Study of the packing of double-walled carbon nanotubes into bundles by transmission electron microscopy and electron diffraction

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The structure of bundles of double-walled carbon nanotubes synthesized by catalytic chemical vapour deposition is investigated using transmission electron microscopy and electron diffraction. Small and well-crystallized bundles are observed and characterized by transmission electron microscopy and electron diffraction and display particular features that reveal unambiguously the presence of double-walled nanotubes constituting the bundles. Other remarkable results are obtained focusing our interest on the rings of double-walled nanotube bundles. The experimental results are analysed with the help of the kinematical theory of diffraction. We conclude this study by the discussion of the growth mechanism of these bundles.

Introduction

Since their discovery in 1991,1 carbon nanotubes have been the subject of intensive research. Most effort has been devoted to single-walled carbon nanotubes (SWNTs) due to their extraordinary mechanical2 and electronic3 properties. More recently, double-walled carbon nanotubes (DWNTs), which consist of two concentric cylindrical graphene layers, have attracted the interest of researchers because they offer a nice transition between single-walled carbon nanotubes and multi-walled carbon nanotubes (MWNTs). Moreover, they allow to investigate the effect of interactions between coaxial graphitic layers.

The selective syntheses of DWNTs have been recently reported, offering an opportunity to further study their structure. The DWNTs can be synthesized by different methods such as electric arc discharge,4 coalescence of C60 peapods,5 and catalytic chemical vapour deposition (CCVD) using supported9 or floating10–12 catalysts. Depending of these synthesis methods, different values of the intertube spacing have been reported. Large and isolated DWNTs synthesized by CCVD, using supported5–9 or floating10–12 catalysts, have been reported elsewhere.9 The synthesized carbon material was extracted by treatment in concentrated aqueous HCl solution.9 Concerning the TEM characterization, we followed the regular procedure for carbon nanotubes. A few milligrams of carbon material was dispersed ultrasonically in ethanol and one droplet was put onto a holey-carbon TEM grid and examined in a JEOL 200CX microscope working at 200 kV. The selected-area electron diffraction (SAED) patterns were recorded with a typical exposure time of 90 s on usual photographic films.

Experiment and theory

Experimental

The sample was synthesized by a CCVD method. The catalyst is composed of a Mg1–xCoO solid solution containing Mo oxide and reduced in a H2–CH4 atmosphere at a maximum temperature of 1000 °C, following the experimental procedure reported elsewhere.9 The synthesized carbon material was extracted by treatment in concentrated aqueous HCl solution.9 Concerning the TEM characterization, we followed the regular procedure for carbon structures. A few milligrams of carbon material was dispersed ultrasonically in ethanol and one droplet was put onto a holey-carbon TEM grid and examined in a JEOL 200CX microscope working at 200 kV. The selected-area electron diffraction (SAED) patterns were recorded with a typical exposure time of 90 s on usual photographic films.

Kinematical theory of diffraction

The experimental ED patterns of carbon nanotubes, and particularly the so-called equatorial lines, can be analyzed with the kinematical theory of diffraction.15 Since the distances (in real space) associated with low momentum transfer (k < 2.5 Å−1) are larger than the C–C distance, we can use the continuum theory for analysing the equatorial lines (the individual tubes being considered as continuous surface density of carbon atoms on a cylinder).17,18 Within this approximation, the scattering form factor of a single tube of radius ρ is given by \( A(k) = f(k)pJ_0(kp) \) (where \( J_0 \) is the Bessel function of order 0 and \( f(k) \) is the carbon atomic scattering factor). For a double-wall carbon nanotube, the diffracted amplitude is

\[
A(k) = f(k)(\rho_1J_0(k\rho_1) + \rho_2J_0(k\rho_2))
\]

(\( \rho_1 \) and \( \rho_2 \) being the radii of the inner and outer tubes, respectively).
The simulations of the equatorial lines performed here are based on this continuum theory, whereas the atomistic description of carbon nanotubes is taken into account for the simulation of the full diffraction pattern.\textsuperscript{16}

**Straight bundles of double-walled carbon nanotubes**

**Real space evidence**

The observed sample is constituted by a majority of double-walled nanotubes isolated and organized into bundles. Focusing our interest on these bundles, the packing of double-walled nanotubes in a hexagonal arrangement is exemplified in Fig. 1. As in the case of bundles of SWNTs, TEM observations of a bundle of DWNTs are possible with the electron beam perpendicular (Fig. 1(a)) or parallel (Fig. 1(b)) to its axis. When the observations are made perpendicular to the bundle axis, in the (10) direction (Fig. 1(a)), the image consists of a set of fringes with two different spacings, the larger one is related to the inner tube diameter and the smaller one to the interlayer distance between the two walls, for a focus close to the Scherzer focus. However, the observations of DWNT bundles generally show a variable sequence of fringe spacings, corresponding to different crystallographic orientations of the bundle with respect to the electron beam. This observation is due to the twisting of the bundles around their axes.

