21G [32,33] as basis set to better describe structural characteristics and electronic properties of chiral CNTs.

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The first step involves structure optimization and determination of a stable geometrical configuration. The structure optimization of infinitely long chiral SWCNTs and MWCNTs are performed by imposing periodic boundary conditions (PBC) [34] and choosing B3LYP function with 3-21G basis set. Fig. 1 shows that the optimized structures of the infinite SWCNT (12, 6) (a); DWCNT (6, 3) @ (12, 6) (b); and TWCNT (4, 2) @ (8, 4) @ (12, 6) (c) obtained by PBC-B3LYP/3-21G. The second step involves analysis of the energy band structures. The 240k-points to describe all of the energy band structures of infinitely long single- and multi-walled chiral CNTs. And 10 energy levels are selected up and down around the Fermi level. Subsequently, the wave functions of output coefficient matrix to calculate the density of states (DOS) and the discrete peaks are set to 0.3 eV by Gaussian functions.

3. Results and discussion

First, the infinitely long chiral SWCNTs, DWCNTs, and TWCNTs 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; and $(n, n/2)$ @ $(n + 4, n/2 + 2)$ @ $(n + 8, n/2 + 4)$ $(n = 4)$ and $(n, n/2)$ @ $(n + 6, n/2 + 3)$ @ $(n + 12, n/2 + 6)$ $(n = 6)$ for TWCNTs.

3.1. Structural stability

Binding energy (E_b) is applied to assess the structural stability of single- and multi-walled CNTs. E_b is defined as follows:

$$E_b = \frac{kE(c) - E(c_k)}{k} \tag{1}$$

where k is the total number of carbon atoms. $E(c_k)$ and $kE(c)$ are the total ground state energies of carbon nanotubes and carbon atoms, respectively.

Fig. 2a–c shows the binding energies of infinitely long chiral SWCNTs, DWCNTs, and TWCNTs obtained by imposing PBC. Fig. 2a shows that E_b of chiral SWCNTs gradually increases as pipe diameter increases. For instance, the pipe diameter of (12, 6) infinite SWCNT is larger than that of (10, 5) infinite SWCNT, and their E_bs are 9.01 and 8.99 eV, respectively. Fig. 2b and c shows that E_b of chiral DWCNTs and TWCNTs gradually increases as the pipe diameter or pipe distances increase. For instance, when the pipe distances (Table 1) of (4, 2) @ (8, 4) and (8, 4) @ (12, 6) DWCNTs are the same, the pipe diameter and E_b of (8, 4) @ (12, 6) are larger than those of (4, 2) @ (8, 4) CNT. When the outer diameter of (6, 3) @ (12, 6) and (8, 4) @ (12, 6) CNTs are the same, the pipe distance and E_b of (6, 3) @ (12, 6) are larger than those of (8, 4) @ (12, 6) DWCNT. The pipe diameter and pipe distance of (6, 3) @ (12, 6) @ (18, 9) TWCNT is larger than that of (4, 2) @ (8, 4) @ (12, 6) TWCNT, and their E_bs are 8.98 and 8.79 eV, respectively. This finding indicates that chiral CNTs further stabilize as pipe diameter or distance increases. Obviously, the reason large-diameter CNTs are easily synthesized during manufacture is that E_b of large-diameter CNTs is higher than that of small-diameter CNTs.

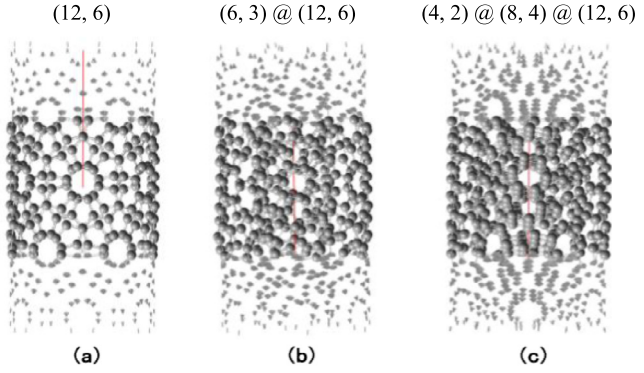

Fig. 1. The optimized structures of the infinite SWCNT (12, 6) (a); DWCNT (6, 3) @ (12, 6) (b); and TWCNT (4, 2) @ (8, 4) @ (12, 6) (c) obtained by PBC-B3LYP/3-21G.

