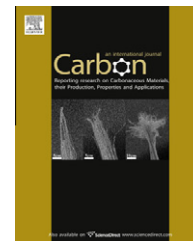


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Structure, energetics, and heteroatom doping of armchair carbon nanotori

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ABSTRACT

Based on armchair carbon nanotubes (CNTs), we construct the structural models of symmetric armchair carbon nanotori of different tubular/radial diameters. Tight-binding (TB) calculations show that the energetic stabilities of these carbon nanotori rely on their symmetries and tubular diameters closely. Density functional theory (DFT) calculations on a carbon nanotorus with substitutional B/N doping reveal that B(N) dopant prefers to occupy heptagonal (pentagonal) sites in order to form a steady six π -electrons orbital. After B/N doping, the electron density of states (DOSs) near the Fermi energy are notably enhanced. The pristine and doped carbon nanotori with diverse geometric and electronic properties provide new opportunities in the applications of nanotechnology.

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1. Introduction

In various superstructures formed from carbon nanotubes (CNTs), a unique member with toroidal (donut-like) structure, namely carbon nanotorus [1,2], has attracted peculiar attention as an ideal nanoscale electromagnetic structural element [3–5] in the future nano-electromechanical systems (NEMS). In 1997, carbon nanotori with typical diameters between 300 and 500 nm were first synthesized by Liu et al. using the laser-growth method [2]. Later, a variety of experimental approaches, such as ultrasonic treatments [6,7], organic reactions [8,9], and chemical vapor deposition (CVD) [10–12], were developed to fabricate carbon nanotori. In particular, the tubular diameter of carbon nanotori is now controllable. Nanotori formed from single-walled [6–9], double-walled [13], triple-walled [14], and multi-walled CNTs [10,15] have been achieved.

Prior to the experimental synthesis, the structural models of carbon nanotori were proposed by Dunlap [1] and researchers in Hitachi Ltd. [16–19]. So far, there have been six major

ways to construct the structural models of carbon nanotori: (1) bending a finite CNT and connecting its ends together [20,21]; (2) connecting two CNTs with different radii [1,22]; (3) constructing from fullerenes [16]; (4) employing the prescription of Goldberg [23] that was previously used in deriving the large-scale fullerenes [17]; (5) constructing through the connection of one zigzag-edged chain of hexagons and another armchair-edged chain of hexagons [19]; (6) sewing the walls of a double-walled CNT at both ends [24]. Itoh and Ihara [19] classified carbon nanotori into five types using the parameters of the inner (r_i) and outer (r_o) diameters, and the height (h) of a nanotorus.

Based on those structural models, atomistic simulations on the physical properties of carbon nanotori were performed with hope in the potential applications in NEMS and other nanoscale devices. Using molecular dynamics simulations incorporated with the Stillinger–Weber-type potential [16–19] or semiempirical quantum chemical approaches [25], it was shown that carbon nanotori are energetically more stable

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than the C_{60} . Due to their unique spatial geometry, carbon nanotori are expected to possess many interesting physical properties, including larger reversible tension (up to 39%) [26] than that of the CNTs (about 5%) [27,28], deformation-related metallic and deformation-insensitive semiconducting electronic properties [29], oscillating Aharonov–Bohm (AB) effects [30–32], and single-file diffusion of water molecules inside the nanotori [33], and so on.

In addition to the pristine samples, doping (especially with B/N) can effectively tailor the chemical and physical properties of the carbon nanostructures. Previous studies on doped C_{60} fullerenes demonstrated that B/N doping could modify their electronic properties to enable the B/N doped C_{60} fullerenes as building units in molecular electronic devices (like molecular rectifiers) [34,35]. Investigations on B/N doped single-walled CNTs showed that the doped CNTs could act as gas sensors with controllable sensitivity [36]. Furthermore, B/N doping can distinctly modify the electronic conductance and band structures of CNTs [37,38]. In 2007, Rodriguez-Manzo et al. [39] revealed that doped carbon nanotori presented unusually large paramagnetism when a small percentage of extra electrons or holes were introduced.

