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Measurement of handedness in multiwalled carbon nanotubes by electron diffraction

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Abstract

It is shown that the intensities of electron diffraction from a commensurate multiwalled carbon nanotube are sensitive to the angle of rotation of the nanotube about its axis. This dependence is usable to measure the handedness of the commensurate graphene shells of multiwalled carbon nanotubes. The period of intensity oscillation of the scattering intensity for graphene shells of the same handedness is much larger than that for nanotube shells of opposite handedness. By examining the angular dependence of the scattering intensities, the relative handedness, having the same or opposite handedness, of the commensurate shells can, therefore, be determined.

Carbon nanotubes possess many extraordinary electrical properties such as being metallic or semiconducting depending on their diameter and helicity [1–3]. The diameter of a carbon nanotube is usually a few nanometers, although its length can extend up to tens of microns [4]. Carbon nanotubes usually exhibit a large aspect ratio and are excellent electron field emitters [5,6]. A single-walled carbon nanotube can be formed by wrapping up a two-dimensional graphene along a chosen tubule axis and, therefore, can be characterized by a pair of integer indices (chiral indices) (u,v) [7]. The folding can occur in two possible directions resulting in two enantiomers that are each other's mirror image: left-handed and right-handed carbon nanotubes. If we choose to designate the chiral indices satisfying $u > v \geqslant 0$ for the right-handed nanotubes, the chiral indices (u,v) for the left-handed nanotubes satisfy $v > u \geqslant 0$. For the special class of nanotubes with an achiral structure, i.e., the armchair structure ($u = v$)

and the zigzag structure ($v = 0$), the two enantiomers are degenerate into one unique structure.

The chiral structure of carbon nanotubes has been studied extensively by various analytical techniques such as scanning tunneling microscopy (STM) [8,9], Raman spectroscopy [10], optical photoluminescence [11], electron imaging and electron diffraction [12–20]. However, information on the handedness of carbon nanotubes is still limited, though handedness is also an important structural parameter in affecting the properties of carbon nanotubes such as the magnetochiral conductance [21]. Although STM is capable of determining the handedness of single-walled carbon nanotubes, the inner structure of multiwalled carbon nanotubes can hardly be revealed [22]. Raman scattering and optical photoluminescence provide no information on the handedness of carbon nanotubes. Due to the 2mm symmetry of electron diffraction patterns [23], the handedness of carbon nanotubes is not revealed in any single electron diffraction pattern. Recently, we have proposed a procedure to determine the handedness of single-walled carbon nanotubes by observing the moving directions of the layer lines in electron diffraction patterns before and after twisting a chiral

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carbon nanotube about the tubule axis [24]. Though this procedure can also be applied to determine the handedness of multiwalled carbon nanotubes in principle, it may prove difficult experimentally. On the other hand, as encountered experimentally sometimes, the periodicities of some graphene shells in multiwalled carbon nanotubes are commensurate in the axial direction and such nanotubes also have interesting properties [25].

In this Letter, we present an analysis of electron diffraction from a special class of multiwalled carbon nanotubes, where commensurate shells are present and establish a practical procedure for measuring the relative handedness of the commensurate shells.

Multiwalled carbon nanotubes consist of a number of concentric shells nested each other with intertubular distances similar to the interlayer spacing of graphite. The scattering amplitude for a multiwalled carbon nanotube structure consisting of N concentric shells can be expressed as [26]

$$F(R, \Phi, Z) = \sum_j \sum_{n,m} f \zeta_j \chi_j(n,m) \gamma_j(n,m) J_n(\pi d_j R)$$
$$\times \exp[in(\Phi + \pi/2)], \tag{1}$$

where

$$\zeta_j = \exp\left[-in\varphi_j + 2\pi l^{(j)} z_j/c_j\right]$$
$$= \exp\left[i2m\varphi_j\left(u_j^2 + v_j^2 + u_j v_j\right)/(u_j + 2v_j)\right], \tag{2}$$

$$\chi_{u_j,v_j}(n,m) = 1 + \exp\{2\pi i[n + (2u_j + v_j)m]/3u_j\}, \tag{3}$$

and

$$\gamma_{u_j,v_j}(n,m) = \frac{1 - \exp[-2\pi i(n + mv_j)]}{1 - \exp[-2\pi i(n + mv_j)/u_j]}$$
$$= \begin{cases} u_j, & (n + mv_j)/u_j = \text{integer} \\ 0, & \text{otherwise} \end{cases}, \tag{4}$$

