Unambiguous atomic structural determination of single-walled carbon nanotubes by electron diffraction

Hua Jiang a,*, Albert G. Nasibulin b, David P. Brown b, Esko I. Kauppinen a,b,*

a VTT Technical Research Center of Finland, Biologinkuja 7, P.O. Box 1000, FIN-02044 VTT, Finland
b NanoMaterials Group, Laboratory of Physics and Centre for New Materials, Helsinki University of Technology, P.O. Box 1000, FIN-02044 VTT, Finland

Received 16 June 2006; accepted 18 July 2006
Available online 11 December 2006

Abstract

We introduce a novel non-dimensional “intrinsic layer-line spacing” concept for electron diffraction analysis of single-walled carbon nanotubes (SWCNTs). Accordingly, we develop a unique method for direct determination of chiral indices \((n,m)\) of the carbon nanotubes from their electron diffraction patterns (EDPs). The new method is totally calibration-free. Errors due to the nanotube inclination are specified. The tilt angle of the carbon nanotube with respect to the incident electron beam is simultaneously evaluated, thus the effect of the tube tilting is compensated for in the \((n,m)\) determination. Several effective procedures are proposed to cross-check the results by using abundant information contained in the diffraction patterns. The efficiency of the method is demonstrated on both simulated and experimental diffraction patterns from single-walled nanotubes. The technique can be extended to structural analysis of nanotubes of structure similar to carbon nanotubes, such as boron nitride nanotubes.

© 2006 Published by Elsevier Ltd.

1. Introduction

A fundamental problem in both basic and applied research on single-walled carbon nanotubes (SWCNTs) exists because many physical properties of nanotubes are extremely sensitive to their atomic structure [1]. The structure of a SWCNT can be conveniently described by a pair of integers known as the chiral indices \((n,m)\) [2]. A well-known example of the sensitivity of structure to properties is that a carbon nanotube can be metallic if \((n/m)\) is divisible by 3, otherwise they are semiconducting [1,2]. A slight change in the value \(n\) or \(m\) can, thus, dramatically alter the electronic properties of a nanotube. For instance, a (13,1) tube is metallic while a (14,1) tube is semiconducting though they are geometrically very similar to each other [3]. Therefore, unambiguous \((n,m)\) determination of individual SWCNTs is of crucial value for progressing CNT-based nanotechnology.

Current efforts for structural characterization of SWCNTs can be categorized into two broad classes, i.e., optical and non-optical. Optical spectroscopy includes, for example, resonant Raman scattering [3,4] and photoluminescence [5], where \((n,m)\) are identified by using the characteristic optical transition energies and photon frequencies (in Raman scattering) or optical absorption and emission energies (in photoluminescence). Optical measurements are usually limited in that they require a range of laser wavelengths for detecting a variety of tubes and they are only valid for a limited range of tube diameters. Laborious tasks are usually involved for both measurement and data interpretation. Photoluminescence has an additional drawback since the method can only detect semiconducting nanotubes. In addition, the insufficient spatial resolution of optical measurements makes it impossible to probe individual SWCNTs for analysis without considering effects from the tube environment. Moreover, there is no known calibration technique to correlate the intensity of excitations.
for tubes of given chiral indices to their concentrations, thus it is difficult to accurately map the chirality distribution in a SWCNT sample with optical measurements.

In the non-optical communities, the chiral indices are usually assigned by first determining the characteristic tube diameter $D_0$ and chiral angle $\chi$ by means of direct imaging techniques in real space (e.g., scanning tunneling microscopy (STM) [6,7] and high-resolution transmission electron microscopy (HRTEM) [8]), or in reciprocal space by the electron diffraction technique [9–19]. Direct imaging techniques are faced with the problem that the tubes are usually not stable enough for acquiring high-quality images with atomic-resolution at a high magnification.

