PHYSICAL REVIEW B **71**, 033404 (2005)

First-principles study of the (2,2) carbon nanotube

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(Received 10 July 2004; published 7 January 2005)

Using first-principles calculations, we investigate the structural stability and electronic properties of the smallest (2,2) carbon nanotube as the inner wall of the double-walled carbon nanotubes. The results indicate that an isolated (2,2) carbon nanotube is unstable upon unrolling in free space, while it can exist within (6,6) and, especially, within (7,7) carbon nanotubes. In addition, a spontaneous symmetry breaking of the isolated (2,2) nanotube produces an energy gap at Fermi level converting it into a semiconductor.

DOI: 10.1103/PhysRevB.71.033404 PACS number(s): 61.46.+w, 31.10.+z, 31.15.Ar

Carbon nanotubes (CNTs) have attracted much attention owing to their special properties and intriguing applications in many fields.[1–7] It has been demonstrated that they possess remarkable mechanical properties and interesting electric transport behavior.[8] The novelty of these tubes, caused mainly by the small diameter, may motivate great achievement of CNTs with the smallest possible diameter. The diameter of free-standing single-walled carbon nanotubes (SWCNTs) can be as large as a few tens of nanometers, while the fabrication of small diameter nanotubes advances step by step. Carbon nanotubes with a diameter smaller than that of C_{60} fullerene (0.7 nm) were first discovered in the spatially confined environment. Xie *et al.*[9] and Qin *et al.*[10] subsequently reported multiwall carbon nanotubes with the diameter of the inner core of as small as 0.5 and 0.4 nm, respectively. And 0.4-nm SWCNTs have also been proved to exist in the 1-nm-sized channels of zeolite channels.[11] In 2003, 0.4-nm free-standing SWCNTs were successfully grown on small catalyst particles deposited on porous materials.[12,13] Using high-resolution transmission electron microscopy (HRTEM), Zhao *et al.*[14] further found that a stable 0.3 nm CNT can be grown inside multiwalled carbon nanotubes (MWCNTs).

For energetic considerations, Sawada *et al.*[15] pointed out that 0.4 nm was the minimum diameter limit of a CNT in free space. Tight-binding molecular dynamics simulations[16] show that the carbon tubes with diameters smaller than 0.4 nm are energetically less favorable than a graphene sheet but some of them are indeed mechanically stable at temperatures as high as 1100 °C. Sano *et al.*[4] investigated an open ended (4,0) CNT as a possible candidate for the sub-0.4 -nm CNT formed in the center of a MWCNT. In their results, the 0.4-nm diameter constraint suggested by Sawada *et al.* was not necessary to apply in the tightly restricted reaction zone, for example, within a SWCNT. In addition, it is expected that the structural and electronic properties of ultrasmall nanotubes are different from those of larger ones due to the large curvature effect. Local density approximation (LDA) calculations[17,18] shows that (5,0) tube becomes a metal, rather than a semiconductor predicted by the band-folding scheme. Compared with large nanotubes, 0.4-nm nanotubes exhibit more remarkable electronical, optical properties, such as one-dimensional superconducting fluctuation, polarized light adsorption,[19] etc. These facts imply that the nanotube with diameter smaller than 0.4 nm is of significant importance. Density functional calculations indicate that the 0.3 nm CNT is the armchair CNT (2,2) with a radial breathing mode at 787 cm^{-1}.[14] In view of these findings, there are some open questions such as the following. (1) Whether the (2,2) armchair CNT is capable of existence? (2) How about its electronic properties of this ultrathin CNT? (3) As the innermost shell of the multiwalled nanotubes, does it match with the outer shell? In order to justify these questions, we study here the structures and properties of (2,2) nanotube as inner wall of various (n,n) armchair CNTs using the first-principles calculations.

We use first-principles plane-wave pseudopotential density functional theory as implemented in the CASTEP code.[20] For the exchange and correlation term, the generalized gradient approximation (GGA) is used as proposed by Perdew, Burke, and Ernzerhof.[21] We use ultrasoft pseudopotentials[22] for the carbon atoms and a plane-wave cutoff of 350 eV. The Brillouin zone integration is performed within the