Obviously, the atomic structure of a carbon nanotorus plays an essential role in determining its physical/chemical properties. However, the carbon nanotori in most previous structural models possessed no explicit chirality related to the CNTs, even though they are actually formed from curved CNTs. Furthermore, little is known about doping effects in the carbon nanotori. In this paper, we proposed a simple way to construct the structural models of carbon nanotori from the armchair CNTs. The energetic stabilities of the nanotori with different symmetries and sizes have been systematically examined within a tight-binding (TB) total energy model. To extend the potential applications of these carbon nanotori, density functional theory (DFT) calculations were carried out to study the effects of heteroatom doping on the electronic properties. We found that substitutionally doping B (N) into the heptagonal (pentagonal) sites in the nanotori is energetically favorable and the electronic properties of these carbon nanotori can be tuned by B/N doping.

2. Structural models and computational methods

In our previous work [40], we have developed a simple way to construct the atomistic structural model of carbon nanocoils from an armchair (n, n) CNT. In a similar manner, a single-walled armchair carbon nanotorus can be obtained from a single-walled armchair CNT. As shown in Fig. 1 (left), one pair of pentagons and another pair of heptagons were first introduced in two sides of a piece of an armchair CNT individually. Simply relaxing this structure using an empirical force field would lead to a bent nanotube segment. Using these bent segments as building blocks, armchair carbon nanotori with different shapes (including quadrangle with 280 carbon atoms, pentagon with 350 carbon atoms, hexagon with 420 carbon atoms, heptagon with 490 carbon atoms, and octagon with 560 carbon atoms, see Fig. 1 (right)) can be built, depending on how many building blocks were connected together.

Starting from a CNT with the given chiral vector (n, n) , we constructed nanotori of different radial diameters by varying the length of the tube segment, which is thus equivalent to the side length of polygon of the nanotorus (see Fig. 2). Since the armchair carbon nanotori were constructed on the basis of the armchair CNTs, we denominated the nanotori using chiral vector (n, n) of the corresponding armchair CNTs. Here we introduced a symbol $(n, n)_S^m$ to represent an armchair carbon nanotorus built from a (n, n) armchair CNT, where superscript m (also called side length) denotes the number of sixfold ring between any two nearby heptagons along the circumference orientation, and subscript S defines the shape of a nanotorus (S = quadrangle, pentagon, hexagon, heptagon, and octagon, respectively).

Using a nonorthogonal TB model developed by our group [41], we investigated the energetic stability of a number of armchair carbon nanotori with different tubular diameters and symmetries. In our previous work [41], the TB parameters were carefully fitted to achieve a satisfactory agreement with the experimental or *ab initio* data of the hydrocarbon molecules and nanostructures. Our recent calculations on the carbon nanocoils [40] also validated this TB model, whereas the structures of carbon nanocoils are in analogy with the carbon nanotori.

In addition to TB calculations, the substitutional energy and electronic properties of a 420-atom $(5, 5)_{\text{hexagon}}^1$ armchair carbon nanotorus doped with B or N atoms were investigated using all-electron DFT calculations, as implemented in the DMol³ program [42]. We adopted the double-numerical plus *d* polarization (DND) basis set and the generalized gradient approximation (GGA) with the PW91 parameterization [43] for describing the exchange–correlation interaction.

3. Results and discussion

3.1. Energetic stability of the armchair carbon nanotori

Based on the $(5, 5)$ armchair CNT, we constructed a series of armchair carbon nanotori with different symmetries and radial diameters. Each nanotorus was fully optimized by TB calculations. As shown in Fig. 3a, all armchair $(5, 5)$ carbon nanotori considered here are more stable than C_{60} (−6.51 eV of the binding energy from our TB calculations), in good agreement with the previous calculations [16–19,25]. On the other hand, their binding energy per atom are all less than that of the closed-ended $(5, 5)$ CNTs with the same tubular diameter and number of carbon atoms (see the insert graph of Fig. 3a). This can be easily understood by the curved geometry of nanotori as well as the existence of large portions of pentagonal and heptagonal (6.45% for $(5, 5)_{\text{hexagon}}^1$) rings that are energetically unfavorable. Accordingly, a nanotorus would become more stable as its side length increases (see Fig. 3a, from $m = 1$ to 4) since it is getting closer to a straight tube. We further discuss the energetic stabilities of carbon nanotori with different tubular diameters, which were constructed from the armchair (n, n) CNTs with $n = 5, 6, 7$. As shown in Fig. 3b, with the same side length, stability of the carbon nanotorus almost increases as its tubular diameter becomes larger, which is simply due to the curvature effect as in the case of straight CNTs [44].