in which f is the atomic scattering amplitude of carbon for electrons, (R, Φ, Z) are cylindrical coordinates in the reciprocal space, j ranges from 0 to $N - 1$ denoting the sequential number of the tubular graphene shell (u_j, v_j) relative to a reference shell of the nanotube, d_j is the diameter of the jth shell, c_j and Δ_j stand for the axial periodicity and the axial distance between neighboring atoms along a helix on the jth shell, (φ_j, z_j) specify the rotational and translational shifts of the jth shell relative to the reference shell in the real space, n, m and $l^{(j)}$ are all integers governed by the selection rule for the jth shell in the nanotube [12,23],

$$l^{(j)} = [(u_j + 2v_j)n + 2(u_j^2 + v_j^2 + u_j v_j)m]/(u_j p_j), \tag{5}$$

with p_j being the maximum common divisor of $(u_j + 2v_j)$ and $(2u_j + v_j)$ for the jth shell. The scattering intensity distribution in the electron diffraction patterns of a multiwalled carbon nanotube is $I(R, \Phi, Z) = |F(R, \Phi, Z)|^2$.

A multiwalled carbon nanotube is commensurate if the ratios of the axial periodicities of its composing shells are fractional numbers [25]. For commensurate multiwalled nanotubes, certain layer lines from different shells in the electron diffraction patterns overlap, resulting in interfered scattering intensities on these layer lines. These interfered scattering intensities are very sensitive to the angular orientation Φ of the nanotube in the reciprocal space. Experimentally, only the principal layer lines show significant scattering intensities in the electron diffraction patterns of carbon nanotubes.

To simplify the mathematical equations but without loss of generality in principle, we can consider a double-walled carbon nanotube with two composing shells of the same helicity and chiral indices (u_1, v_1) and (u_2, v_2), respectively. Their diffraction layer lines in the electron diffraction pattern overlap completely. It is more informative to examine the intensity distribution along the principal layer lines which give the most significant scattering intensities in the electron diffraction patterns of this double-walled carbon nanotube. If the two composing shells have the same handedness, by reference to Eq. (1), the scattering intensities on the layer lines l_1, l_2 and l_3 are:

$$I(R, \Phi, l_1) = \chi_0^2 f^2 \{|u_1 J_{-v_1}(\pi d_1 R)|^2 + |u_2 J_{-v_2}(\pi d_2 R)|^2$$
$$+ 2u_1 u_2 J_{-v_1}(\pi d_1 R) J_{-v_2}(\pi d_2 R)$$
$$\times \cos[(v_1 - v_2)(\Phi + \pi/2) + \Delta\varphi_1]\}, \tag{6}$$

$$I(R, \Phi, l_2) = \chi_0^2 f^2 \{|u_1 J_{u_1}(\pi d_1 R)|^2 + |u_2 J_{u_2}(\pi d_2 R)|^2$$
$$+ 2u_1 u_2 J_{u_1}(\pi d_1 R) J_{u_2}(\pi d_2 R)$$
$$\times \cos[(u_2 - u_1)(\Phi + \pi/2) + \Delta\varphi_2]\}, \tag{7}$$

$$I(R, \Phi, l_3) = \chi_0^2 f^2 \{|u_1 J_{-(u_1+v_1)}(\pi d_1 R)|^2 + |u_2 J_{-(u_2+v_2)}(\pi d_2 R)|^2$$
$$+ 2u_1 u_2 J_{-(u_1+v_1)}(\pi d_1 R) J_{-(u_2+v_2)}(\pi d_2 R)$$
$$\times \cos[(u_1 - u_2 + v_1 - v_2)(\Phi + \pi/2) + \Delta\varphi_3]\}, \tag{8}$$

where χ_0 is a constant determined by Eq. (3), $\Delta\varphi_1 = \Delta\varphi_3 = 152\varphi/7$ and $\Delta\varphi_2 = 0$ by assuming the outer shell as the reference shell and the rotational shift of the inner shell as φ. However, if the two composing shells have opposite handedness, the scattering intensities on the principal layer lines l_1, l_2 and l_3 then become