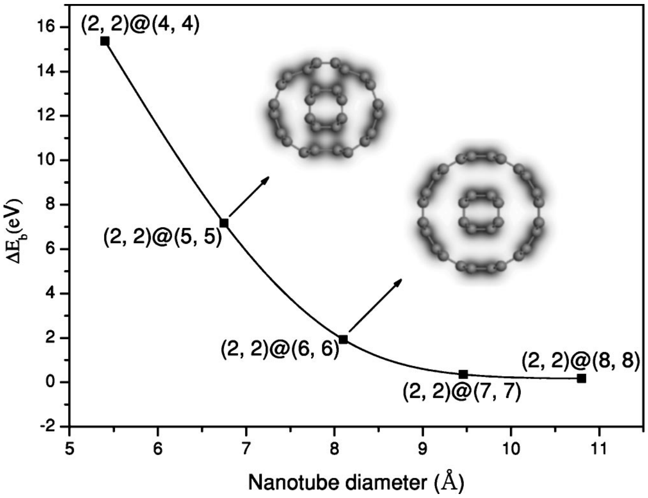

FIG. 1. Binding energy as a function of diameter for (2, 2)@(n, n), $n=4-8$. The inset shows the charge density of (2, 2)@(5, 5) and (2, 2)@(6, 6) DWCNTs.

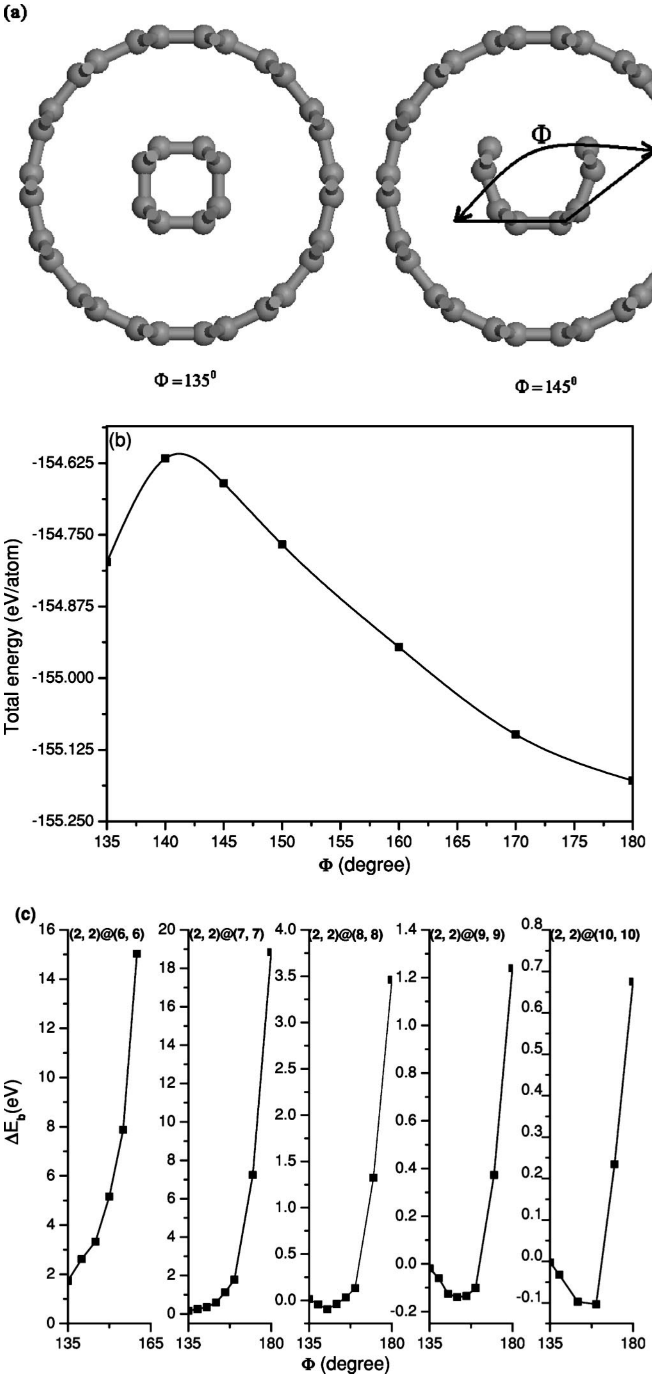

FIG. 2. (a) Schematic illustration of the the (2, 2) ribbon inside (7, 7) CNT. The projected bond angle Φ determines the degree of uncurling of the (2, 2) CNT. As Φ is 135°, the inner structure is a (2, 2) CNT. $\Phi=140°$ and $\Phi=150°$ corresponds to the different uncurling ribbon obtained from the splitting of the (2, 2) CNT. (b) The total energy versus the uncurling angle Φ for a (2, 2) CNT in free space. (c) The binding energy ΔE_b versus the uncurling angle Φ for a (2, 2) CNT in a larger $(n,\ n)$ $(n=6-10)$ CNT.

