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Smallest Carbon Nanotube Assigned with Atomic Resolution Accuracy

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ABSTRACT

The smallest carbon nanotubes with the chiral index (3,3), (4,3), or (5,1) were unambiguously identified for the first time. They were grown inside single-wall carbon nanotubes with the diameter of 1.0–1.2 nm, and the chiral indices were experimentally assigned beyond a doubt by an aberration-corrected high-resolution transmission electron microscopy (HR-TEM). In contrast to a theoretical prediction, the (3,3) nanotube is rather unstable and extremely sensitive to the electron beam and, therefore, may not survive alone without the protection of outer nanotube. The cap structure of (3,3) nanotube is also well-explained by a half-dome of C_{20} fullerene, which consists of six pentagons only.

What is the smallest diameter that a carbon nanotube can really have? Since a theoretical calculation predicted that the smallest diameter is ∼0.4 nm for a stable single-walled carbon nanotube (SWNT),[1] many efforts have been made to produce the smallest carbon nanotube and identify its atomic structure. Qin et al. and Tang et al. both claimed that they found a smallest nanotube with the diameter of ∼0.4 nm as an innermost layer inside multiwalled carbon nanotubes[2] or confined inside the channel of porous zeolite.[3] However, they simply measured the diameter as a distance between two dark lines associated with tube walls in conventional high-resolution transmission electron microscopy (HR-TEM) images. Regrettably, the image simulation has already revealed that the simple measurements of diameters with a ruler will exhibit systematic and substantial deviation from the true diameters (the diameter can be underestimated as large as 30%),[4,5] which indeed undermines the reliability of the reported works. In order to unambiguously identify the diameter of smallest carbon nanotube by TEM, the assignment of its chiral index with the relevant image simulation[4] or the nanoprobe diffraction is indispensable.[6] In this viewpoint, the smallest carbon nanotube, which has been experimentally identified so far, is the (5,5) nanotube (the diameter is ∼0.7 nm) within a double-wall carbon nanotube (DWNT).[7] As for the SWNT with diameter of about 0.4 nm, there are three possible structures, zigzag (5,0) (0.39 nm in diameter), armchair (3,3) (0.41 nm in diameter), and chiral (4,2) (0.41 nm in diameter), none of which has ever been identified experimentally. In this study, we attempted to produce the smallest carbon nanotube with the diameter of ∼0.4 nm as an inner tube of DWNT and successfully identified their chiral indices by using a modern HR-TEM with a post-specimen aberration corrector, which has a large merit for decreasing the delocalization effect and reaches its point resolution better than 0.14 nm at 120 kV accelerating voltage.[8] Using this technique, the carbon network of the smallest carbon nanotube can be faithfully imaged (as a moiré pattern) with hardly any error in measurement and therefore the chiral index assignment can be performed beyond a doubt.

A suitable sample is a prerequisite in order to assign the smallest SWNT. Free-standing SWNTs with the smallest diameters are intrinsically unstable under electron beam irradiation and supposed to be quite sensitive to oxidation from the atmosphere; therefore, it should be hard to identify.[9] Also those nanotubes confined in the thick multiwalled carbon nanotubes or lying on the supporting amorphous carbon film can always disturb observation. To bypass these problems, the smallest SWNTs were directly synthesized by pyrolysizing the ferrocene molecules ($FeCp_2$) inside the commercial available high-pressure CO conversion (HiPCO) SWNTs, which have a mean diameter of ∼1.1 nm. The HiPCO SWCNTs were annealed in air at 723 K for 1 h to open the end of the SWNTs. Ferrocene ($FeCp_2$) was inserted in SWNTs by exposure of SWNTs to a vapor phase of $FeCp_2$. A glass tube with two separated sub-tubes was chosen as the reaction vessel. SWNTs and some $FeCp_2$ were loaded in the sub-tubes, respectively. This tube was evacuated to 10^{-3} Pa. The sub-tube loaded with SWNTs was heated up to 723 K for 2 h to remove the adsorbed impurity, whereas the sub-tube loaded with $FeCp_2$ was kept at room temperature. The tube was then sealed and heated in a furnace up