$$I(R, \Phi, l_1) = \chi_0^2 f^2 \{|u_1 J_{-v_1}(\pi d_1 R)|^2 + |u_2 J_{v_2}(\pi d_2 R)|^2$$
$$+ 2u_1 u_2 J_{-v_1}(\pi d_1 R) J_{v_2}(\pi d_2 R)$$
$$\times \cos[(v_1 + v_2)(\Phi + \pi/2) + \Delta\varphi_1^*]\}, \tag{9}$$

$$I(R, \Phi, l_2) = \chi_0^2 f^2 \{|u_1 J_{u_1}(\pi d_1 R)|^2 + |u_2 J_{-u_2}(\pi d_2 R)|^2$$
$$+ 2u_1 u_2 J_{u_1}(\pi d_1 R) J_{-u_2}(\pi d_2 R)$$
$$\times \cos[(u_1 + u_2)(\Phi + \pi/2) + \Delta\varphi_2^*]\}, \tag{10}$$

$$I(R, \Phi, l_3) = \chi_0^2 f^2 \{|u_1 J_{-(u_1+v_1)}(\pi d_1 R)|^2 + |u_2 J_{(u_2+v_2)}(\pi d_2 R)|^2$$
$$+ 2u_1 u_2 J_{-(u_1+v_1)}(\pi d_1 R) J_{(u_2+v_2)}(\pi d_2 R)$$
$$\times \cos[(u_1 + u_2 + v_1 + v_2)(\Phi + \pi/2) + \Delta\varphi_3^*]\}, \tag{11}$$

where $\Delta\varphi_1^* = 0$ and $\Delta\varphi_2^* = -\Delta\varphi_3^* = 152\varphi/7$.

From Eqs. (6)–(11), we observe that the scattering intensities on the principal layer lines are all related to the rotational orientation of the nanotube by a cosine function due to the coherent interference between the waves coming from the two shells and the intensities vary periodically with the azimuth angle Φ. The periodicity of varying scattering intensities relative to the azimuth angle Φ depends not only on the layer lines, but also on the relative handedness of the composing shells in the nanotube. Focusing on the scattering intensities on the second layer line l_2, referring to Eqs. (7) and (10), the angular periodicity of the scattering intensities for the nanotube in which the two shells have the same handedness is $2\pi/|u_2 - u_1|$, while the angular periodicity for the case of opposite handedness is $2\pi/|u_2 + u_1|$. Since the chiral indices u_1 and u_2 are usually large numbers for the shells of multiwalled carbon nanotubes, the difference in angular periodicity between the two cases illustrated above is generally very large. As an example, for a double-walled carbon nanotube composed of shells of the same handedness with chiral indices of (18, 12) and (12, 8), the angular periodicity of the scattering intensities on the principal layer line l_2 with respect to the azimuth angle Φ is $2\pi/6$, whereas the angular periodicity is $2\pi/30$ for the nanotube with composing shells of opposite handedness with chiral indices (18, 12) and (8, 12). Fig. 1a shows the structure model of the nanotube with its two shells having the same right-handedness, where the constituting carbon helices revolve in the clockwise direction viewed top down against the tubule axis. The nanotube structure made of shells of opposite handedness is shown in Fig. 1b.

The above theoretical analysis has been further corroborated by the calculated electron diffraction patterns of the model structures of the double-walled carbon nanotubes depicted in Fig. 1. Fig. 2 shows a series of simulated electron diffraction patterns of the double-walled carbon nanotube (Fig. 1a) with the two shells having the same handedness at various rotational orientations with azimuth angle $\Phi = 0°$, $3°$, $6°$, $15°$, $30°$, and $45°$. Since the angular periodicity is $60°$ as shown in Fig. 2a in which the maximum scattering intensity on layer line l_2, indicated by the arrow in Fig. 2b–g, is plotted against the azimuth angle Φ, the scattering intensity varies rather slowly as the azimuth angle Φ changes. It should be noted that, for example, when the azimuth angle increased from $0°$ to $6°$ (Fig. 2b–d), the intensity changed very little. Only when the azimuth angle is increased by large values, such as $30°$, significant change of intensity is observed as shown in Fig. 2e–g.

