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Bundles of identical double-walled carbon nanotubes

J.-F. Colomer,*[a] L. Henrard,[a] P. Launois,[b] G. Van Tendeloo,[c] A. A. Lucas[a] and Ph. Lambin[a]

[a] *Laboratoire de Physique du Solide, FUNDP, 61 rue de Bruxelles, 5000 Namur, Belgium. E-mail: jean-francois.colomer@fundp.ac.be; Fax: +32(0)81724707; Tel: +32(0)81724708*

[b] *Laboratoire de Physique des Solides (UMR CNRS 8502), Bât. 510, Université Paris-Sud, 91405 Orsay Cedex, France*

[c] *EMAT, University of Antwerp (RUCA), Groenenborgerlaan 171, 2020 Antwerp, Belgium*

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In a sample produced by catalytic chemical vapor deposition (CCVD), the structure of the carbon nanotubes (diameter and helicity) which governs their electronic properties, is determined by electron diffraction. We found that most of the smallest bundles are constituted of identical double-walled carbon nanotubes.

Since their discovery in 1991,[1] carbon nanotubes have attracted great attention, with a particular interest for the single-walled carbon nanotubes (SWNTs)[2,3] because they constitute ideal one-dimensional systems. One of their most spectacular properties is that they can be metallic or semi-conducting depending on their diameter and helicity.[4] Recently, selective syntheses[5] of double-walled carbon nanotubes (DWNTs) have offered the opportunity to further study their structure, as intermediates between SWNTs and multi-walled nanotubes. Indeed, the DWNTs constitute a remarkable object for the investigation of the effects of the intershell interaction and the relationship between the chiral angles of two walls.

A powerful technique for the determination of the helicity of nanotubes is electron diffraction (ED), as first demonstrated by Iijima *et al.*[1,2] Experimentally, only few results on DWNTs have been reported so far. The determination of the chiral indices of individual DWNTs with large radii has been performed[6] and linked to the transport properties.[7] In previous works, we have evidenced particular features in the transmission electron microscopy (TEM) images and on the ED patterns related to the triangular arrangement of the DWNTs packed in bundles, either straight[8] or in the form of loops.[9] Recently, we have analysed an ED pattern from a small bundle of DWNTs with helicities of 0° and 15.3° and deduced the most probable wrapping indices.[10] We present here new experimental selected-area electron diffraction (SAED) data obtained on a CCVD sample which reveal that small bundles are often made of identical DWNTs, each bundle having a peculiar helicity. This interpretation is based on a detailed analysis of the ED patterns using the kinematical theory of diffraction.[11]

The CCVD sample was synthesized by decomposition of methane on Co/MgO catalyst in a temperature range from 900 to 1000 °C and purified by a hydrochloric acid treatment to remove the catalyst.[12] Long isolated straight bundles are required to achieve good-quality diffraction but due to the vibrations of the bundles under the electron beam, the TEM images are then difficult to obtain.[10] Note that the SAED experiments are insensitive to vibrations. To minimize blurring effects due to vibrations, we have performed high-resolution TEM close to the parts of the bundles attached to the carbon grid. Fig. 1a shows a straight bundle exhibiting different fringe spacings along the axis, related to different crystallographic orientations of the two-dimensional lattice with respect to the electron beam, revealing the twist of the bundle around its axis. The two other views (Fig. 1b and c) are magnifications of two parts of this bundle, where it is possible to show direct evidence that the bundle is made of DWNTs.[8] Indeed, these enlarged images can definitively not be attributed to single-walled nanotubes packed into bundles, because fringes with at least two different spacings are observed. The larger one is related to the inner diameter and the smaller one is related to the interlayer distance inside the double-walled nanotube.

