Determination of Optical Isomers for Left-Handed or Right-Handed Chiral Double-Wall Carbon Nanotubes

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The handedness relationship between adjacent layers in nested double-wall carbon nanotubes (DWNTs) has been investigated for the first time. Our high-resolution electron microscopy analysis on a series of specimen tilts can successfully tell the handedness of each constituent nanotube in a DWNT, and therefore the chiral indices (n, m) including their optical isomers [(n, m) or (m, n)] of inner and outer nanotubes can be uniquely determined. It is shown that right-handed and left-handed nanotubes are equally distributed for both the inner and outer nanotubes in the examined specimens and a preferable handedness relationship between the adjacent layers in DWNT may exist.

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Optical isomer determination of single quantum objects is of great scientific and technological importance. The chiral structure of carbon nanotubes was first demonstrated by Iijima in 1991 [1], but since then very little attention has been paid to its handedness (optical isomers) so far. Although a wrapping vector $\boldsymbol{C}_h = n\boldsymbol{a}_1 + m\boldsymbol{a}_2$ is generally used for the structural assignment of a single-wall carbon nanotube (SWNT) where $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ are the unit vectors of a two-dimensional graphene sheet and n and m are integers [2,3], the chiral index (n, m) often ignores the optical isomers (handedness) of the SWNT. It should be noted that any chiral nanotube with a chiral index (n, m) has a mirror image of the (m, n) nanotube [4]. The determination of the carbon nanotube handedness will become of great consequence since it has recently been shown that their optical properties are firmly correlated to circularly polarized light [5]. In this study, a careful and systematic high-resolution electron microscopy (HREM) study on the determination of handedness of each constituent nanotube of double-wall carbon nanotubes (DWNTs) is demonstrated for the first time.

Raman spectroscopy and electron diffraction are widely used for the determination of nanotube atomic structure, but neither technique in principle allows us to distinguish the optical isomers. Except for the limited cases where the SWNTs' handedness has been investigated by scanning probe microscopy (SPM) and HREM [6,7], the handedness assignment of the constituent nanotubes in nested (multi-wall) nanotubes has never been achieved experimentally. The interlayer interaction is quite dependent on the handedness of constituent nanotubes for the nested carbon nanotube, e.g., for a DWNT. Even though the chirality relationship in a DWNT has been previously investigated by HREM [8], a huge uncertainty still remains in the atomic correlation between the layers since the inner and outer nanotubes could have either left- or right-handed structures, which essentially results in two possible $\Delta\alpha(= \alpha_1 - \alpha_2)$, where α_1 and α_2 are the chiral angles of inner and outer nanotubes in a DWNT, respectively. In other words, a simple determination of the two chiral indices $(n_1, m_1)@(n_2, m_2)$ for inner and outer nanotubes in a DWNT cannot be discriminated among the following four combinations of the structural isomers: $(n_1, m_1)@(n_2, m_2)$, $(m_1, n_1)@(n_2, m_2)$, $(n_1, m_1)@(m_2, n_2)$, and $(m_1, n_1)@(m_2, n_2)$ when $n_1 > m_1 > 0$ and $n_2 > m_2 > 0$ [see Figs. 1(a)–1(d) for example].

By using transmission electron microscopy (TEM), the handedness of a carbon nanotube can be determined if the