3.2. Electronic properties

Fermi energy (E_F) and energy gap (E_g) are calculated to investigate electronic properties of chiral CNTs. Energy gap refers to the energy difference between the lowest unoccupied orbital (*LUMO*) and highest occupied orbital (*HOMO*). Energy gaps are generally caused by curvature of the tube wall, and they are more remarkable as diameters decrease [35]. The smaller the E_g, the easier the electronic transition will be from *HOMO* to *LUMO*. Moreover, the *HOMO* of an electron likely forms chemical bonds with the electron of other atoms. Additionally, E_g determines the electrical conductivity of CNTs; the smaller the E_g, the stronger the conductivity will be. E_F and E_g are respectively defined as follows:

$$E_F = (E_{LUMO} + E_{HOMO})/2 \tag{2}$$

$$E_g = E_{LUMO} - E_{HOMO} \tag{3}$$

Chiral index (n, m) is directly associated with the electronic and optical properties of CNTs [36]. When $n - m \neq 3q$ (for integer q, $n > m$), electronic DOS of SWCNTs near the Fermi level show obvious band gap, producing a semiconductor. When $n - m = 3q$, the valence band and conduction band of SWCNTs overlap each other, producing a conductor [28]. Fig. 3a shows that (8, 4) and (10, 5) chiral SWCNTs are wide and direct band gap semiconductors at *X*-point, whereas (4, 2) SWCNT are wide and indirect band gap semiconductor. The E_g values of (6, 3) and (12, 6) SWCNTs are 0.33 and 0.10 eV, respectively, which are lower than that of conductors (0.40 eV). Fig. 3b shows that (4, 2) @ (8, 4) DWCNT is a conductor with narrow band gap, whereas (8, 4) @ (12, 6) DWCNT is a wide and indirect band gap semiconductor. In addition, (6, 3) @ (12, 6) DWCNT with valence band and conduction band that pass through the Fermi level but do not overlap, is a half metal. By contrast, (12, 6) @ (18, 9) DWCNT with overlapping valence band and conduction band, is a conductor. Fig. 3c shows that (4, 2) @ (8, 4) @ (12, 6) and (6, 3) @ (12, 6) @ (18, 9) TWCNTs are conductors.

Overall, for chiral (n_1, m_1) @ (n_2, m_2) DWCNTs we investigated, when $n_1 - m_1 \neq 3q$ @ $n_2 - m_2 \neq 3q$ (or $n_1 - m_1 = 3q$ @ $n_2 - m_2 = 3q$), producing a conductor; When $n_1 - m_1 \neq 3q$ @ $n_2 - m_2 = 3q$, producing a semiconductor; For chiral (n_1, m_1) @ (n_2, m_2) @ (n_3, m_3) TWCNTs we investigated, when $n_1 - m_1 \neq 3q$ @ $n_2 - m_2 \neq 3q$ @ $n_3 - m_3 = 3q$ (or $n_1 - m_1 = 3q$ @ $n_2 - m_2 = 3q$ @ $n_3 - m_3 = 3q$), producing a conductor. Moreover, when $n - m \neq 3q$, E_g gradually decreases as the pipe diameter of SWCNTs increases; $n - m = 3q$ SWCNTs also conform to this rule (Table 1). For instance, E_g of (4, 2) (1.41 eV) is larger than that of (8, 4) gap (1.32 eV). E_g of (6, 3) (0.33 eV) is also larger than that of (12, 6) (0.10 eV). Although (4, 2) @ (8, 4) and (8, 4) @ (12, 6) DWCNTs have the same pipe distance (2.07 Å), the pipe diameter and E_g of (8, 4) @ (12, 6) are larger than those of (4, 2) @ (8, 4).

In principle, DOS can be used as visual representation of energy band structures. Fig. 4(a)–(c) shows the total DOS (TDOS) and the partial DOS (PDOS) of (4, 2) (a); (4, 2) @ (8, 4) (b); and (4, 2) @ (8, 4) @ (12, 6) (c) CNTs, respectively. The Fermi level is set at zero. As shown in Fig. 4a, (4, 2) SWCNT is a wide energy gap semiconductor. On top of the valence band area at −9.01 eV, TDOS mainly contributes to carbon atom p_x- and p_z-orbital, resulting in formation of π-bonds.

Below the top of the valence band in range from −11.61 eV to −12.53 eV, TDOS mainly contributes to carbon atom *s*- and