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Determination of helicities in unidirectional assemblies of graphitic or graphiticlike tubular structures

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Here we propose a universal method for the determination of all helicities present in unidirectional assemblies of hexagon-based graphitic or graphiticlike tubular structures, e.g., multiwalled or bundled carbon nanotubes (CNTs) or boron-nitride nanotubes and their structural analogs. A critical dimension characteristic of a fundamental structural property, i.e., the atomic bond length, is discerned from electron diffraction patterns by which all helicities present in the assemblies are identified. Using this method, we determine the helicity population in a single-walled CNT sample produced by laser ablation technique. © *2008 American Institute of Physics*.
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Since the recognition of carbon nanotubes (CNTs) by Iijima in 1991,[1] nanoscale tubular structures, including graphitic CNTs[2] and graphiticlike boron-nitride nanotubes (BNNTs),[3] have generated tremendous interest. Single-walled CNTs (SWCNTs) are either metallic or semiconducting depending on the tube diameter and the chiral angle, i.e., helicity. BNNTs show an insulating character due to their large band gap regardless of the helicity or diameter.[4] To better understand nanotube properties, develop practical applications, and control synthesis, it is crucial to advance our capability for structural characterization of nanotubes.

A number of techniques have been used to characterize nanotube structures. In contrast to optical measurements that generally depend on whether or not a nanotube has a detectable optical response to the illuminating light,[2] electron diffraction allows direct analysis of single-walled, multiwalled, bundled, or isolated nanotubes. Moreover, in combination with high-resolution electron microscopy, the morphology of nanotubes, i.e., whether the tubes are individual, bundled, or multiwalled, can simultaneously be established. In particular, electron diffraction analysis of individual SWCNTs[5–9] or BNNTs[10] enables explicit determination of their atomic structures specified by chiral indices (n,m).

Nanotubes often form bundles or exist as coaxial multiwalled tubes, i.e., as unidirectional assemblies. Efforts have been undertaken to analyze the structures of such assemblies in CNTs[11–16] and in BNNTs[17–19] from their electron diffraction patterns (EDPs), usually with uncertainties due to unmeasured tilt effects of the nanotube with respect to the electron beam and the streaking effects of reflections forming the so-called diffraction "layer lines."[8] Errors are especially large when layer lines overlap, if two or more helicities are close to each other. In general, current methods for electron diffraction analysis are inadequate and there is an urgent need for a reliable and universal method to characterize structural helicity properties in nanotube assemblies.

In this letter, we propose a method for electron diffraction characterization of unidirectional assemblies of graphitic or graphiticlike tubular structures. We discovered that from EDPs of such tubular structures, whether or not they are coaxially aligned or packed in bundles, a critical dimension can be calculated, which can then be used to identify all helicities present in the groups. This enables a fast and reliable approach to determine the helicities present in CNTs, BNNTs, or other such similar structures.

For simplicity, but without loss of generality, we illustrate our method by using a simulated EDP (Fig. 1) of a small SWCNT bundle that consists of four tubes: (13,2), (18,7), (20,6), and (26,6). The EDP was calculated using the DIFFRACT program[20] by assuming a bundle tilt angle of 15° with respect to the electron beam. In addition to the equatorial line at the center of the EDP, the pattern is mainly composed of a number of layer lines, which are spaced in parallel by certain distances from the equatorial line. An arbitrary individual tube i is characterized by a set of layer line distances d_1^i, d_2^i, and d_3^i assigned for the first-order hexagon and d_4^i, d_5^i, and d_6^i for the second-order hexagon.[9] In this work, only d_2^i and d_3^i will be involved in the analysis though theoretically any two pairs could be used. The chiral angle of tube i is determined by the ratio of d_2^i and d_3^i.[5] We notice that as the chiral angle of the nanotube increases from 0° (zigzag)