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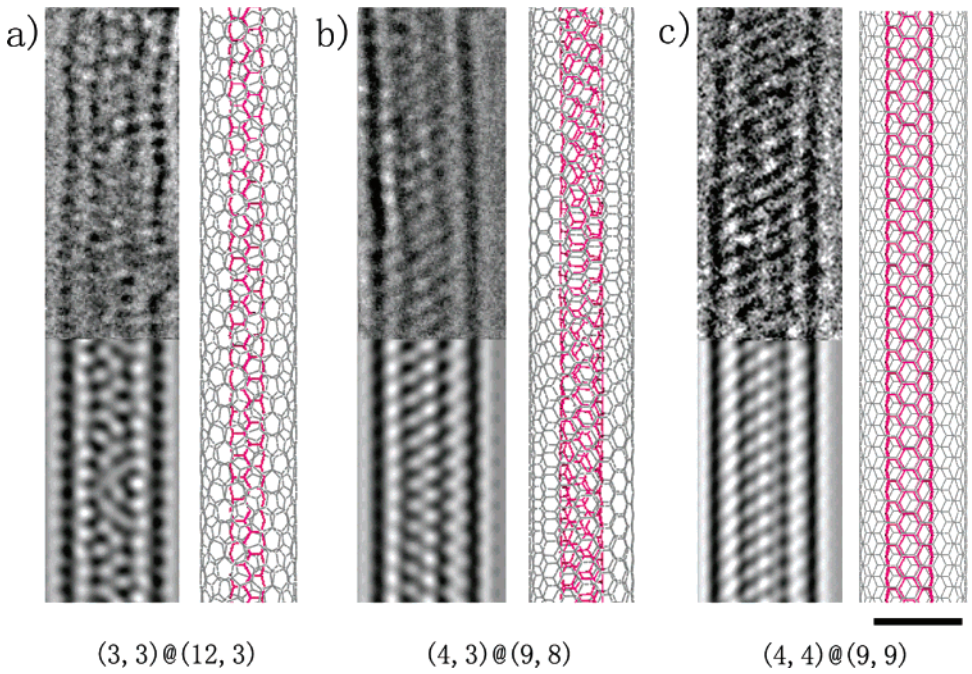

Figure 1. Set of HR-TEM image (up left), simulation (down), and schematic model (right) for (a) (3,3)@(12,3) DWNTs, (b) (4,3)@(9,8) DWNTs, and (c) (4,4)@(9,9) DWNTs. Scale bar = 1 nm.

to 573 K. After maintaining the temperature for 48 h, the tube was cooled to room temperature. The so-obtained materials were $FeCp_2$@HiPCO SWNTs. In order to remove $FeCp_2$ coated on the SWNT surface, the SWNTs were washed with alcohol for several times until the solvent was colorless. Conversion of the $FeCp_2$ inside HiPCO SWNTs to the inner SWNTs was carried out via annealing at 1273 K in 10^{-3} Pa for 24 h. After annealing, the yield of the smallest SWNTs was about 15∼20%, other products were carbon graphite materials. The mean diameter of HiPCO SWNT is relatively small and well suited for the inner tube growth with 0.4 nm diameter when the typical interlayer distance ∼0.35 nm is taken into account. (Note that, in a previous study, annealing $FeCp_2$ inside larger SWNTs with mean diameter of ∼1.4 nm at high temperature converted the filled $FeCp_2$ into the inner tubes, forming the DWNTs with the mean inner diameter of 0.7 nm.[10])

The prepared "DWNTs", i.e., the smallest tubes grown inside the outer SWNTs, were put on a holey carbon grid for TEM observations. A field emission TEM (JEOL-2010F, operated at 120kV) equipped with a post-specimen spherical aberration coefficient (C_s) corrector (CEOS) was used for the HR-TEM imaging. The C_s value was set to 0.02−0.1 μm and the defocus condition was slightly underfocused (Δf = −5 to −10 nm) in this study, so that the spatial point resolution of the HR-TEM was 0.14 nm, which is sufficient to visualize the typical carbon−carbon distance (0.14 nm). Carbon nanotubes are sensitive to electron irradiation; for instance, Ajayan et al. observed nanotubes shrank from 1.4 to 0.4 nm under continuous electron beam irradiation.[11] In order to minimize the electron irradiation effect, we employed optimized parameters for imaging by reducing the exposure time (1 s for one frame) and electron dose as low as possible. A sequence of HR-TEM frames were acquired and superimposed (four frames for 1 image shown below) to increase the signal-to-noise (S/N) ratio for display. In the HR-TEM image, the apparent chiral angle can be measured with accuracy of ∼5°; the apparent diameter can be converted to the approximate true diameter with an error of ∼0.05 nm. A systematic image simulation for the smallest DWNTs with various diameters has been performed for the wide range of diameters with 0.01 nm step to achieve the final set of chiral indices.

Table 1. Summary of the Assigned Best Fit Chiral Indices, Diameter, and Interlayer Distance of Inner and Outer Tubes[a]

DWNT	chiral index (inner/outer)	calculated diameter D_{inner}/D_{outer} (nm)	calculated interlayer distance (nm)
1	(3,3)@(12,3)	0.407/1.077	0.335
2	(3,3)@(10,6)	0.407/1.097	0.345
3	(4,3)@(9,8)	0.476/1.154	0.339
4	(4,4)@(9,9)	0.542/1.221	0.340
5	(5,1)@(11,5)	0.436/1.110	0.337
6	(5,2)@(15,0)	0.489/1.175	0.343
7	(5,3)@(9,9)	0.548/1.221	0.336

[a] The C−C bond lengths are assumed unchanged.