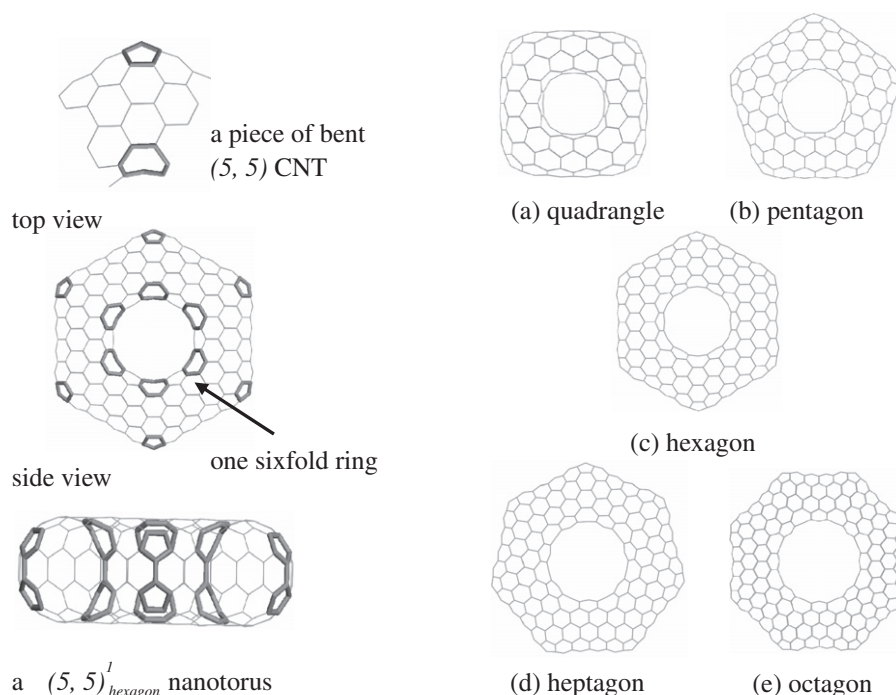


Fig. 1 – Procedures to construct a $(5, 5)_{\text{hexagon}}^1$ armchair carbon nanotorus from a piece of (5, 5) armchair CNT (left) and armchair carbon nanotori constructed with different shapes are shown (right).

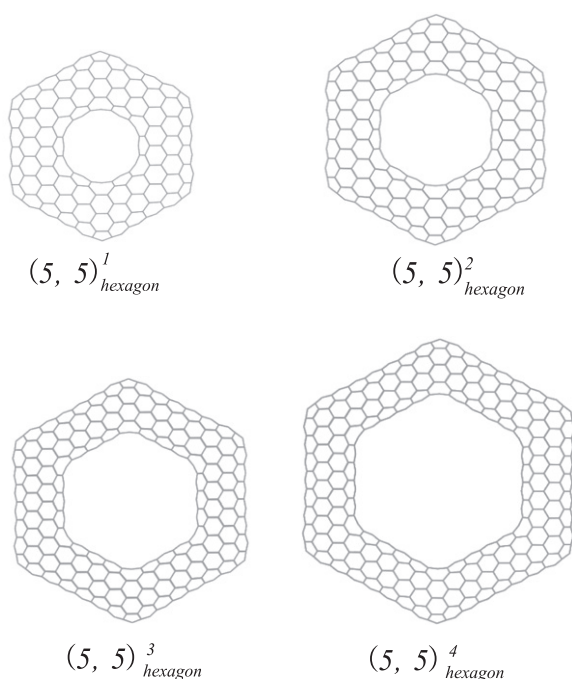


Fig. 2 – Armchair carbon nanotori built from the (5, 5) armchair CNT with different radial diameters are given.