Fig. 2a and 4a show experimental ED patterns where the two characteristic features of diffraction from a bundle of carbon nanotubes are observed: (i) intense spots along a line perpendicular to the bundle axis and crossing the 000 central spot, the so-called equatorial line (EL), where the spot positions are determined by the Bragg diffraction conditions imposed by the two-dimensional lattice of the bundle and the intensity is modulated by the form factor of the nanotubes; (ii) a distribution of non-equatorial spots in the so-called layer-lines, elongated in the direction normal to the axis and localized on two concentric circles (related to the graphite reflections) having their centers on the 000 spot. The distribution of the layer-lines depends on the helicity of the nanotubes and the tilt angle of the bundle with respect to the incident electron beam. In Fig. 2a, the layer-lines localized on the first circle are arranged in two sets of hexagons suggesting the presence of identical (or very close) helicity of the nanotubes (see ref. 11 for further information)

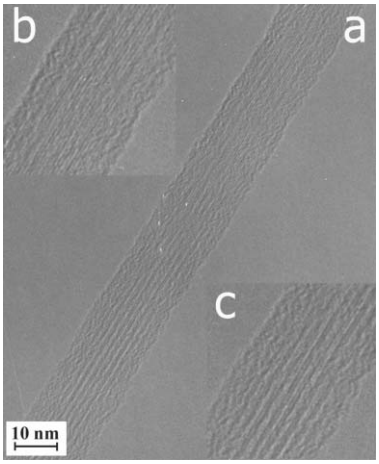

Fig. 1 (a) TEM image of a bundle of DWNTs and, (b) and (c) enlarged TEM images of two parts of this bundle.

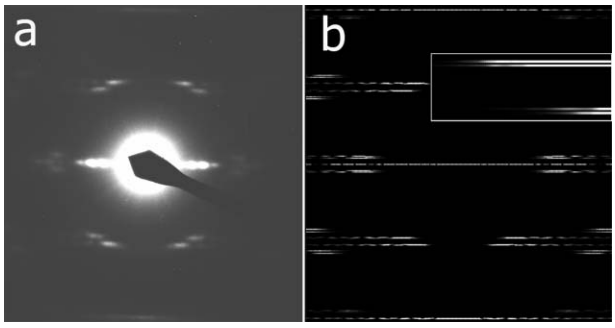

Fig. 2 (a) Experimental and (b) simulated ED patterns for a bundle of (9,7)@(15,11) DWNTs where an enlargement shows that the layer-lines are split, due to two close but different helicities.

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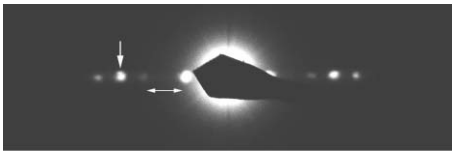

Fig. 3 Magnification of the equatorial line of the ED pattern in Fig. 2a.

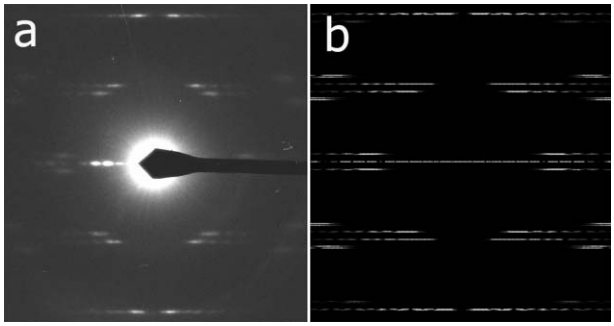

Fig. 4 (a) Experimental ED pattern compared with (b) the simulated ED pattern for a bundle of (8,6)@(14,10) DWNTs.

with a chiral angle of 25.4° estimated by the method described in ref. 13.

Other information about the packing of the nanotubes into bundles is extracted from the analysis of the equatorial line, magnified in Fig. 3. This EL exhibits unambiguously the characteristic features of the packing of double-walled nanotubes into bundles, with weak diffracted intensities around a momentum transfer of about 1 $Å^{-1}$ (see the horizontal double-headed arrow in Fig. 3) and a more intense spot localised at larger momentum transfer values ($k \geqslant 1.5$ $Å^{-1}$, see the vertical arrow in Fig. 3).[8–10] The first intense spot close to the 000 central spot and localised at 0.60 $Å^{-1}$ can be attributed to the (11) Bragg spot. The lattice parameter is then calculated to be equal to 20.9 Å.