Figure 1 shows some HR-TEM images of the DWNTs, accompanied with the schematic models and the simulated images based on the models. Unlike previous HR-TEM images in which the DWNTs appeared only four dark lines,[5] the HR-TEM images taken by the C_s-corrected microscope does exhibit fine structure of graphene layer network with atomic resolution. It is generally more complicated to assign the (n, m) value of the constituent tubes because of the intense interference of the Fresnel fringes arising from two adjacent layers.[12] Systematic image simulations are therefore

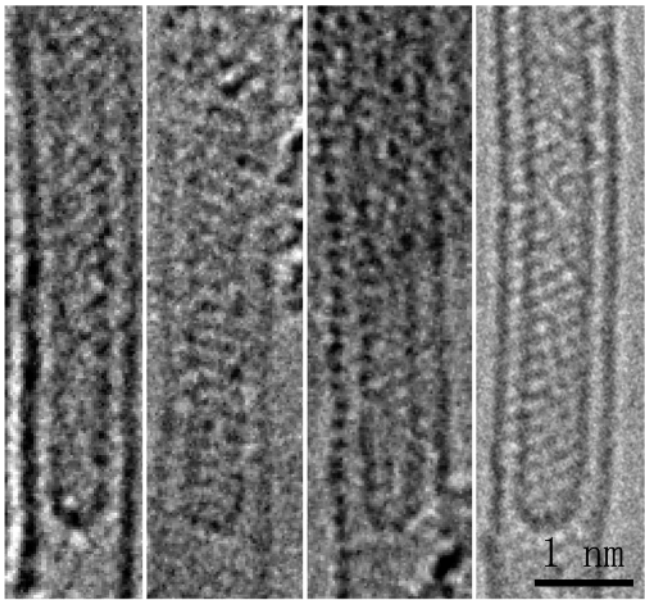

Figure 2. Typical HR-TEM images of the newly formed inner capped tubes.

necessary to corroborate the observed images and carefully extract the pair of chiral indices.[6,12,13] By carefully comparing the simulated images with the observed images, the structures of both inner and outer tubes can be unambiguously assigned.

The HR-TEM image in Figure 1a (up left) represents a DWNT with diameters of 0.4 nm/1.1 nm. There are three possible structures for the 0.4 nm inner tube: (3,3), (4,2), and (5,0). The experimental image is well reproduced by a simulation (down left in Figure 1a) arising from a DWNT (3,3)@(12,3) (right in Figure 1a). The inner (3,3) tube (in red) shown in Figure 1a is an achiral SWNT. The simulations were also performed on the (4,2) and (5,0) tubes (see the Supporting Information for more details). It is worth noting that the DWNT with inner tube of 0.4 nm in diameter is the smallest possible DWNT. It definitively broke the smallest record (~0.7 nm for inner tube) held by DWNT derived from C_{60} peapods.[14]

Various DWNTs with innertubes of ~0.5 nm in diameter were also identified. After the comparison with the systematic simulations, the innertubes of 0.5 nm were identified as (4,3), (4,4), or (5,1). The results with the detailed chirarity analysis are summarized in Table 1. There are no chiral correlations between the constituent nanotubes in the examined DWNTs; that is, the chiral angles in the both constituent nanotubes in DWNT do not show any preference. The interlayer distances of the ultra-small DWNTs are quite uniform (0.340 ± 0.005 nm) in comparing with other reported DWNTs with larger diameters which have relatively broad distribution (from 0.36 to 0.40 nm).[12] This difference is significant and suggests that the inner tube of smaller diameter should have much more interaction with the outer tubes.

The innertubes produced in this method are always capped. There is no iron particle (catalyst) found near the cap (Figure 2). The caps of SWNTs can be associated with the related half-fullerene structures, which are composed of pentagons and hexagons. Although a (5,5) (0.68 nm in diameter) SWNT should have a cap structure of half a C_{60} fullerene (six pentagons and ten hexagons),[15] a (3,3) SWNT (0.41 nm in diameter) can be capped by a half dodecahedron (C_{20}) (the smallest fullerene composed only pentagons).[16] Much attention has been paid to the cap structure in an effort to reveal the growth mechanism of SWNT, since the structure of a cap may determine the chirality of the nanotube.[17] However, the cap structures have never been experimentally determined so far. The difficulty in observing the cap structure lies in its instability during the observation as well as the resolution problem. Especially as for the possible smallest C_{20} fullerene, it has been found only in gas-phase with a lifetime of only 0.4 ms, and its structure has not yet been definitely assigned.[15] The smallest cap is therefore reasonably considered as a most labile part of the SWNT and may not survive during the TEM observation. Nevertheless, we have focused on the cap structure of the smallest