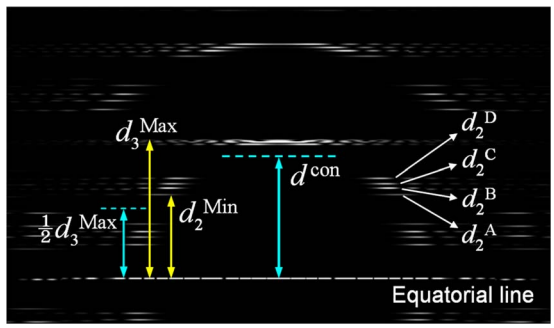

FIG. 1. (Color online) A simulated EDP of a SWCNT bundle containing four individual tubes: (13,2), (18,7), (20,6), and (26,6).

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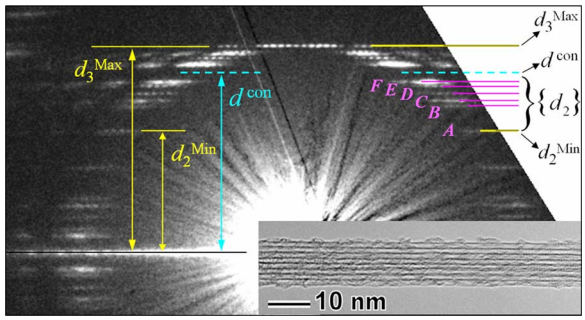

FIG. 2. (Color online) An EDP from a laser-produced SWCNT bundle with its high-resolution image as an inset.

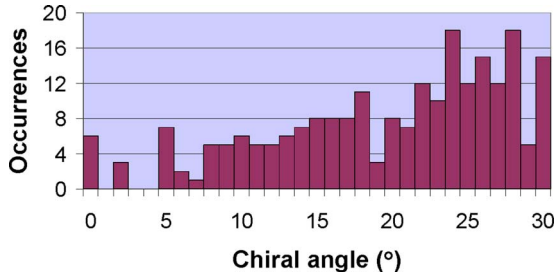

FIG. 3. (Color online) Helicity distribution in the laser-ablation SWCNT sample.

to 30° (armchair), the value of d_3^i is reduced while the value of d_2^i rises. Layer lines d_2^i and d_3^i merge or converge for an armchair tube, i.e., $d_3^i = d_2^i$.[9] The distance from the convergent line to the equatorial line is defined by the pair (d_2^i, d_3^i) of an arbitrary tube i

$$d^{con} = \sqrt{(d_2^i)^2 + (d_3^i)^2 - (d_2^i d_3^i)}. \quad (1)$$

Because the convergent line is located where layer lines d_3^i and d_2^i of an armchair tube appear as a single line, d^{con} can be also determined by $d^{con} = K/\sqrt{3}r$. Here, r is the atomic bond length in the hexagonal networks, e.g., the C–C bond length r in graphite is ~0.142 nm.[21] K is the diffraction camera constant. In other words, for a certain EDP, d^{con} is an intrinsic constant describing the fundamental structural property, i.e., the atomic bonding distance r in graphitic or graphiticlike tubular structures. As a result, d_3^i and d_2^i are conjugated to each other, and thus form a conjugated pair.

Based on the above analysis, in the EDP of a CNT bundle, layer line distances d_3^i for all possible helicities must appear in the range $d^{con} \leqslant d_3^i \leqslant d_3^{max}$, where d_3^{max} is the largest possible d_3^i (Fig. 1). On the other hand, all layer-line distances d_2^i in the bundle are bounded by $d_3^{max}/2 \leqslant d_2^i \leqslant d^{con}$. In practice, the smallest possible d_2^i denoted by d_2^{min} (Fig. 1) is measured from the layer line that is closest to $d_3^{max}/2$. d_2^{min} and d_3^{max} form a conjugated pair that corresponds to a single helicity in the assembly with the smallest chiral angle. With d_2^{min} and d_3^{max}, one can calculate the intrinsic constant d^{con} based on Eq. (1), by which all visible layer lines located between $d_3^{max}/2$ and d^{con} can then be paired, thus allowing corresponding helicities in the assemblies to be identified. For the example in Fig. 1 by the above-described means, helicities corresponding to layer lines d_2^A, d_2^B, d_2^C, and d_2^D are determined to be 7.00°, 10.35°, 12.79°, and 15.90°, respectively, with an accuracy better than 0.2°. The analysis is fully independent of the tilting effect[8] of the nanotube with respect to electron beam.