As shown in Fig. 3a and b, the nanotori of hexagonal shape (D_{6h} symmetry) are always more stable than the other shaped nanotori with the same tubular diameters and side length index m . To understand this phenomenon, Fig. 4 displays the average bond lengths (left) and bond angle distributions

(right) for armchair (5, 5) nanotori of different shapes. It can be seen that the hexagonal nanotorus possesses an average bond length of 1.444 Å, closest to that of the straight CNT (1.426 Å) from the same TB calculation. The bond angle distribution of the hexagonal nanotorus (with two major peaks at 118.6° and 119.7°) is also closer to that of the straight CNT (with only two peaks at 118.7° and 119.4°) than the other nanotori. The structural similarity between the D_{6h} hexagonal nanotorus and the straight nanotube implies less bond distortion (and consequently less curvature energy) with regard to the CNT, which may account for its relatively higher stability compared with the other shaped nanotori.

3.2. 2 B/N doping in the carbon nanotorus

The effects of substitutional B/N doping on a $(5, 5)_{\text{hexagon}}^1$ nanotorus with 420 carbon atoms were investigated by all-electron DFT calculations using the DMol³ code. For an individual B or N dopant, we explored all possible heptagonal and pentagonal sites, as well as some representative hexagonal sites for comparison. The substitutional formation energy (E_{sub}) can be calculated from the total energies of all relevant systems using the following equation:

$$E_{\text{sub}} = E(\text{C}_{419}\text{X}) + E(\text{C}) - E(\text{C}_{420}) - E(\text{X}) \quad (\text{X} = \text{B}, \text{N})$$

where $E(\text{C}_{420})$ and $E(\text{C}_{419}\text{X})$ are the total energies for pristine and doped nanotorus, respectively; $E(\text{C})$, $E(\text{B})$, and $E(\text{N})$ are the total energies for an individual C, B, and N atom, respectively. For each type of site, the substitutional formation energies are listed in Table 1. Interestingly, substituting a B atom into heptagonal sites or an N atom into pentagonal sites is energetically more favorable than substitutional doping in

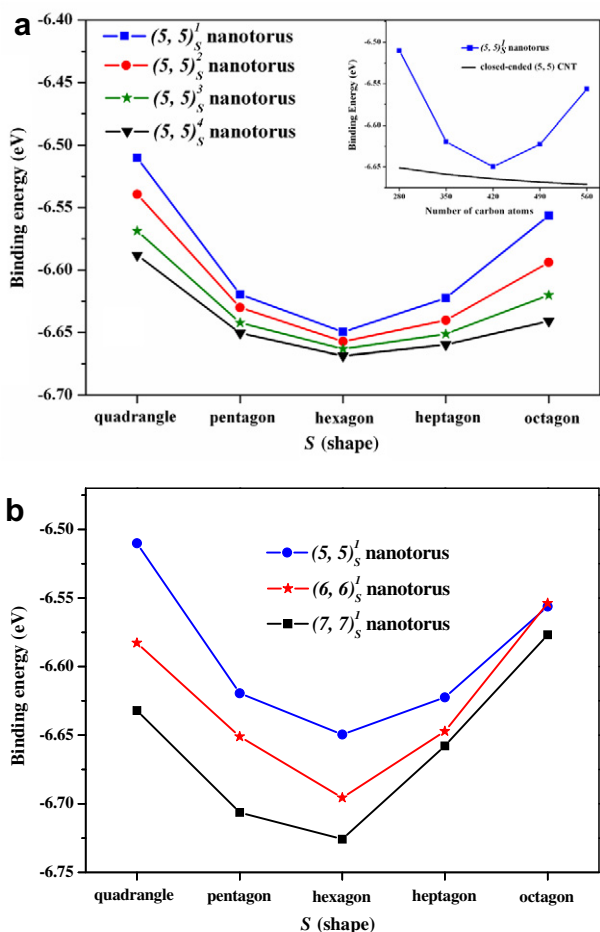


Fig. 3 – Binding energies of armchair carbon nanotori (a) with a given diameter but different side lengths, and (b) with a given side length but different sizes are plotted. The insert graph in figure (a) compares the energies of the $(5, 5)_S^I$ nanotori and the closed-ended $(5, 5)$ CNTs with the same number of C atoms.

the hexagonal sites in either nanotorus or nanotube. In particular, the negative substitutional formation energies for the B dopant suggest that doping a B atom into carbon nanotori is exothermic.