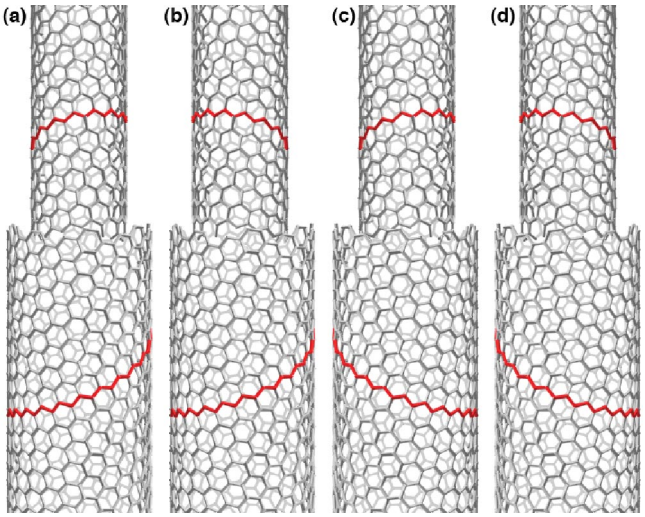

FIG. 1 (color). Schematic models of a chiral DWNT with four different combinations of handedness. (a) (14, 3)@(17, 10), (b) (3, 14)@(17, 10), (c) (14, 3)@(10, 17) and (d) (3, 14)@(10, 17). Here a chiral index (n, m) indicates two of three zigzag chains are right-handed when $n > m$ and left-handed when $n < m$ (see the definition in the Ref. [5]).

inclination relationship between the nanotube and the incident electron beam is known. By tilting the nanotube relative to the incident electron beam within 30°, asymmetric lattice fringes, which are corresponding to the center-to-center spacing of $1.5d_{c-c}(= 0.216$ nm) between the neighboring of the zigzag chain, will appear at either wall of any chiral carbon nanotube [9]. As for achiral nanotubes, these lattice fringes will show up on both sides of the walls when the relative tilting angles are 0 and 30° for zigzag and armchair nanotubes, respectively. Knowing the inclination angle (ϕ) between the nanotube and the incident electron beam (as shown in Fig. 2), when the zigzag chains show their fringe contrasts, we are certainly able to determine the chirality and handedness of chiral nanotube from the asymmetric lattice image. Strictly speaking, the projection of the zigzag chains will show their fringe contrasts within a range of several degrees, the angle ϕ should be defined when the projection of lattice fringes are the longest. Note that the right side of nanotube is up relative to the electron beam when $\phi > 0$. In this study, the definition of left and right handednesses of chiral nanotube is based on Ref. [5], namely, we denote here the right-handed nanotube as one with two of three zigzag chains are right handed (see Fig. 1 and its caption).

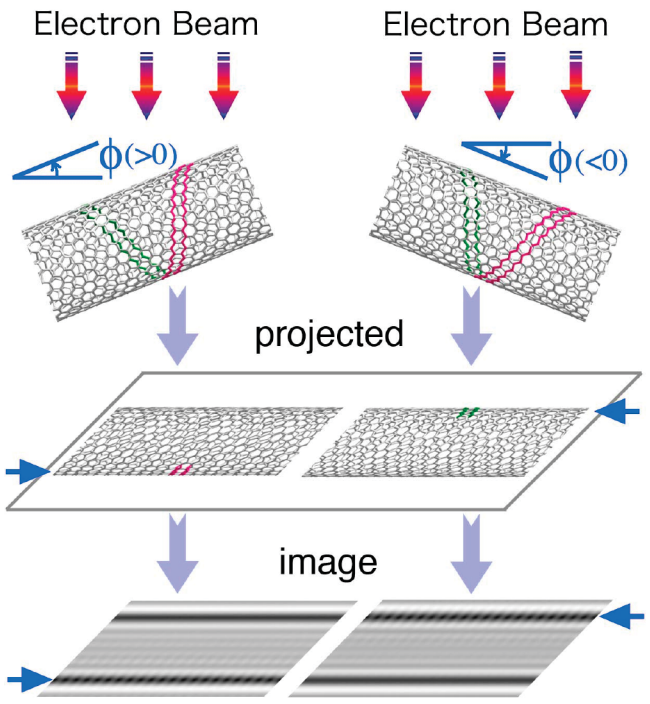

FIG. 2 (color). A schematic sketch for the definition of inclination angle. The right side is up relative to the electron beam when $\phi > 0$. As seen in the figure, asymmetric lattice fringes shown by the blue arrows appear at either side of the tube wall when the zigzag chains are parallel to the incident beam. To be seen easily, two sets of zigzag chains are shown in colors. Red and green correspond to the zigzag chains on the front and back surfaces, respectively.