Now, we apply our method for the analysis of an EDP taken from a bundle of SWCNT produced by a laser ablation technique.[22] The transmission electron microscopy (TEM) sample has been so prepared (to be published elsewhere) that SWCNT bundles are typically well isolated, straight, and appropriate for electron diffraction analysis. Figure 2 shows a typical EDP from a CNT bundle with its high-resolution image as an inset. The TEM image and the EDP were taken on a Philips CM-200FEG microscope operated at 80 kV. A Gatan 794 multiscan charge coupled device camera (1 k ×1 k) was used for digital recording. The EDP shown in Fig. 2 is superior in that all the layer lines are clearly resolved and they are straight with clear features in contrast to the previously published EDPs from similar samples, where layer lines are weak and form dim arcs. This means that the nanotubes are not twisted in the bundle and helicities are well defined.[16]

In Fig. 2, two characteristic diffraction layer lines d_3^{max} and d_2^{min} are denoted by their distances measured from the equatorial line. d^{con} is calculated from d_2^{min} and d_3^{max} and it separates all d_2 and d_3 layer lines. Six d_2 layer lines indicated by A, B, C, D, E, and F, respectively, are observed between layer lines d_2^{min} and d^{con}. For each d_2 layer line, a corresponding d_3 can be calculated based on Eq. (1) with the aid of d^{con}, thus resulting in a corresponding helicity. From this particular EDP, six individual helicities are recognized. However, this does not necessarily imply that there exist only six nanotubes in the bundle. It is possible that two or more tubes in the bundle may have the same helicity and thus produce diffraction layer lines that overlap. Due to the fact that the diffraction intensity depends not only on the helicity of the nanotube, but also on the nanotube diameter, the integrated intensity of a certain layer line is typically not a linear function of occurrence of a given helicity. Attempting to evaluate the helicity density from one single EDP by analyzing the diffraction intensity is beyond the scope of this work. Instead, for a reliable statistical analysis of helicity distribution in a CNT sample, a large number of diffraction patterns are required to reduce the effects due to possible overlap.

We now apply the above-introduced method to the analysis of helicity distribution in the laser-produced SWCNT sample. Fifty-eight EDPs from 48 SWCNT bundles and 10 individual SWCNTs have been acquired under the same microscope settings as previously mentioned. Altogether 228 helicities are extracted resulting in the helicity distribution as shown in Fig. 3. The sample number is large enough so that further increasing sampling size do not dramatically change the character of the helicity distribution, which is biased toward large chiral angles with deficiencies around 3°, 7°, 19°, and 28°. This result is in contrast to previous reported electron diffraction studies of similar samples. Qin *et al.*[11] claimed that SWCNTs in the bundles display a rather uniform distribution of helicities, Bernaerts *et al.*[13] claimed a narrow dispersion around the armchair configuration, while Colomer *et al.*[14] concluded that their sample contains multiple but well-defined helicities. It is interesting to note that each of the three previous results represents a portion of the helicity distribution determined in this work.