The present finding may be simply related to a previous DFT prediction that introducing pentagon–heptagon defects can enhance the chemical reactivity of CNT [46]. Recently, Gao et al. [47] found that heteroatom-doped carbon-conjugated-materials could be more energetically stable compared with their pure-carbon counterparts, for example when heteroatom (such as B, N) is doped into the heptagonal or pentagonal sites of the carbon-conjugated-materials, six π -electrons can be formed and enjoy a similar π -conjugation with that of the hexagonal ring, according to the Hückel's rule. In such a picture, in a carbon nanotorus the substitutional B (N) dopant prefers to occupy the heptagonal (pentagonal) site, as revealed by our DFT calculations.

We further discuss the effects of B/N doping on electronic properties of the $(5, 5)_{\text{hexagon}}^I$ armchair nanotorus. From our DFT calculations, the pristine $(5, 5)_{\text{hexagon}}^I$ nanotorus is a semiconductor with a small HOMO–LUMO gap of about 0.3 eV. When one B atom is incorporated into a heptagon of a $(5, 5)_{\text{hexagon}}^I$ nanotorus, it slightly enhances the electron density of states (DOS) near the Fermi energy of the nanotorus. When more B atoms are doped, the HOMO–LUMO gap vanishes gradually, which illustrates that the DOS near the Fermi energy of a carbon nanotorus can be tuned through B doping (see Fig. 5). Substitutionally doping N atoms into nanotori shows similar effect. The $(5, 5)_{\text{hexagon}}^I$ nanotorus with one and more N dopants presents no gap, corresponding to metallic properties (see Fig. 5). In addition, simultaneously doping B and N atoms into a nanotorus also enhance its metallicity.

Since the armchair carbon nanotori belong to the graphic systems, their electronic structures are dominated by the delocalized π electrons. It is well known that the straight $(5, 5)$ armchair CNT is metallic [44,45]; but why the $(5, 5)_{\text{hexagon}}^I$ armchair nanotorus constructed from the metallic $(5, 5)$ CNT becomes a semiconductor? Within our structural model,

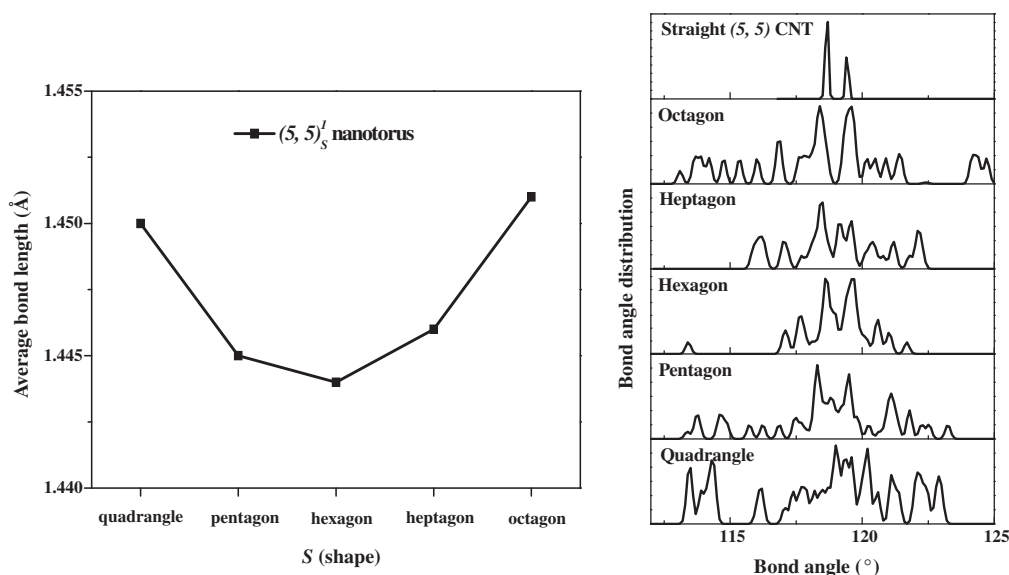
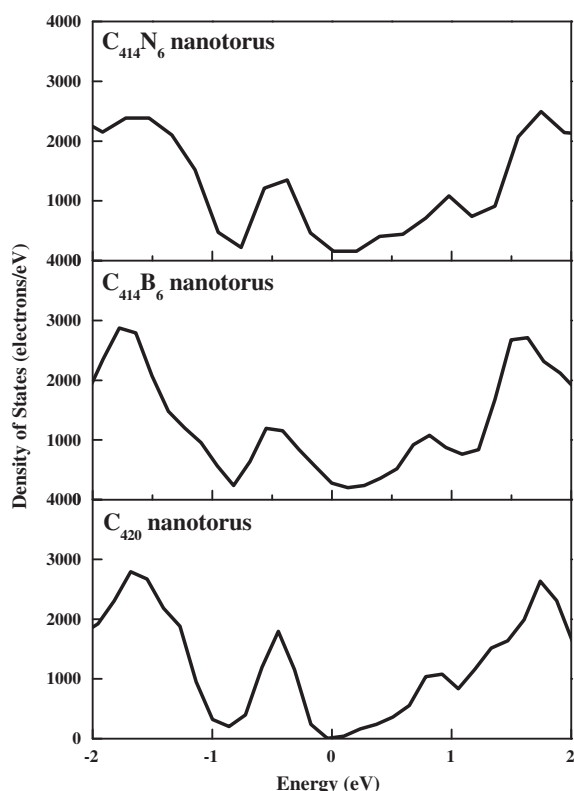


