Chiral penta-graphene nanotubes: Structure, bonding and electronic properties

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ABSTRACT

In this work, we carry out a computational study on the structure and electronic properties of penta-graphene nanotubes (penta-CNTs), based on a periodic plane wave-pseudopotential approach. We consider chiral structures, among zigzag and armchair structures which were reported previously. Interestingly, the energetic stability (Binding energy per atom or BEA) of chiral penta-CNTs is comparable with (n,n) penta-CNTs. In such manner that chiral (5,10) and (6,3) penta-CNTs displayed structural stability (phonon dispersion curves), while their thermal stability was sustained by Born-Oppenheimer molecular dynamics (BOMD) calculations. Moreover, penta-CNTs displayed bandgap values which are not directly related to their diameters.

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1. Introduction

Since the discovery of zero-, one- and two-dimensional carbon nanostructures, they have attracted considerable interest due to their remarkable properties and devised applications in nanodevices [1–3]. In 2015, a new two-dimensional carbon allotrope named as penta-graphene (penta-C), was reported as metastable based on theoretical calculations. This means that penta-C represents a local minimum in the potential energy surface and it sustains a binding energy slightly less negative than the ones displayed by graphite and diamond [4]. Penta-C is formed by pentagonal rings of carbon atoms with sp^2 or sp^3 hybridization, and they are organized in a pattern known as Cairo pentagonal tiling [5]. In addition, penta-C was obtained experimentally from the exfoliation of the T12-carbon phase. This new 2D carbon allotrope exhibited interesting mechanical and electronic properties. Unlike graphene, it is considered as an indirect bandgap semiconductor with an estimated bandgap value of 3.24 eV based on Heyd-Scuseria-Ernzerhof (HSE06) functional calculations [6].

In order to construct penta-c nanotubes, we rolled up their 2D monolayers along a chiral vector defined as $c = na_1 + ma_2$, where a_1 and a_2 constitute an orthonormal set (Fig. S1). Noteworthy is that the arrangement of the carbon atoms at the endings of penta-CNTs cannot be denoted as zigzag or armchair as on carbon nanotubes. We named as *chiral* penta-CNTs those structures where the 2D unit cells are forming a spiral along each tube axis. A figure

is provided in the supporting in order to clarify this notation (Fig. S2).

Worthy of note is that previous studies have considered only penta-CNTs with equal n and m indexes. Zhang et al. [4] reported that (n,n) penta-CNTs had thermal (up to 1000 K) and dynamical stability, with calculated GGA/PBE bandgap values spanning a 2.334–2.608 eV range. Regarding penta-CNTs bandgap values, they were independent of their chirality. Avramov et al. [7] reported the binding energy per atom for (n,n) penta-CNTs, finding the (7,7) penta-CNT as the most energetically stable. They found that structures with different n and m indexes, failed to converge to stable tubular structures. Herein we extent the study of penta-CNTs to include structures with a chiral atomic arrangement (where n and m are different). Furthermore, we carried out their structural characterization (bonding), and we calculate their electronic properties (bandgap values).

The present work offers new insight into the study of penta-graphene nanotubes, where contrary to the claim that (n,0) and (0, m) are not enantiomers, we found that they present translational symmetry indeed, and therefore they constitute a pair of enantiomers (Figs. S3–S6). In addition, penta-CNTs with reversed indexes (i.e. penta-CNTs with index (n,m) and (m,n)) are equal, because of their chiral angles which are comprised between 0 and 45 degrees.

2. Computational methods

In this manuscript, first-principles calculations are based on dispersion-corrected density functional theory (DFT-D),

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implemented in the CASTEP package [11], which is able to account for van der Waals interactions by using the method of Grimme et al. [8–10]. We have used a plane wave-pseudopotential approach, which uses plane waves and a norm-conserving pseudopotential to describe the electron-ion interactions [11,12]. The pseudo potential used for C atoms considered a $2s^2 2p^2$ configuration for its valence electrons. We employed the generalized gradient approximation (GGA), and the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional [13]. In all calculations the energy cutoff was at least 680 eV. Noteworthy is that, the selected convergence criteria (force (0.03 eV/Å) and energy (1×10^{-5} eV/atom)) provides support to our main results. Moreover, all atomic positions and lattice parameters of the unit cells were relaxed without any symmetry constrains. The dynamical stability of the proposed structures was examined by their phonon dispersion curves, while Born-Oppenheimer molecular dynamics (BOMD)[8,9] calculations provided insight into their thermal stability, and their energetic stability was tested by binding energy per atom calculations (BEA).