In conclusion, we propose a universal method for quantitative helicity analysis in unidirectional assemblies of hexagon-based tubular structures from their EDPs. A critical dimension d^{con} is discerned from an EDP, which is a unique

intrinsic structural property of the atomic bonding distance in graphitic or graphiticlike tubular structures. With the aid of d^{con}, diffraction layer lines from bundles of single-walled or multiwalled graphitic or graphiticlike tubular structures are easily identified. Every individual layer line paired with its conjugated layer line reveals a single helicity contained in the assembly. If the layer lines are clustered into bunches, helicity bounds can be defined. The method has been used to analyze helicity in a SWCNT sample produced by a laser ablation technique, resulting in a reliable helicity distribution. This result helps to resolve a ten-year dispute over the helicity population in such samples. We attribute the reliability of our results to improvements in TEM sample preparation and to the improved helicity evaluation technique introduced here.

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[1]S. Iijima, Nature (London) **354**, 56 (1991).
[2]A. Jorio, E. Kauppinen, and A. Hassanien, *Carbon Nanotubes*, Topics in Applied Physics Vol. 111, edited by A. Jorio, G. Dresselhaus, and M. S. Dresselhaus (Springer, Berlin, 2008), pp. 63–100.
[3]D. Golberg, Y. Bando, C. Tang, and C. Zhi, Adv. Mater. (Weinheim, Ger.) **19**, 2413 (2007).
[4]X. Blase, A. Rubio, S. G. Louie, and M. L. Cohen, Europhys. Lett. **28**, 335 (1994).
[5]M. Gao, J. M. Zuo, R. D. Twesten, I. Petrov, L. A. Nagahara, and R. Zhang, Appl. Phys. Lett. **82**, 2703 (2003).
[6]Z. Liu, Q. Zhang, and L.-C. Qin, Phys. Rev. B **71**, 245413 (2005).
[7]J. C. Meyer, M. Paillet, G. S. Duesberg, and S. Roth, Ultramicroscopy **106**, 176 (2006).
[8]H. Jiang, D. P. Brown, A. G. Nasibulin, and E. I. Kauppinen, Phys. Rev. B **74**, 035427 (2006).
[9]H. Jiang, A. G. Nasibulin, D. P. Brown, and E. I. Kauppinen, Carbon **45**, 662 (2007).
[10]R. Arenal, M. Kociak, A. Loiseau, and D.-J. Miller, Appl. Phys. Lett. **89**, 073104 (2006).
[11]L.-C. Qin, S. Iijima, H. Kataura, Y. Maniwa, S. Suzuki, and Y. Achiba, Chem. Phys. Lett. **268**, 101 (1997).
[12]H. Z. Jin, R. R. He, and J. Zhu, J. Electron Microsc. **48**, 339 (1999).
[13]D. Bernaerts, A. Zettl, N. G. Chopra, A. Thess, and R. E. Smalley, Solid State Commun. **105**, 145 (1998).
[14]J.-F. Colomer, L. Henrard, Ph. Lambin, and G. Van Tendeloo, Eur. Phys. J. B **27**, 111 (2002).
[15]Z. Liu, Q. Zhang, and L.-C. Qin, Appl. Phys. Lett. **86**, 191903 (2005).
[16]L. Henrard, A. Loiseau, C. Journet, and P. Bernier, Eur. Phys. J. B **13**, 661 (2000).
[17]D. Golberg, Y. Bando, K. Kurashima, and T. Sato, Solid State Commun. **116**, 1 (2000).
[18]T. Laude and Y. Matsui, Eur. Phys. J.: Appl. Phys. **28**, 293 (2004).
[19]A. Celik-Aktas, J. M. Zuo, J. F. Stubbins, C. Tang, and Y. Bando, Appl. Phys. Lett. **86**, 133110 (2005).
[20]Ph. Lambin and A. Lucas, Phys. Rev. B **56**, 3571 (1997).
[21]M. F. Budyka, T. S. Zyubina, A. G. Ryabenko, S. H. Lin, and A. M. Mebel, Chem. Phys. Lett. **407**, 266 (2005).
[22]T. Guo, P. Nikolaev, A. Thess, D. T. Colbert, and R. E. Smalley, Chem. Phys. Lett. **243**, 49 (1995).