Knowing the helicity and the lattice parameter value, we can now try to identify the wrapping indices of the DWNT tubes in the bundle.[10] However, in spite of the ED pattern suggesting a single helicity, it is not possible to constitute double-walled nanotubes with the two tubes having the same helicity close to 25.4° packed in a bundle with the estimated lattice parameter. That means that the two tubes have close but different helicities. Only few possibilities are realistic, the best fit is obtained with a bundle made of (9,7)@(15,11) double-walled nanotubes with a lattice parameter of 20.91 Å (see Fig. 2b). The (9,7) and the (15,11) tubes, with radii of 5.44 and 8.85 Å, possess chiral angles of 25.9 and 24.9° respectively. The spots corresponding to the two helicities are not resolved experimentally (Fig. 2a) but can be observed in the simulation (inset in Fig. 2b). Note that a small tilt angle (5°) of the bundle with respect to the incident electron beam has been introduced to describe completely the experimental ED pattern.

The detailed analysis of another ED pattern leads to similar conclusions. Fig. 4a shows an experimental ED pattern suggesting a helicity of 24.7°. The study of the EL gives a lattice parameter of 19.8 Å. As in the previous case, the double-walled nanotubes made by two tubes with the same helicity cannot be constituted. The best theoretical result is obtained for a bundle made of (8,6)@(14,10) double-walled nanotubes with a lattice parameter of 19.9 Å. The (8,6) and (14,10) tubes, with radii of 4.76 and 8.18 Å, possess chiral angles of 25.3 and 24.5° respectively. The simulated ED pattern (Fig. 4b) is in agreement with the experimental one. As in the first case, the split of the layer-lines is not resolved experimentally. Note that the electron beam here is normal to the bundle axis (no tilt). The profile of the experimental EL (Fig. 5) shows the two characteristic features of DWNT bundles (weak diffracted intensities at about 1 $Å^{-1}$ and a more intense spot localized at

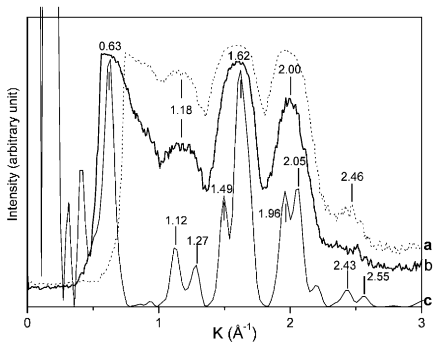

Fig. 5 (a and b) Comparison between the experimental ELs with two different exposure times , and (c) the computed EL for a (8,6)@(14,10) DWNT bundle.

1.62 $Å^{-1}$). The experimental EL profile is nicely reproduced by the computed EL for a bundle made of (8,6)@(14,10) double-walled nanotubes. Note that all the simulations are realized with 13 DWNTs packed in a triangular arrangement into bundles.

We have shown examples of CCVD double-walled carbon nanotubes that are formed by identical nanotubes when packed into small bundles. Of course, these observations were made on a small number of bundles, which were found suitable for performing reliable ED experiments, and no definitive conclusions can be drawn statistically about the preferential helicity values. But the observed helicities offer keys for the detailed investigation of the growth mechanisms, which should account for them. Moreover, our finding of identical DWNT bundles gives a strong indication that their growth is the result of a collective growth mechanism from a larger metal catalytic particle. Indeed, a mechanism involving the coalescence of isolated DWNTs that have grown individually and have then gathered in bundles after their formation by van der Waals forces could not easily explain the identical structure of the DWNTs inside a small bundle.

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