Preparation method for the DWNTs used in this experiment can be found in the literature [10]. For TEM measurements, DWNT samples were suspended in hexane (99.9 vol. %) by ultrasonication. This suspension was dropped onto a carbon microgrid for TEM observation. HREM observations were performed with JEM-2010F at an accelerating voltage of 120 kV at room temperature. A CCD (Gatan 794) was used for the image acquisition. A typical exposure time is 1 sec. Because we have only a high-resolution pole piece for our microscope, with which the inclination angle of the specimen is limited to ±18°, therefore not all the chiral nanotubes' handedness can be identified in our experiments. It is, however, merely a mechanical problem and the technique can be basically applied for any chiral nanotube to be investigated if the specimen tilt could go as far as 30°.

Figures 3(a)–3(d) show a series of HREM images of a DWNT taken under inclination angles with a range of $-10° < \phi < +21°$. At first, there are no lattice fringes on either wall of the DWNT when the DWNT is perpendicular to the incident electron beam ($\phi = 0$) as shown in Fig. 3(a). On the basis of fast-Fourier-transform (FFT)

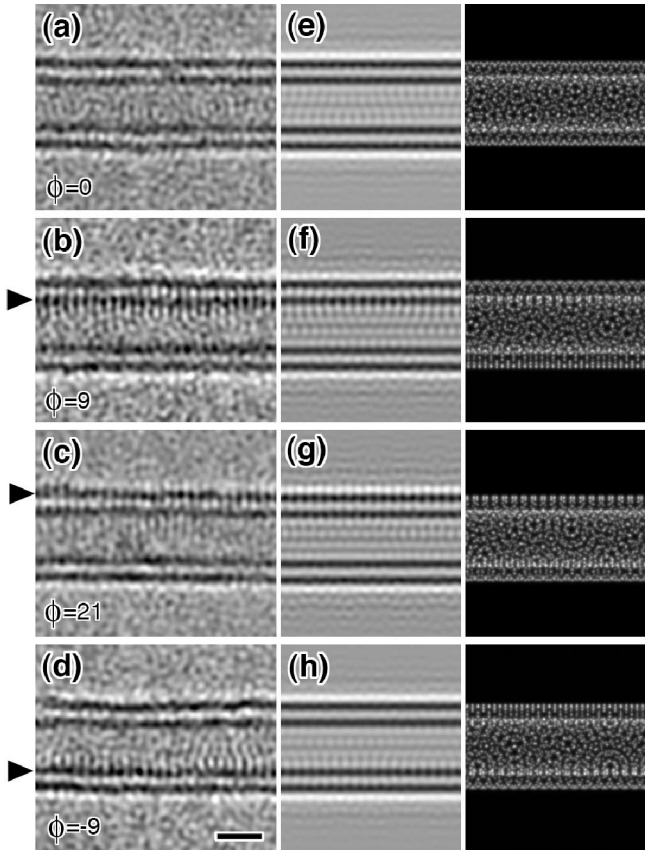

FIG. 3. A series of HREM images of a DWNT acquired with an inclination angles range of $-10 < \phi < +21$. The layers with zigzag contrast are indicated by arrows. The simulated images inclined with the same angles are inserted for each HREM image. The scale bar is 1 nm.

analysis of the moiré pattern between layers, the indices of the inner and outer nanotubes in this DWNT can be identified [8]. Through the measurements of the inner diameter $d_{in} = 1.05(\pm 0.03)$ nm, outer diameter $d_{out} = 1.81(\pm 0.03)$ nm, the apparent chiral angle $\alpha_{in} = 11(\pm 2)^\circ$, and $\alpha_{out} = 21(\pm 2)^\circ$, and after the relevant calibration [11,12], this DWNT is determined to a unique solution as (14, 3)@(17, 10) but with the unidentified handedness. Note that the measured diameters and apparent chiral angles in FFT analysis are systematically different from the true values (see Ref. [11]). However, at this stage, the unique structure of this DWNT cannot be distinguished among the following four combinations of different isomers described in Fig. 1, namely, (14, 3)@(17, 10), (3, 14)@(17, 10), (14, 3)@(10, 17) and (3, 14)@(10, 17).