Electron diffraction was the first technique to be used to characterize SWCNTs at the time of their discovery [9] and has remained one of the most powerful means for their structural analysis. Advanced nanobeam electron diffraction techniques uniquely allow direct probing of individual nanotubes and characterization of their structure [12–14]. However, the measurements are typically made by assuming a normal incidence condition [13,18] or a small tube tilting angle, e.g., less than $6^\circ$ [16]. In contrast, it is not rare for a nanotube to have a tilt angle of $20^\circ$ from the horizontal plane. In practice, it is difficult to establish an experimental setup to ensure such small tilt angle requirements. Although determination of the chiral angle $\chi$ from electron diffraction patterns (EDPs) was shown to be independent of tube inclination [12], evaluation of the tube diameter may rely on the tilt of the tube unless the diffraction patterns are actually calibrated by internal standard materials, which are in practice unavailable in the measurement. In the absence of such standards, absolute calibration of an EDP of a SWCNT depends on the value of the carbon–carbon (C–C) bond distance, which has uncertainty between 0.142 nm and 0.144 nm [16]. Additionally the C–C bond can be stretched when the tube diameter is small [17]. Also, calibration of the EDP by using the C–C bonding distance is either tilt sensitive or complicated by the curvature of the tube. In order to take into account the tilting effect of the tube on the determination, a tedious trial-and-error simulation procedure has to be applied [14–16].

Moreover, when $D_0$ and $\chi$ are required to be determined prior to $(n,m)$ assignment, as by previous methods [9–17], they must both be determined with high accuracy in order to determine chiral indices $n$ and $m$ unambiguously. For instance, the metallic (13,1) tube where $D_0 = 1.06$ nm and $\chi = 3.7^\circ$, is very similar to the semi-conducting (14,1) tube where $D_0 = 1.14$ nm and $\chi = 3.4^\circ$. Obviously, a slight error in either $D_0$ or $\chi$ easily leads to an ambiguity in indexing a SWCNT.

Recently an approach for direct $(n,m)$ determination was reported based on Bessel function analysis of the diffraction layer-lines in the EDPs [18,19]. However, it has been shown that the intensity distribution along a non-equatorial layer-line is sensitive to the tilt of the tube [19]. Thus, a confident structural determination of SWCNTs requires an accurate determination of the tilt angle of the nanotube with respect to the electron beam.

In this paper, we introduce a new concept of “intrinsic layer-line spacing” for electron diffraction analysis of SWCNTs. Based on this novel concept, we develop an efficient and unambiguous method for direct determination of $(n,m)$ chiral indices of SWCNTs from their EDPs. The proposed method is absolutely calibration-free. Uniquely, errors in $(n,m)$ determination due to the nanotube inclination are specified. The tilt angle of the carbon nanotube with respect to the incident electron beam is simultaneously evaluated, thus the effect of the tube inclination is totally compensated for in the determination of the chiral indices. In addition, several independent procedures are proposed to cross-check the results based on the new perceptions of the electron diffraction from carbon nanotubes. The efficiency of the method is convincingly demonstrated on both simulated and experimental diffraction patterns of single-walled carbon nanotubes. The technique can be readily extended to structural analysis of nanotubes of other materials with structure analog to carbon nanotubes, such as boron nitride nanotubes [20].

2. Method

Fig. 1 shows a simulated EDP from a (12,7) SWCNT in normal incidence. The diffraction pattern is composed of many separate layer-lines parallel to each other but perpendicular to the tube axis. Discrete hexagons can be constructed as schematically illustrated in Fig. 1. According to the kinematical diffraction theory of carbon nanotubes [21–24], the intensity profile along a certain layer-line is described by the sum of a series of squared Bessel functions. In particular, along the equatorial line

---

1 Meyer JC. Private communication 2006.
at the center, the dominant Bessel function is \( J_0(xR) \), where \( R \) is the radial distance measured along the equatorial line from the diffraction center.

Mathematically, Bessel functions have an infinite number of zeros (roots) pseudo-periodically spaced. In practice, when \( x = \pi D_0 R \gg 0 \), the zero-order Bessel function \( J_0(xR) \) or simply \( J_0(x) \), can be approximated by \( J_0(x) \approx \sqrt{\frac{2}{\pi x}} \cos(x - \frac{\pi}{4}) \) \cite{23}, of which the roots are given by \( x_j = \pi D_0 R_j = \left(j - \frac{1}{2}\right) \pi \), where \( j \) is an integer greater than 1, and the interval between the neighboring roots is \( x_{j+1} - x_j = \pi \). By this approximation we have then

\[
\Delta \theta = \theta_1 - \theta_2 = 1, \quad \text{where} \quad \theta = R_{j+1} - R_j.
\] (1)

It is worth remarking that the intensity profile on the equatorial line is totally independent of tube tilting \cite{24}, and thus so is the measurement of the value \( \delta \).