Monkhorst-Pack scheme[23] using between $1\times1\times10$ to $2\times2\times10k$ points. Optimal atomic positions are determined until the magnitude of the forces acting on all atoms became less than 0.1 eV/Å, which also converge the total energy within 0.5 meV. In addition, finite basis set corrections are also included. We adopt a supercell model in which double walled carbon nanotubes (DWCNTs) are arranged with their adjacent outer walls separated by 1 nm.

The relative stabilities of $(2,2)@(n,n)$ $(n=4-8)$ nanotubes are determined by the binding energies. For instance, a small binding energy means strong binding of the (2,2) to the outer CNT, which are defined by the formula

$$\Delta E_b = E_{\text{tot}}[(2,2)\ @\ (n,n)] - E_{\text{tot}}(2,2) - E_{\text{tot}}(n,n),$$

where $E_{\text{tot}}(2,2)$ and $E_{\text{tot}}(n,n)$ $(n=4-8)$ are the total energies of isolated (2,2) and (n,n) $(n=4-8)$ CNTs, and the $E_{\text{tot}}[(2,2)@(n,n)]$ $(n=4-8)$ is the total energy of the

DWCNT. The binding energy as a function of nanotube diameter is shown in Fig. 1. As shown in Fig. 1, the binding energy between (2,2) inner and outer single-walled nanotubes decrease as the outer tube's radius increase. One finds that the (2,2)@(4,4) has an unfavorable binding energy (15.37 eV) compared with other DWCNTs. However, binding energy becomes much more favorable as nanotube diameter increases. In the (2,2)@(7,7) case, the binding energy still has a small positive value (0.36 eV). The calculated binding energy of 0.36 eV represents the interlayer interaction which include van der Waals effect corresponding to the interlayer distance.[24,25] This indicates that the interaction between (2,2) and (7,7) tubes are still repulsive. If the formation of (2,2) tube inside (7,7) tube might be possible as a metastable state, the overall double-walled nanotube is endothermic. The binding energy of (2,2)@(8,8) is 0.18 eV. It implies that binding energy would tend to zero as CNT diameter increases. However, the fact that the binding energy approaches zero for large n does not mean that the DWCNT is stable. Indeed, each tube may adopt a configuration close to the one it has in free space when the interwall distance is large. In the inset of Fig. 1, we show the charge density of (2,2)@(5,5) and (2,2)@(6,6) DWCNTs. It is found that the radius of (5,5) CNT is contracted in the *y* direction, while it is elongated along the *x* direction. As a result, the circular cross section is distorted to an elliptical one. From the charge density, there is clear covalent character in the interaction between the carbon atoms of (2,2) and the carbon atoms of (5,5). This may mean that it is less favorable to form individual (2,2) CNT in the (5,5) CNT. Similar phenomena can be seen for the (2,2)@(4,4) arrangement as well (not shown in Fig. 1). However, in the charge density plot of (2,2)@(6,6) DWCNT, it displays that the (2,2) CNT locates at the central position inside the (6,6) CNT. Insertion of (2,2) into (6,6) does not result in deformation of (6,6) CNT. No significance electron density overlap is found in the intersticial space between (2,2) and (6,6) CNT. So, from the charge density point of view, the smallest armchair CNT accommodating (2,2) nanotube may be (6,6) CNT.

Whether all of CNTs with diameter larger than (6,6) can contain stable (2,2) CNT? To further analysis the stability of (2,2) confined in CNTs, we develop a method similar to that of Sano *et al.*[4] In our work, we use (2,2) CNT and the uncurling ribbon obtained from the splitting of the CNT. We compare the energy of the CNT and the ribbon inside a larger CNT (n,n) $(n=6-10)$. The top view of the (2,2) CNT placed inside (7,7) CNT is shown in Fig. 2(a). The projected bond angle Φ determines the degree of uncurling of the (2,2) CNT. As Φ is increased from 135° to 180°, the inner structure opens from a (2,2) CNT to a flat ribbon. The total energy versus the uncurling angle Φ for a (2,2) CNT in free space is shown in Fig. 2(b). When the tube is only slightly open with a small Φ (about 135° to 140°), there is an increase in the energy of the structure due to creation of dangling bonds at the open edges. As the uncurling angle is increased beyond 140°, the total energy decreases due to the reduction in the stress induced by curvature. In free space, the total energy is lower for $\Phi=180°$ than for $\Phi=135°$ indicating that the tubular structure is energetically less preferable than the graphene ribbon in this small size, consistent with the reports by Sawada *et al.*[15] However, the dependency of the binding energy versus the uncurling angle in a larger CNT is dramatically different as shown in Fig. 2(c). It can be seen that the binding energy increases sharply with Φ in the cases of (2,2)@(6,6) and (2,2)@(7,7). In the cases of $(2,2)@(n,n)$ $(n=8-10)$, there are distinctive minimum points on the ΔE_b curve between $\Phi=135°$ to $\Phi=180°$. It means that the (2,2) tubular structure would be stable inside (6,6) and (7,7) CNTs with the tightly restricted of the outer tube. With the diameter of outer nanotube larger than (7,7), (2,2) tubular structure is unlikely to be stable inside CNT. In our calculation, the minimum interatomic distance between (2,2) and (6,6) is 0.286 nm, which is smaller than that of interlayer distance in graphite (0.34 nm). However, the minimum interatomic distance between (2,2) and (7,7) is 0.33 nm, close to the interlayer distance in graphite and is consistent with HRTEM measurements.[14] So the most favorable geometry of DWCNT containing (2,2) is (2,2)@(7,7). Moreover, if there are any other host materials with diameter comparable to (7,7) tube, the formation of (2,2) tube might also be possible.