Then, by tilting the DWNT to $\phi = +9^\circ$, the lattice fringes appear on the upper wall of the inner nanotube as shown by the arrowhead in Fig. 3(b), and these fringes disappear for a time by further tilting. However, the lattice fringes turn up again on both the upper walls of inner and outer nanotubes through a continuous tilting ($\phi = +21^\circ$) as can be seen in Fig. 3(c). At this time, we must be careful concerning the fringes on the inner nanotube because it can easily be confused with the fringes on the outer nanotube which is continuously seen in the inward [13]. Finally, the lattice fringes emerge on the lower side wall of the inner nanotube when the DWNT is tilted to the opposite direction relative to the incident electron beam and $\phi = -9^\circ$, as shown in Fig. 3(d). Unfortunately, the lattice fringes showing up on the lower side wall of the outer nanotube could not be observed because of the tilting limitation of our sample holder. Nevertheless, the data obtained here are enough to determine the handedness of inner and outer nanotubes. Through this inclination experiment, it can be easily known that this DWNT has the zigzag right-handed chirality for both inner and outer nanotubes and the indices are (14, 3)@(17, 10). The real framework structure is therefore the one shown in Fig. 1(a). We should be very careful in judging the handedness of a nanotube when the nanotube does not lie perpendicular to the electron beam at the beginning stage of the tilting, since if a nanotube lies at an angle larger than 30° relative to the electron beam when the tilting begins, the tilting results will give an incorrect solution of the handedness of the nanotube. However, the Fresnel fringes at both ends of the nanotube will show different contrasts because of the different defocus conditions. Thus this situation could be easily resolved through a careful checking of the HREM images.

The simulated images, with each projected potential image inserted on the right side, of a (14, 3)@(17, 10) DWNT with different inclination angles of $\phi = 0$, $\phi = +9$, $\phi = +21$, and $\phi = -9$ are shown in the Figs. 3(e)–3(h) respectively. It can be seen that the simulated images fit very well with those HREM images. Thus, the unique structure of this DWNT was completely determined.

In order to describe the full atomic structure of a DWNT including the atomic correlation between two layers, one might think that, besides the two independent chiral indices, the relative translation (T) and rotation (R) vectors of the inner (or outer) nanotube should be defined. It should be recalled now that the translation (T) and rotation (R) operations of the inner (or outer) tube are basically identical for a chiral DWNT [$(n_1, m_1)@(n_2, m_2)$ when $n > m > 0$ or $m > n > 0$] and there is no unit cell defined unless the $\Delta\alpha = 0$. Therefore the relative T and R vectors cannot be defined for the chiral DWNT without a unit cell. The atomic correlation in a chiral DWNT should therefore be fully defined only by two chiral indices (n_1, m_1) and (n_2, m_2) in most cases. But this is not the case if any achiral nanotubes involved (zigzag or armchair type).

The chiral angle (α) should be identical to the specimen inclination angle (ϕ) when the projected fringes of zigzag chain are longest in the HREM images. The allowance of the inclination angle (ϕ) is, however, quite wide when the zigzag chain contrast could be visible in this experiment and therefore the measured ϕ is not suitably used for the chiral angle determination (α). On the other hand, the simultaneous measurements of ϕ and α are in principle a good cross-check for the chirality assignment.

Table I summarizes our measurements of the handedness of 18 chiral DWNT specimens. Three achiral DWNTs are also found but excluded here. Not all the constituent nanotubes' handedness can be determined because of the specimen tilting limitation of our microscope apparatus.

TABLE I. A summary of the handedness measurements of the 18 chiral DWNTs. (R: right-handed, L: left-handed.) The notation "unidentified" means that the handedness cannot be determined due to the technical limitation of our microscope apparatus.

Specimen	Inner nanotube	Outer nanotube
1	R	R
2	L	L
3	L	L
4	L	L
5	R	R
6	R	R
7	L	R
8	L	L
9	R	L
10	L	R
11	L	L
12	L	L
13	R	R
14	R	L
15	R	R
16	L	L
17	unidentified	R
18	unidentified	R

The chiral indices are not described for each DWNT because similar results can be found in our previous work [8]. As seen in the Table I, the right- and left-handed nanotubes are equally distributed for outer and inner nanotubes. The results can be regarded as natural but indeed prove that any selective formation of handed nanotubes has not occurred during the nanotube growth. A synthesis of nanotubes within an intensive magnetic field would be intriguing in order to obtain the nanotubes of the selected handedness.