The spacing \( d_0 \) (Fig. 1) of each non-equatorial layer-line measured from the equatorial line is subject to scaling by a tilt factor \( \frac{1}{\cos \tau} \), where \( \tau \) represents the tilt angle of the nanotube with \( \tau = 0^\circ \) in the normal incidence condition. \( d_0 \) of the three layer-lines for the first-order hexagons are assigned \( d_1, d_2, d_3 \) and \( d_{n1}, d_{n2}, d_{n3} \) for the second-order hexagons.

Now let us introduce a new term, the intrinsic layer-line spacing \( (\xi_i) \), corresponding to each non-equatorial layer-line, which is defined by

\[
\xi_i = D_0 \cdot d_i.
\] (2)

By geometrical considerations, expressions for \( \xi_i \) of the six most important layer-lines corresponding to \( d(j = 1, 2, \ldots, 6) \) can be derived as

\[
\begin{align*}
\xi_1 &= \frac{n - m}{\sqrt{3} \pi}, & \xi_2 &= \frac{n + 2m}{\sqrt{3} \pi}, & \xi_3 &= \frac{2n + m}{\sqrt{3} \pi}, \\
\xi_4 &= \frac{3m}{\pi}, & \xi_5 &= \frac{3m}{\pi}, & \xi_6 &= \frac{3(n + m)}{\pi}.
\end{align*}
\] (3)

\( \xi_i \) are non-dimensional parameters and they are functions of only the chiral indices \( (n,m) \). On the other hand, \( \xi_i \) can be readily measured from the diffraction pattern by \( \xi_i \approx \frac{x_i}{s} \) if Eqs. (1) and (2) are combined. It is obvious that the measured values of the intrinsic layer-line spacings \( (\xi_i) \) are scaled by \( \frac{1}{\cos \tau} \).

The simultaneous solution of any two expressions of \( \xi_i \) from Eq. (3) will give chiral indices \( (n,m) \). For instance, the solution of \( n \) and \( m \) from \( \xi_2 \) and \( \xi_3 \) is

\[
n = \frac{\pi}{\sqrt{3}}, \quad m = \frac{\pi}{\sqrt{3}}, \quad \xi_2 = \frac{2\pi}{\sqrt{3}}, \quad \xi_3 = \frac{4\pi}{\sqrt{3}}.
\] (4)

Or equivalently from \( \xi_3 \) and \( \xi_6 \), we have

\[
n = \frac{\pi}{\sqrt{3}}, \quad m = \frac{\pi}{\sqrt{3}}, \quad \xi_3 = \frac{4\pi}{\sqrt{3}}, \quad \xi_6 = \frac{8\pi}{\sqrt{3}}.
\] (5)

In more general cases, when the tilt angle \( \tau \) is non-zero, the actual measured results \((n',m')\) are given by

\[
n' = n - \frac{1}{\cos \tau}, \quad m' = m - \frac{1}{\cos \tau}, \quad n' = n + e_n, \quad m' = m + e_m,
\] (6)

where \( e_n \) and \( e_m \) are tilt-effect errors, which are positive numbers. It is calculated that \( e < 2 (n = 0 \text{ or } m) \) for nanotubes with \( n \text{ or } m \approx 30 \) at a tilt angle of \( \tau = 20^\circ \). When the tilt angle is small, so that \( 0 < \epsilon < 1 \), then,

\[n = \text{TRUNC}(n') \quad \text{or} \quad m = \text{TRUNC}(m'),\] (7)

when the tilt angle becomes relatively large, so that \( 1 < \epsilon < 2 \), then,

\[n = \text{TRUNC}(n') - 1 \quad \text{or} \quad m = \text{TRUNC}(m') - 1.\] (8)

Here, TRUNC is a function to truncate a number into an integer by removing the fractional part of that number.