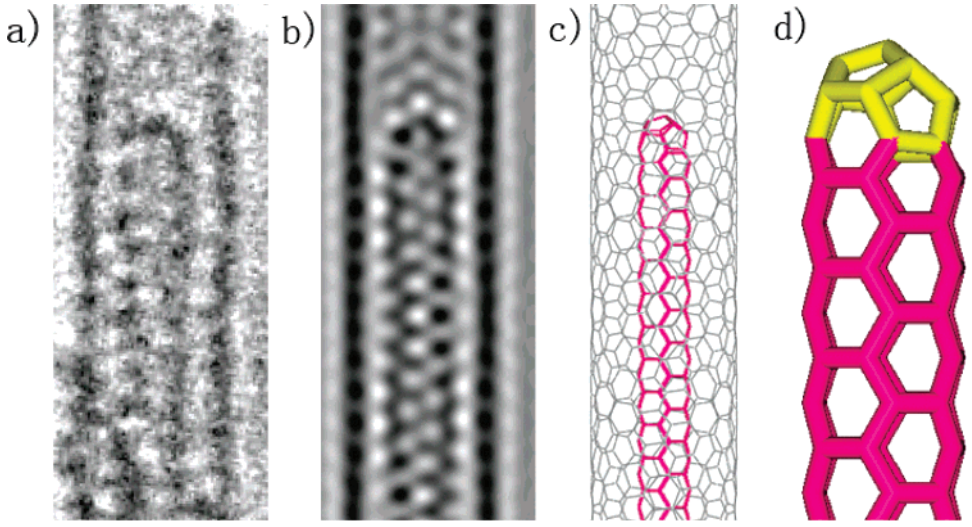

Figure 3. (a) HR-TEM image of the cap region of (3,3)@(10,6) DWNT, (b) simulated images, and (c) schematic model. (d) The inner cap structure can be modeled as half a C_{20} fullerene consists of six adjacent pentagons (shown in yellow).

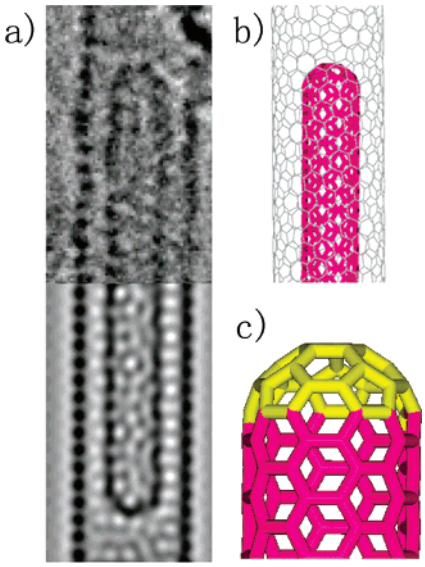

Figure 4. Capped (5,5) SWNT inside a (16,3) SWNT. (a) The observed HR-TEM image (up) showing a moiré pattern and the simulated image (down). (b) The schematic model. (c) The (5,5) SWNT can be exactly capped with half a C_{60} fullerene (yellow), the smallest fullerene that avoids adjacent pentagons.

SWNT in the hope that the outer tube can protect and stabilize the inner cap structure.

Figure 3 shows a comparison of the configuration of a capped (3,3) tube inside a (10,6) tube with the experimentally observed image (Figure 3a). Although the atomic structure cannot be directly derived from the HR-TEM image, the size and curvature are quite similar to the expected C_{20} half dome. The quick electron beam damage is also noticed. The cap of the (3,3) tube (Figure 3c) is modeled of six adjacent pentagons (shown in yellow), which indeed violate the isolated pentagon rules.[18] The image of the capped (3,3) SWNT demonstrates the positive relationship between the smallest fullerene and the smallest SWNTs for the first time. The (5,5) SWNT capped with half a C_{60}, the smallest fullerene that avoid adjacent pentagons,[19] has also been observed.

The assignment of the SWNT structure by means of Raman spectroscopy on the present specimen is extremely difficult for the following reasons: (i) the interaction between two concentric tubes is robust and (ii) the curvature and anisotropic effect, which affect the C−C bond nature, may not be negligible for the smallest SWNT.

In conclusion, we have synthesized the smallest SWNTs and assigned their chiral indices unambiguously by using the HiPCO SWNTs as reaction cells to directly grow the smallest SWNTs and as specimen support to observe them with the lowest background noise. The successful imaging of the smallest (3,3) SWNT and its possible cap structure of the half C_{20} might allow us to understand the growth mechanism of the smallest SWNT more comprehensively.

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Supporting Information Available: Additional simulations also performed on the (4,2) and (5,0) tubes. This material is available free of charge via the Internet at http://pubs.acs.org.

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