A faint tendency of the same handedness for the inner and outer constituent nanotubes in DWNTs can be noticed. No more than four DWNTs with mixed handedness ($R@L$ or $L@R$) are found over 16 investigated. The DWNTs with mixed handedness should be the same in the number as the DWNTs with the same handedness ($R@R$ or $L@L$) if the right-handed or left-handed nanotubes are randomly generated for constituent nanotubes in a DWNT. This is therefore suggestive that some interaction may have been exerted during the simultaneous growth of two layers to prefer the same handedness for the inner and outer nanotubes.

In conclusion, a systematic HREM analysis on a series of specimen tilt was performed to determine the handedness of each constituent nanotube of DWNTs. By comparing with the simulated images, the unique structure of DWNTs can be completely determined. The method demonstrated here can be applied to any multiwall carbon nanotubes and is the only way to determine the handedness of the inner nanotube, since the SPM can only tell the handedness of the outer nanotube. And this work may open up a huge possibility for the realization of nanotube optical devices, which could function with a circularly polarized light. Optical measurements of isolated carbon nanotubes with known handedness would be of great interest [5]. Also the nanotubes with a selected handedness should be certainly of important concern for specific biological applications involving chiral molecules.

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[1] S. Iijima, Nature (London) **354**, 56 (1991).
[2] N. Hamada, S. Sawada, and A. Oshiyama, Phys. Rev. Lett. **68**, 1579 (1992).
[3] R. Saito, G. Fujita, G. Dresselhaus, and M. S. Dresselhaus, Appl. Phys. Lett. **60**, 2204 (1992).
[4] The definition of chiral index is slightly different in the Refs. [2,3] for the unit vectors of a two-dimensional graphene sheet ($\boldsymbol{a}_1$ and $\boldsymbol{a}_2$) with an angle of $\pi/3$ or $2\pi/3$ respectively. We follow the chiral index defined in the Ref. [3] in this paper.
[5] Ge. G. Samsonidze, A. Grüneis, R. Saito, A. Jorio, A. G. Souza Filho, G. Dresselhaus, and M. S. Dresselhaus, Phys. Rev. B **69**, 205402 (2004).
[6] J. W. G. Wildoer, L. C. Venema, A. G. Rinzler, R. E. Smalley, and C. Dekker, Nature (London) **391**, 59 (1998).
[7] R. R. Mayer, S. Friedrichs, A. I. Kirkland, J. Sloan, J. L. Hutchison, and M. L. H. Green, J. Microsc. **212**, 152 (2003).
[8] A. Hashimoto, K. Suenaga, K. Urita, T. Shimada, T. Sugai, S. Bandow, H. Shinohara, and S. Iijima, Phys. Rev. Lett. **94**, 045504 (2005).
[9] S. Friedrichs, J. Sloan, M. L. H. Green, J. L. Hutchison, R. R. Meyer, and A. I. Kirkland, Phys. Rev. B **64**, 045406 (2001).
[10] T. Sugai, H. Yoshida, T. Shimada, T. Okazaki, H. Shinohara, and S. Bandow, Nano Lett. **3**, 769 (2003).
[11] M. Kociak, K. Hirahara, K. Suenaga, and S. Iijima, Eur. Phys. J. B **32**, 457 (2003).
[12] A. Hashimoto, K. Suenaga, A. Gloter, K. Urita, and S. Iijima, Nature (London) **430**, 870 (2004).
[13] There can be a simple overlap of the outer and inner tube fringes for a DWNT and the overlap fringes may extend to the inner tube from the outer tube. This effect makes it difficult to distinguish whether the fringes at the inner tube come from the inner tube or the outer tube when the fringe contrasts show up on both the inner and outer tubes. Nevertheless, it could be theoretically distinguished by a continuous tilting of the specimen under the electron beam from 0 to 30°.