After \((n,m)\) is determined, the tilt angle \( \tau \) can be calculated from Eq. (6) by \( \cos \tau = \frac{1}{n'} \) or \( \cos \tau = \frac{1}{m'} \). Since the intrinsic layer-line spacings \( \xi_i \) are more sensitive to the tube tilting, the tilt angle is more robustly evaluated by \( \cos \tau = \frac{\xi_3}{\xi_6} \) for instance,

\[
\begin{align*}
\cos \tau &= \frac{\xi_3}{\xi_6} = \frac{2n + m}{2m} = \frac{\xi_3}{\xi_6} = \sqrt{\frac{3(n + m)}{\pi}}.
\end{align*}
\] (9)

With the tilt angle \( \tau \) taken into account, the absolute calibration of the diffraction pattern can be carried out \textit{a posteriori} by any of the layer-line spacings \( d_n \), for example,

\[
d_3 = 2\sqrt{3} \frac{\cos \tau}{\pi \cos \tau}.
\] (10)

Here, the graphene lattice constant \( a \) is known to be 0.246 nm \cite{1}.

3. Results

In order to test the proposed method, we simulate a tilted series of EDPs of a \((12,7)\) SWCNT. Two of them are shown in Fig. 2. By applying the \((\xi_3, \xi_6)\) set of equations, chiral indices \((n,m)\) and the tilt angles \( \tau \) are determined as summarized in Table 1, in which \( 2\xi_i (i = 3 \text{ or } 6) \) are measured from the simulated patterns; \( 2\xi_i (n,m) \) are calculated from Eq. (3). The tilt angles, \( \tau (i = 3 \text{ or } 6) \), are determined by using the intrinsic layer-line spacings based on Eq. (9).

It is clearly seen that, when the tilt angle is less than \( 20^\circ \), the chiral indices can be directly measured without ambiguity. The error for the case when the tilt is \( 5^\circ \) (Fig. 2(a)) and \( e_n = -0.02 < 0 \) is due to the pixel resolution limitation, which can be avoided by improving the pixel resolution of the EDP.

As the tilt angle increases as large as \( 25^\circ \), \( e_n = 1.21 > 1 \), while \( e_m = 0.74 < 1 \). When the tilt angle reaches \( 30^\circ \), both \( e_n \) and \( e_m \) become larger than 1. In such situations, one must be cautious when calculating \((n,m)\) from Eq. (7) or Eq. (8). This will be discussed later in more detail.

To apply the method to real problems, high-quality EDPs of individual SWCNTs are essential but in reality difficult to obtain because of their weak scattering power and the tendency for the tubes to be easily modified by the electron beam. An optimized electron micro-diffraction technique has been developed on a conventional transmission electron microscope (TEM) with the aim of enhancing signal-to-noise ratio of the diffraction pattern. \(^3\) Fig. 3 shows (a) a high-resolution TEM image of an individual SWCNT and (b) its corresponding EDP, both of which were taken by a Philips CM200-PEG TEM operating at the highest possible accelerating voltage of 200 kV to reduce the Ewald sphere curvature effect. The microscope is equipped with a Gatan 794 multiscan CCD camera (1k x 1k) for digital recording. The sample of carbon nanotubes was synthesized by a novel aerosol method using ethanol as carbon precursor, and iron aerosol nanoparticles as catalysts \cite{25}.

\(^2\) For example, since \( D_0 = \frac{\sqrt{2} \pi m + \pi}{\pi}, d_3 = \frac{1}{\sin \tau} \cos \tau \), where \( d_{100} = \frac{\sqrt{3}}{2} a \), and \( \cos \tau = \frac{\sqrt{3}}{2 m} \), we have \( \xi_3 = D_0 \cdot d_3 = \frac{2m}{\sqrt{3} \pi} \), \( (a \text{ is known to be the graphene lattice constant.)} \)

\(^3\) To be published elsewhere.
The \((n_2, n_3)\) set of equations and the \((n_3, n_6)\) set of equations are independently employed for the calculations with results summarized in Table 2 (a) and (b), respectively. The chiral indices \((n, m)\) of the SWCNT are thus determined to be \((23, 10)\) and the tilt angle \(\tau\) is determined to be \(10^\circ\) from both equation sets. Accordingly, this is a semiconducting nanotube. It is interesting to note that, from the same EDP (Fig. 3(b)), the nanotube was previously evaluated to be a \((21, 9)\) metallic tube by the method based on \((D_0, z)\) determination wherein the tilt effect was ignored [24,26]. A simple comparison shows that the difference between chiral angles of the \((23,10)\) tube and the \((21,9)\) tube is only 0.19\(^\circ\), but the diameters differ from each other by 10\%. Calibration error due to neglecting the tilt-effect.