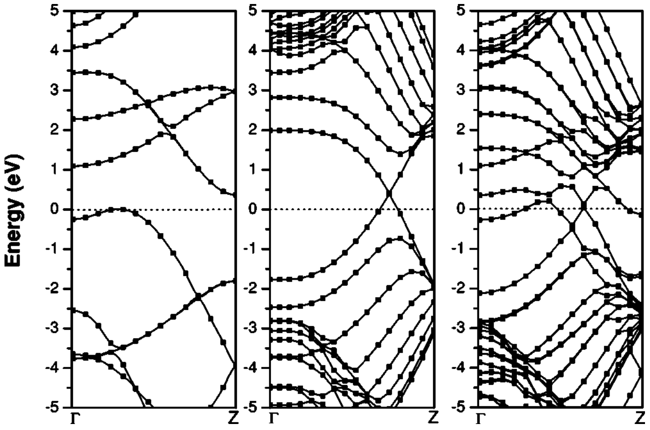

FIG. 3. Band structures for (a) individual (2, 2) nanotube, (b) individual (7, 7) nanotube, and (c) (2, 2)@(7, 7) DWCNT.

The band structures for individual (2,2), (7,7) and (2,2)@(7,7) nanotubes are shown in Fig. 3. In Fig. 3(a), we can find that there is a small energy gap about 0.2 eV near the Fermi level, and this turns it into an indirect semiconductor. The reason may be that severe steric distortion makes the tube far more susceptible to a spontaneous symmetry breaking compared to larger diameter (n,n) tubes, and engenders the Peierls gap near the Fermi level as is held in our case.[26] Figure 3(b) shows that the armchair (7,7) is metallic, due to the fact that there are two energy bands near Fermi energy and the two bands cross with ε_F at $k \simeq 2\pi/3$ of Brillouin zone, which is required by symmetry and suggested by the band-folding theory. In the case of (2,2)@(7,7) [Fig. 3(c)], the band structure seems to be a superposition of the individual (2,2) and (7,7) nanotubes. Thus the (2,2)@(7,7) system exhibits metallic character. Therefore, it is expected that (2,2)@(7,7) DWCNT consisting of the semiconducting (2,2) nanotube would exhibit an interesting variation of electronic structures around the Fermi level. The formation of the (2,2)@(7,7) double-walled structures which introduces a new structural multiplicity in the (2,2) nanotube causes the metallization of the structures. The results indicate that the

DWCNT with thin innermost nanotube (2,2) may has the potentiality of a possible application for electron devices.

In summary, we have investigated the comparative stability and electronic properties of ultrathin (2,2) nanotube as the innermost shell of the multiwalled nanotubes using first-principles calculations. The results indicate that an isolated (2,2) is unstable upon unrolling in free space, while it would be stable at (6,6) and (7,7) CNTs with tightly restricted outer tubes. The minimum interatomic distance between (2,2) and (7,7) is 0.33 nm, which is close to the interlayer distance in graphite and is consistent with HRTEM measurements. So the most favorable geometries with 0.3 nm found in experiments is (2,2)@(7,7). A spontaneous symmetry breaking of isolated (2,2) nanotube produces an energy gap at the Fermi level converting it into a semiconductor, which cannot be explained by the zone-folding theory. This ultrathin nanotube as the innermost shell of the multiwalled nanotubes has potential applications in nanoelectronics, nanomechanics, and nanomaterials.

This work was supported by the Project Supported by Scientific Research Fund of Hunan Provincial Education Department (Grant Nos. 03A046, 03B039, 03JZY3019, and 04C647), and partly by the Science & Technology Foundation for Ministry of Education (Grant Nos. 204099 and 03JJY3010).

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