Fig. 4 – Average bond length (left) and bond angle distribution (right) of $(5, 5)_{\text{hexagon}}^I$ armchair carbon nanotori are presented.

Table 1 – The minimal and maximal (in brackets) E_{sub} (eV) for B/N doping into different type of sites in a $(5, 5)_{\text{hexagon}}^1$ armchair carbon nanotorus or a perfect (5, 5) CNT are given.

Substitutional site	Nanotorus		Nanotube	
	Pentagon	Hexagon	Heptagon	Hexagon
E_{sub} of N dopant	3.62 (3.68)	4.16	4.05 (4.22)	4.42
E_{sub} of B dopant	−0.06 (0.07)	−0.11	−0.55 (−0.23)	1.05

**Fig. 5 – Electron DOS of pristine, B- and N-doped $(5, 5)_{\text{hexagon}}^1$ armchair carbon nanotorus (C_{420}) are presented.**

an armchair carbon nanotorus is nothing but a donut-like structure formed by pieces of straight armchair CNTs by introducing pentagons and heptagons on the corners. Thus, one may interpret the modification of the electronic structure of the armchair carbon nanotorus by the existence of pentagons and heptagons, which breaks the perfect six π -electrons orbitals in the originally straight CNT. When a single B atom is doped into the heptagonal site, it gains one electron from the neighboring C atoms, recovering the six π -electrons orbital and thus enhancing the DOS at Fermi level. Similar effect occurs when an N atom is incorporated into the pentagonal site. As more B/N atoms are introduced into a nanotorus, the modification of DOS near the Fermi energy becomes more pronounced. Therefore, doping of B/N atoms into carbon nanotori provides us a way to tailor the electronic properties of carbon nanotori.

4. Conclusions

By introducing pentagons and heptagons appropriately, we constructed a series of structural models of armchair carbon

nanotori with the chirality corresponding to the armchair CNTs. TB calculations revealed that the energetic stability of an armchair carbon nanotorus depends on its symmetry, tubular diameters, and side length. Among the (n, n) carbon nanotori of different shapes (symmetries), the hexagonal one with D_{6h} symmetry is most energetically preferred. Substitutionally doping B/N atoms into the heptagonal/pentagonal defect sites in a carbon nanotorus is more favorable than the hexagonal sites owing to the recovery of the six π -electrons orbitals. Moreover, B/N doping can efficiently modify the electronic properties of the armchair carbon nanotori by enhancing the electron DOS at the Fermi level. The tunable electronic properties of the carbon nanotori as well as the energetic preference of B/N incorporation in the heptagonal/pentagonal sites imply many opportunities in designing novel nanoscale devices using (doped) carbon nanotori as building blocks.