![Fig. 2. Simulated EDPs of a (12,7) SWCNT at tilt angles (a) 5\(^\circ\) and (b) 30\(^\circ\).](image)

![Fig. 3. (a) A high-resolution TEM image of an individual SWCNT; (b) the corresponding experimental EDP and (c) a simulated EDP of a (23,10) nanotube at a tilt angle 10\(^\circ\).](image)
accounts for the large error in the earlier determination of the tube diameter.

With the tilt angle \( \tau = 10^\circ \) taken into account, we can accurately calibrate the diffraction pattern by using, for instance, \( d_3 = \frac{2\sqrt{3}}{3a} \cos \hat{\tau} \approx 4.554 \text{ nm}^{-1} \); hence the tube diameter is determined to be 2.29 nm from the EDP based on Eq. (1), which accurately matches the (23,10) tube.

A simulated EDP of the (23,10) nanotube at a tilt of 10\(^\circ\) is presented in Fig. 3(c), on which a similar measurement is is presented in Fig. 3(c), on which a similar measurement is performed. The corresponding results are also listed in Table 2(a) and (b) for comparison. Again, there is an excellent match between results from the simulated diffraction pattern and the experimental pattern.

4. Discussion

Let us now discuss the error analysis, validity, advantages and limitations of the proposed method. The major sources of error in the method arise from the intrinsic measurement errors of \( \delta = R_{6,1} - R_{1} \) and \( d_6 \), especially the relatively small magnitude of \( \delta \) as a divisor to calculate the intrinsic layer-line spacing \( \xi_i^m \). Actually this has been a common difficulty faced by other methods involved in electron diffraction analysis of SWCNTs. High-resolution CCD cameras or Imaging Plate recorders which enable a high camera-length for the diffraction pattern would be useful in minimizing such errors.

Another error source arises when the tilt angle is large so that there is no confident criterion in practice to make a correct selection between Eq. (7) or Eq. (8) to determine \((n,m)\). In order to stay in the range where Eq. (7) is valid (i.e., so as not to invoke Eq. (8)), we introduce the tolerated tilt angle \( \tau_{\text{max}} \) for nanotubes of different \((n,m)\). Theoretically \( \tau_{\text{max}} \) for a certain \( n \) can be estimated by \( \cos(\exp(\tau_{\text{max}}) = \lim_{\exp(-\tau)} \left( \frac{n}{n + \frac{\varepsilon_{\text{max}}}{m}} \right) \). As the integer \( n \) increases, the tolerated tilt angle \( \tau_{\text{max}} \) decreases. For instance, supposing \( \varepsilon_{\text{max}} = 0.9 \), the tolerated tilt angle is allowed to be as large as 20\(^\circ\) for \( n = 15 \). In addition, based on Eq. (6), an intrinsic index ratio \( A \) which is a function of \((n,m)\) is introduced where \( A = m \frac{n + \varepsilon_{\text{max}}}{n + \varepsilon_{\text{max}}} \leq 1 \), hence \( \varepsilon_{\text{max}} \leq \varepsilon_{\text{min}} \). It can be seen that the method allows equal or higher tilt angle to be tolerated when determining \( m \) than \( n \). In other words, it is favorable to first calculate \( m \) based on Eq. (7). \( n \) can then be more reliably derived by applying the intrinsic index ratio \( A \), since \( A \) can be tilt-independently determined by \( A = \frac{m}{n} = \frac{2\xi_2 - \xi_3}{2\xi_3 - \xi_2} \) according to Eq. (4); or by \( A = \frac{m}{n} = \frac{2\xi_6 - 3\xi_3}{3\xi_3 - \xi_6} \) according to Eq. (5).