3. Results and discussion

We considered a set constituted by seven penta-CNTs with outer diameters within a range of 6.0–16.0 Å (see Table 1 for cell parameters and Tables S1 and S2 for some Cartesian coordinates). The set was constituted by three (n,n), two (n,0) and two (n,m) nanotubes; (0,m) structures were not considered because they are enantiomers of (n,0) structures. The number of atoms included in the unit cells of penta-CNTs are calculated as follows: (n,0) penta-CNTs hold six times their index n, while (n,n) penta-CNTs are formed by twelve times their index n, respectively (Table 1).

3.1. Geometrical structures

A further analysis of all relaxed structures revealed that (n,n) penta-CNTs might be explained by considering three concentric cylinders, with inner and outer cylinders conformed by carbon atoms with a sp^2 hybridization, while the middle cylinder is constituted by atoms holding a sp^3hybridization. In the case of (7,7) penta-CNT, the inner, middle and outer diameters are 10.46, 11.59 and 12.71 Å, respectively (Fig. 1a).

On the other hand, the structure of (n,m) and (n,0) penta-CNTs are constituted by four concentric cylinders. (5,10) penta-CNT has cylinders with diameters of 11.93, 13.05, 13.11 and 14.22 Å (Fig. 1b), respectively. We provide a figure displaying each cylinder for all the studied nanotubes on the supporting information (Fig. S7).

In Fig. 2, is displayed the bonding of each unit cell of penta-CNTs. We used same colors to identify bonds and each color is maintained into bond distances graphs (located at left side). In such manner that is easy to identify distinct bonds in penta-CNT structures. For example, C=C bonds hold values below 1.40 Å, while bonds larger than 1.47 Å are attributed to simple C—C bonds. (n,0) penta-CNTs feature five different types of bonds, these penta-CNTs have a larger C—C bond of circa 1.70 Å, that has been theoretical and experimentally found previously [14,15]. On the other hand, (n,m) penta-CNTs include six different bond lengths, while (n,n) penta-CNTs feature four different ones (Fig. 2). In Fig. 3 is depicted the translational vectors of the unit cell of (n,0) or (n, n) penta-CNTs which are circa of 3.6 and 5.2 Å, respectively.

3.2. Relative stability

In order to understand the stability displayed by penta-CNTs and establish the relationship among diameter and chirality, we calculated the binding energy per atom (BEA) using the following formula:

$$BEA = (E_n - nE_{atom})/n \tag{1}$$

where E_{atom} is the total energy of one isolated C atom, and E_n is the total energy of n atoms included in the unit cell of the penta-CNTs. Calculated BEA values of all structures were included within the range 8.08–8.32 eV. It is important to note that BEA values of

Table 1
Structural features of relaxed penta-CNTs (inner and outer diameters, calculated GGA-PBE bandgap values) and some reported ones.

(n,m)	Inner diameter, Å	Outer diameter, Å	Atoms inside unit cell	Calculated bandgap, eV	Reported bandgap, eV
(3,3)	4.09	6.08	36	2.64	2.39
(6,3)	6.85	9.02	90	2.30	
(7,0)	7.21	9.51	42	1.79	
(8,0)	8.31	10.65	48	1.75	
(7,7)	10.46	12.71	84	2.40	2.47, 2.46
(5,10)	11.93	14.22	150	2.36	
(9,9)	13.71	15.99	108	2.47	

Calculated values (last column) are included in Refs. [4,7].
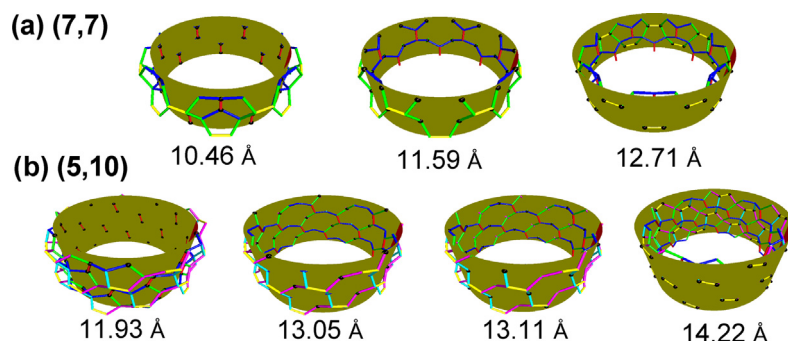

Fig. 1. Unit cells of relaxed penta-CNTs. (a) Three concentric cylinders found in the relaxed unit cell of (7,7) penta-CNT and (b) (5,10) penta-CNT holding four cylinders. Atoms constituting each cylinder are shown in black while their bonds are indicated in various colors.