The calculated electron diffraction patterns of the nanotube structure with two composing shells having opposite handedness are shown in Fig. 3. Similar to Fig. 2, Fig. 3a shows the maximum intensity on layer line l_2 that has angular periodicity of $12°$. The four dots distributed evenly on the intensity curve indicate the
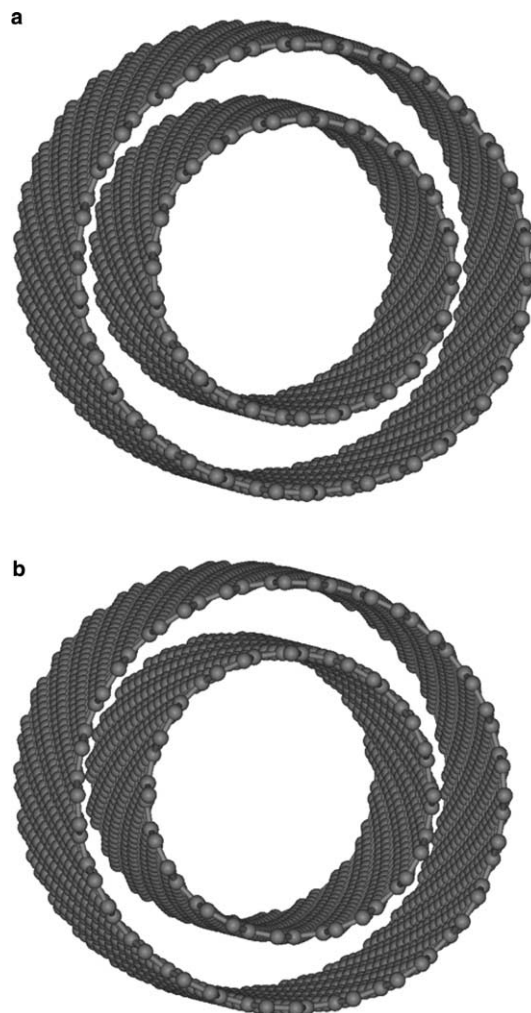

Fig. 1. Model structures of double-walled carbon nanotube where: (a) the two composing shells of (18, 12) and (12, 8) have the same handedness and (b) the two shells (18, 12) and (8, 12) have opposite handedness.

scattering intensities on layer line l_2 at orientations of azimuth angle $\Phi = 0°$, $3°$, $6°$, and $9°$, respectively. The scattering intensities on layer line l_2 enclosed in the narrow rectangles vary in accordance with the dots on the intensity curve given in Fig. 3a. Due to the non-zero value of the original phase shift $\Delta\varphi_2^*$, the starting amplitude is shifted leftward away from the minimum value resulting in the stronger scattering intensities on the principal layer line l_2 as shown in Fig. 3b. In this model structure, the inner shell rotates by $6.2°$ relative to the outer shell. The azimuth angle Φ in Fig. 3b–e changes by an increment of $3°$ and we can see that the angular periodicity of the scattering intensities on layer line l_2 is $12°$, as indicated by Eq. (10).