By this procedure, in general situations when the tilt angle is not larger than 20\(^\circ\), SWCNTs with chiral indices \((n,m) (n \geq 15 \geq m)\) can be directly measured without ambiguity by using Eq. (7) to first derive \( m \). As before, \( n \) can be calculated by using the parameter \( A \). If \( m \) is incorrectly determined due to, for example, pixelation errors, the mistake should be recognized easily from the resultant unreasonable tilt angle; or the results can be cross-checked by the \( n \) measurement based on Eq. (7) or Eq. (8). For example, from Fig. 2(a) \((\tau = 5^\circ)\), if \( m \) is incorrectly determined to be 6, \( n \) then should be 10 by applying the parameter \( A \). The resultant tilt angle is then \( \approx 33^\circ \), which is too large to be a normal case. On the other hand, if \( n \) is incorrectly calculated to be 11, while \( m \) is correctly determined to be 7, this will signal a serious mismatch of the intrinsic ratio \( A \) between the measured value from \( \xi_i^m \) and the calculated value by \( \frac{n}{m} \). Determination of the tube diameter \( D_0 \) after calibration of the EDP based on Eq. (10) can also be independently employed to verify the results. Of course, the results can further be cross-checked by measuring different layer-lines separately. When the tilt angle is beyond the tolerated limit, in addition to the above-mentioned cross-checking procedure, a trial-and-error procedure around all adjacent \((n,m)\) candidates can be applied.

It is worth noting that this method is also applicable for \((n,m)\) determination of achiral nanotubes (i.e., armchair and zigzag tubes), with \( d_1 = 0 \), \( d_2 = d_3 = d_4 = d_5 = 2d_6 = 2d_2 \) for an armchair nanotube; and \( d_1 = d_2 = d_3 = 2d_4 \), \( d_4 = 0 \), \( d_5 = d_6 = 3d_4 \) for a zigzag tube.

Since only the layer-line spacings \( d_i \) and the interval \( \delta \) between the zeros along the equatorial line are involved in the measurement, the present method has no significant limitations. In contrast, the method has a high degree of flexibility and verifiability in that \((n,m)\) can be determined by using many combinations of layer-line spacings. One important remark is that the EDP is required to resolve...
the zeros on the equatorial line so that $\delta$ can be measured with confidence.

5. Conclusions

In conclusion, we have introduced a novel concept of a non-dimensional “intrinsic layer-line spacing” to perceive new insights into electron diffraction of SWCNTs. Accordingly a unique calibration-free method for unambiguous determination of the structural indices $(n,m)$ of SWCNTs has been developed. By this method, the tilt angle of the carbon nanotube is simultaneously evaluated, thus the tilt effect is automatically compensated for in the $(n,m)$ determination. When needed, a precise approach was proposed for absolute calibration of the EDP by using the axial C–C bonding distance with the tilting effect fully considered.

The method has been tested using tilt-series simulated EDPs of a (12,7) SWCNT, and has also successfully been applied to the analysis of experimental electron diffraction patterns from individual SWCNTs produced by an aerosol synthesis process. A carbon nanotube, which was previously evaluated to be a (21,9) metallic tube by a primitive synthesis process, has also successfully been determined to be a (23,10) semiconducting nanotube according to the presented method.

Sources of measurement errors as well as the validity of the proposed method are carefully analyzed in detail. Uniquely, the error due to the tube inclination is specified in the error analysis. Based on the new perceptions of electron diffraction from SWCNTs, several independent procedures are proposed for cross-checking the results by taking full advantage of abundant information contained in the EDPs. Therefore, the determination is free of ambiguity.

The technique is readily extended to structural analysis of nanotubes of other materials with structures analogous to carbon nanotubes, such as boron nitride nanotubes.

Acknowledgements

Prof. Ph. Lambin is kindly acknowledged for providing us with the FORTRAN code of their DIFFRACT simulation program. Hua Jiang is grateful to Dr. M. Kociak for fruitful discussions. This work is supported by the TEKES, VTT and Academy of Finland.

References