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REFERENCES

- [1] Dunlap BI. Connecting carbon tubules. *Phys Rev B* 1992;46(3):1933–6.
- [2] Liu J, Dai HJ, Hafner JH, Colbert DT, Smalley RE, Tans SJ, et al. Fullerene ‘crop circles’. *Nature (London)* 1997;385(6619):780–1.
- [3] Haddon RC. Electronic properties of carbon toroids. *Nature (London)* 1997;388(6637):31–2.
- [4] Liu L, Guo GY, Jayanthi CS, Wu SY. Colossal paramagnetic moments in metallic carbon nanotori. *Phys Rev Lett* 2002;88(21):217204–6.
- [5] Rodriguez-Manzo JA, Lopez-Urias F, Terrones M, Terrones H. Magnetism in corrugated carbon nanotori: the importance of symmetry, defects, and negative curvature. *Nano Lett* 2004;4(11):2179–83.
- [6] Martel R, Shea HR, Avouris P. Rings of single-walled carbon nanotubes. *Nature (London)* 1999;398(6725):299.
- [7] Komatsu N, Shimawaki T, Aonuma S, Kimura T. Ultrasonic isolation of toroidal aggregates of single-walled carbon nanotubes. *Carbon* 2006;44(10):2093–5.
- [8] Sano M, Kamino A, Okamura J, Shinkai S. Ring closure of carbon nanotubes. *Science* 2001;293(5533):1299–301.
- [9] Geng J, Ko YK, Youn SC, Kim YH, Kim SA, Jung DH, et al. Synthesis of SWNT rings by noncovalent hybridization of porphyrins and single-walled carbon nanotubes. *J Phys Chem C* 2008;112(32):12264–71.