This significant difference in their rotational periodicities of electron diffraction patterns relative to the nanotube orientation Φ establishes a practical scheme to measure the relative handedness of the composing shells in a multiwalled carbon nanotube by observing the
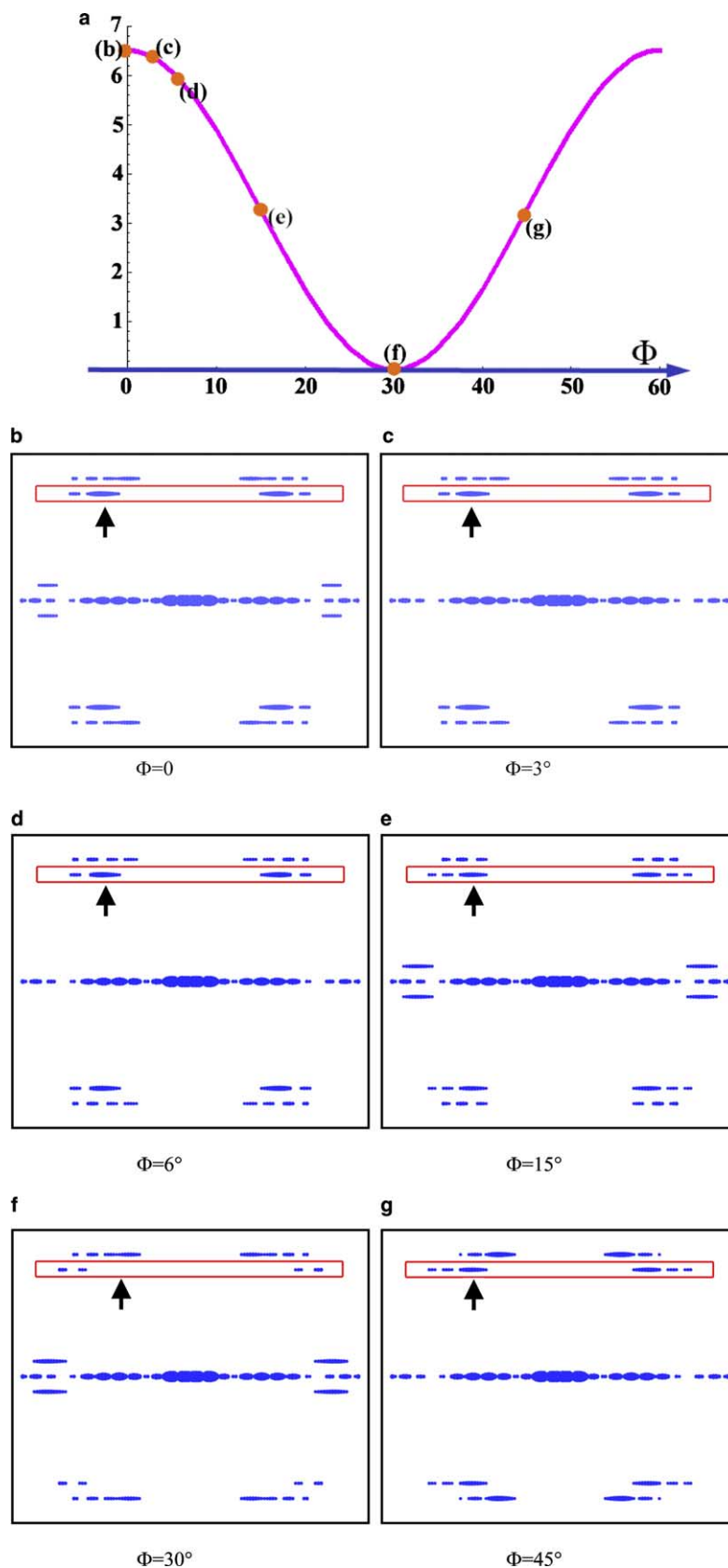
Fig. 2. Simulated electron diffraction patterns of the double-walled carbon nanotube with the two composing shells of chiral indices (18,12) and (12,8) that have the same handedness. (a) Variations of the maximum scattering intensity on principal layer line l_2, indicated by arrow in figures (b–g). Dots on the curve correspond to the rotational orientations shown in subsequent figures. (b) $\Phi = 0°$; (c) $\Phi = 3°$; (d) $\Phi = 6°$; (e) $\Phi = 15°$; (f) $\Phi = 30°$; and (g) $\Phi = 45°$. The rotational periodicity of the scattering intensities on the principal layer line l_2 (enclosed by rectangular frame) is 60°.
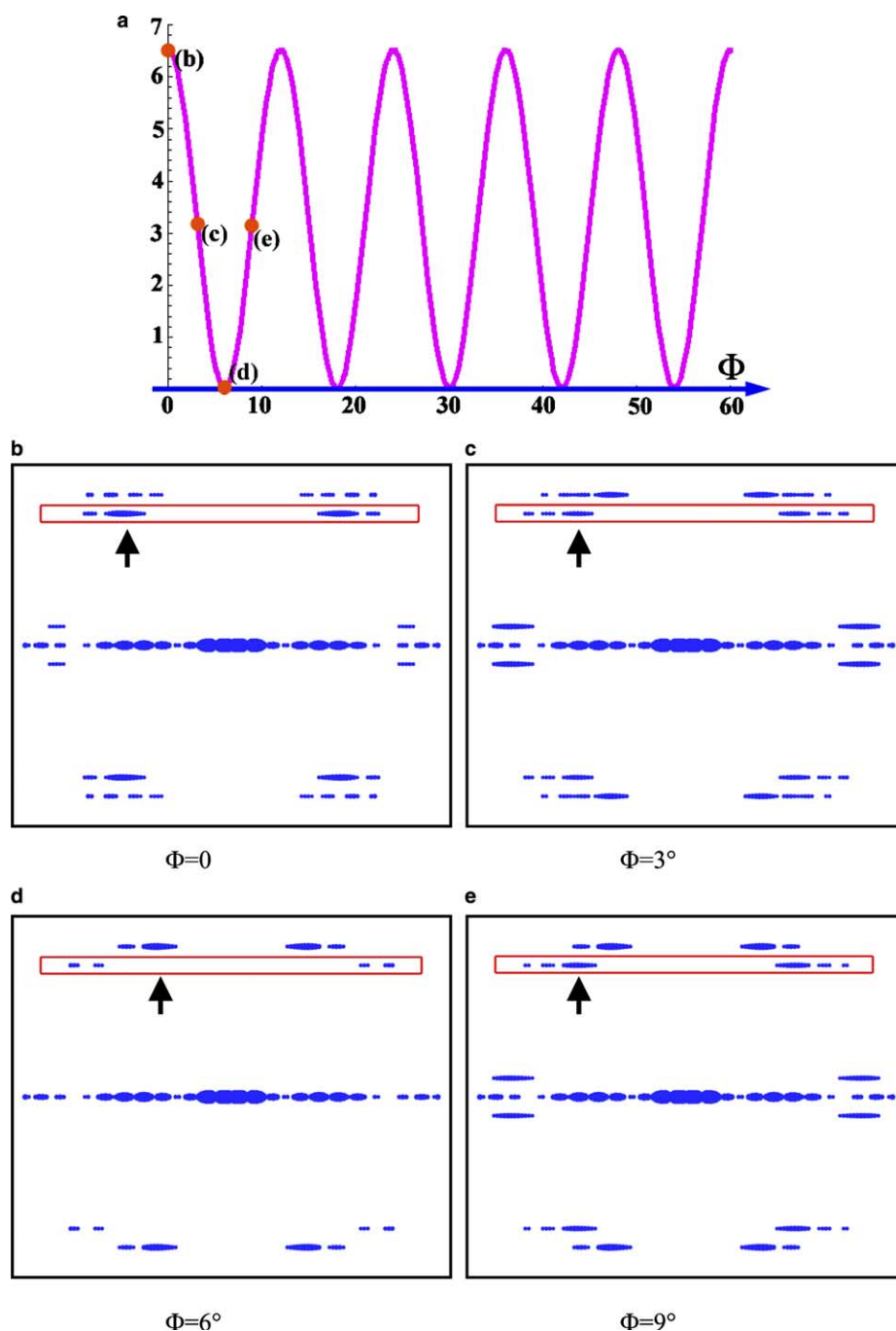
Fig. 3. Simulated electron diffraction patterns of the double-walled carbon nanotube with the two composing shells of chiral indices (18,12) and (8,12) that have opposite handedness. (a) Variations of maximum scattering intensity on principal layer line l_2, indicated by arrow in figures (b–e). Dots on curve correspond to rotational orientations of: (b) $\Phi = 0°$; (c) $\Phi = 3°$; (d) $\Phi = 6°$; and (e) $\Phi = 9°$. The rotational periodicity of the scattering intensities on the principal layer line l_2 (enclosed by rectangular frame) is 12°.

variations of the scattering intensities on the layer lines with respect to the azimuth angle Φ. By locating and finding a multiwalled carbon nanotube with composing shells of the same helicity by using high-resolution transmission electron microscopy and electron diffraction, we can take a series of electron diffraction patterns of the nanotube at different orientations by changing the azimuth angles Φ of the nanotube relative to the incident

electron beam, while still keeping the tubule axis perpendicular to the incident electron beam. This experiment can be carried out conveniently in the transmission electron microscope equipped with a double-tilt sample stage. Experimental investigations are under way and will be reported in a separate publication.

The successful assignment of the relative handedness of multiwalled carbon nanotube may allow us to exam-

ine the distribution of handedness of graphene shells in carbon nanotube samples. It may also see important applications in developing spin-based carbon nanotube electronic devices. Furthermore, since the handedness plays an important role in biological functions, determining the handedness of carbon nanotubes may assist in applying this material in biological applications.

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