- [10] Ahlskog M, Seynaeve E, Vullers RJM, Haesendonck CV, Fonseca A, Hernadi K, et al. Ring formations from catalytically synthesized carbon nanotubes. *Chem Phys Lett* 1999;300(1–2):202–6.
- [11] Song L, Ci L, Sun L, Jin C, Liu L, Ma W, et al. Large-scale synthesis of rings of bundled single-walled carbon nanotubes by floating chemical vapor deposition. *Adv Mat* 2006;18(14):1817–21.
- [12] Zhou Z, Wan D, Bai Y, Dou X, Song L, Zhou W, et al. Ring formation from the direct floating catalytic chemical vapor deposition. *Physica E* 2006;33(1):24–7.
- [13] Colomer JF, Henrard L, Flahaut E, Tendeloo GV, Lucas AA, Lambin P. Rings of double-walled carbon nanotube bundles. *Nano Lett* 2003;3(5):685–9.
- [14] Yu H, Zhang Q, Luo G, Wei F. Rings of triple-walled carbon nanotube bundles. *Appl Phys Lett* 2006;89(22):223103–6.
- [15] Guo A, Fu Y, Guan L, Zhang Z, Wu W, Chen J, et al. Spontaneously formed closed rings of single-wall carbon nanotube bundles and their physical mechanism. *J Phys Chem C* 2007;111(9):3555–9.
- [16] Itoh S, Ihara S, Kitakami Ji. Toroidal form of carbon C₃₆₀. *Phys Rev B* 1993;47(3):1703–4.
- [17] Ihara S, Itoh S, Kitakami Ji. Toroidal forms of graphitic carbon. *Phys Rev B* 1993;47(19):12908–11.
- [18] Itoh S, Ihara S. Toroidal forms of graphitic carbon. II. Elongated tori. *Phys Rev B* 1993;48(11):8323–8.
- [19] Itoh S, Ihara S. Isomers of the toroidal forms of graphitic carbon. *Phys Rev B* 1994;49(19):13970–4.
- [20] Liu L, Jayanthi CS, Wu SY. Structural and electronic properties of a carbon nanotorus: effects of delocalized and localized deformations. *Phys Rev B* 2001;64(3):033412–33414.
- [21] Hod O, Rabani E, Baer R. Carbon nanotube closed-ring structures. *Phys Rev B* 2003;67(19):195407–8.
- [22] Cox BJ, Hill JM. New carbon molecules in the form of elbow-connected nanotori. *J Phys Chem C* 2007;111(29):10855–60.
- [23] Klein DJ, Seitz WA, Schmalz TG. Icosahedral symmetry carbon cage molecules. *Nature (London)* 1986;323(6090):703–6.
- [24] Nagy CL, Nagy K, Diudea MV. Elongated tori from armchair DWNT. *J Math Chem* 2009;45(2):452–9.
- [25] Oh DH, Park JM, Kim KS. Structures and electronic properties of small carbon nanotube tori. *Phys Rev B* 2000;62(3):1600–3.
- [26] Chen N, Lusk MT, van Duin ACT, Goddard WA. Mechanical properties of connected carbon nanorings via molecular dynamics simulation. *Phys Rev B* 2005;72(8):085416–85419.
- [27] Nardelli MB, Yakobson BI, Bernholc J. Mechanism of strain release in carbon nanotubes. *Phys Rev B* 1998;57(8):R4277–80.
- [28] Walters DA, Ericson LM, Casavant MJ, Liu J, Colbert DT, Smith KA, et al. Elastic strain of freely suspended single-wall carbon nanotube ropes. *Appl Phys Lett* 1999;74(25):3803–5.
- [29] Zhang Z, Yang Z, Wang X, Yan J, Zhang H, Qiu M, et al. The electronic structure of a deformed chiral carbon nanotorus. *J Phys: Condens Matter* 2005;17(26):4111–20.
- [30] Lin MF, Chuu DS. Persistent currents in toroidal carbon nanotubes. *Phys Rev B* 1998;57(11):6731–7.
- [31] Shyu FL, Tsai CC, Chang CP, Chen RB, Lin MF. Magnetoelectronic states of carbon toroids. *Carbon* 2004;42(14):2879–85.
- [32] Liu CP, Chen HB, Ding JW. Magnetic response of carbon nanotori: the importance of curvature and disorder. *J Phys: Condens Matter* 2008;20(1):015206–15210.
- [33] Mukherjee B, Maiti PK, Dasgupta C, Sood AK. Single-file diffusion of water inside narrow carbon nanorings. *ACS Nano* 2010;4(2):985–91.
- [34] Esfarjani K, Ohno K, Kawazoe Y. Band structure and chemical bonding in C₅₈BN heterofullerenes. *Phys Rev B* 1994;50(24):17830–6.
- [35] Xie RH, Bryant GW, Zhao J, Smith VH, Carlo AD, Pecchia A. Tailorable acceptor C_{60-n}B_n and donor C_{60-m}N_m pairs for molecular electronics. *Phys Rev Lett* 2003;90(20):206602–4.
- [36] Peng S, Cho K. Ab initio study of doped carbon nanotube sensors. *Nano Lett* 2003;3(4):513–7.
- [37] Latil S, Roche S, Mayou D, Charlier JC. Mesoscopic transport in chemically doped carbon nanotubes. *Phys Rev Lett* 2004;92(25):256804–5.
- [38] Zhao J, Xie RH. Electronic and photonic properties of doped carbon nanotubes. *J Nanosci Nanotech* 2003;3:459–78.
- [39] Rodriguez-Manzo JA, Lopez-Urias F, Terrones M, Terrones H. Anomalous paramagnetism in doped carbon nanostructures. *Small* 2007;3(1):120–5.
- [40] Liu L, Gao H, Zhao J, Lu J. Superelasticity of carbon nanocoils from atomistic quantum simulations. *Nanoscale Res Lett* 2010;5(3):478–83.
- [41] Zhao J, Guo X, Wen B. A nonorthogonal tight-binding model for hydrocarbon molecules and nanostructures. *Mol Simul* 2007;33(8):703–9.
- [42] Delley B. An all-electron numerical method for solving the local density functional for polyatomic molecules. *J Chem Phys* 1990;92(1):508–17.
- [43] Perdew JP, Wang Y. Accurate and simple analytic representation of the electron-gas correlation energy. *Phys Rev B* 1992;45(23):13244–9.
- [44] Dresselhaus MS, Dresselhaus G, Phaeton A. Carbon nanotubes: synthesis, structure, properties, and applications. Berlin: Springer; 2001.
- [45] Martel R, Shea HR, Avouris P. Ring formation in single-wall carbon nanotubes. *J Phys Chem B* 1999;103(36):7551–6.
- [46] Yu LM, Zhao JJ, Qiu JS, Hao C, Wang H. Sidewall fluorination and hydrogenation of single-walled carbon nanotubes: a density functional theory study. *Front Phys China* 2009;4(3):393–7.
- [47] Gao X, Zhang S, Zhao Y, Nagase S. A nanoscale jigsaw-puzzle approach to large π -conjugated systems. *Angew Chem Int Ed* 2010;49(38):6764–7.