When observing a bundle parallel to the tube axis (Fig. 1(b)), the “cross section” consists of a periodic array of two concentric dark circles having a white dot in their center. This image directly displays the close-packed hexagonal arrangement of the double-walled tubes. Indeed, each dark circle is the image of the atomic layer of a tube seen edge on. From this image, the number of double-walled tubes (39) and the periodicity of their arrangement within the bundle are immediately observed. However, the relation between the dark circle dimensions and the diameters of the tubes is valid only for a defocus close to the Scherzer focus.

We must note that these types of TEM images have to be interpreted carefully, if the determination of the numerical values (for example, the inner diameter of the double-walled nanotube or the interlayer spacing), is to be deduced from these images. Note that the easiest value to obtain from the “cross-section” images is the lattice parameter. Indeed, we can estimate this value by measuring the distance between the two centers of two adjacent white dots. From Fig. 1(b) the lattice parameter is evaluated as around 20 Å.

In the sample, different types of bundles are observed. We found bundles that are not well organized, due to the presence of tubes with different numbers of walls and with different diameters (Fig. 2(a)). Considering now the bundles with only double-walled carbon nanotubes, as already exemplified (Fig. 1(b)), the DWNTs can be coherently packed inside small bundles, and exhibit uniform diameters that are generally smaller compared with those found in the case of isolated double-walled tubes. Sometimes we observe larger double-walled tubes that are generally located on the external layers of the bundles (Fig. 2(b)), as already reported in the case of SWNT bundles.\textsuperscript{18} As for larger bundles, they are generally constituted by the coalescence of smaller bundles, the TEM observations showing extensive branching.

**Reciprocal space evidence**

On the same sample, we have realized SAED experiments on the small DWNT bundles that are not the result of the coalescence of other bundles. A typical ED pattern obtained on a straight and small bundle at normal incidence is presented in Fig. 3(a). The ED pattern for a bundle of nanotubes exhibits two main features: (i) a line of spots crossing the 000 central beam, where the helicity can be deduced from the diffracted spots.

In the presented case, the diffracted spots form two perfect hexagons on the inner circle of diffraction and also, spots are visible close to the north and south poles on the second circle. This pattern suggests the presence of a single helicity with a chiral angle estimated at 19.1°. The observation of a single helicity for a small bundle of double-walled nanotubes is a surprising result. This means that, in addition to being identical, the DWNTs are comprised of inner and outer tubes with the same helicity. The single helicity for a bundle composed of DWNTs is due to the small size of the studied

Fig. 1  (a) TEM image of a bundle of DWNTs in the (10) direction and (b) cross section of a bundle of DWNTs exhibiting a hexagonal lattice arrangement.

Fig. 2 (a) Cross section of a bundle constituted by different types of tubes and (b) cross section of a bundle constituted of double-walled carbon nanotubes with larger tubes located on the external layers of the bundle.

Fig. 3 (a) Experimental electron diffraction pattern of a DWNT bundle at normal incidence exhibiting a single chiral angle of 19.1°. (b) Magnification of the equatorial line.
bundle. However, we note that the major portion of the sample is constituted of larger bundles, more or less organised, presenting generally a distribution of helicities.

We now discuss the packing of the double-walled nanotubes inside the bundles by a study of the intensity profile along the equatorial line. The intensity along this line is modulated by the form factor of the nanotubes and the structure factor of the bundle lattice packing. A magnified equatorial line is shown in Fig. 3(b) where four spots can be distinguished. Moreover, we have plotted the experimental EL profile and compared it with a simulation in Fig. 4.

We first notice that the EL presents clearly spots allowing us to conclude high crystallinity of the studied bundle. Further observations are the absence of diffracted intensities around a momentum transfer of about 1 Å⁻¹ (see the horizontal double-headed arrow in Fig. 3(b) and 4) and the rather large intensities of the spots 3 and 4. This fact cannot be attributed to the packing of single-walled nanotubes into bundles where the higher spot intensities are found at about 1 Å⁻¹ with an attenuation of the intensities when moving away from the 000 central beam. However, there are several possibilities to interpret these observations because different DWNTs present a unique helicity of 19.1° and differ only by their lattice parameter: (14,7)@(20,10) (lattice parameter of 23.93 Å), (12,6)@(18,9) (21.85 Å), (10,5)@(16,8) (19.78 Å), (8,4)@(14,7) (17.71 Å), (6,3)@(12,6) (15.64 Å), (4,2)@(10,5) (13.56 Å) and (2,1)@(8,4) (11.49 Å). The best agreement with the experimental EL profile is obtained for a bundle composed of (8,4)@(14,7) double-walled nanotubes with a lattice parameter of 17.7 Å as shown in Fig. 4. The diameter of the (8,4) tube is 8.3 Å and that of (14,7) is 14.5 Å with an interlayer distance between the two tubes of 3.1 Å.

In conclusion, the double-walled nanotubes coherently packed into small bundles have two characteristic signatures along the equatorial line on their ED pattern: (i) the absence of diffracted intensities around k = 1 Å⁻¹; (ii) a spot located at k > 1.5 Å⁻¹ more intense than in the case of single-walled carbon nanotube bundles. Such characteristic signatures of DWNTs packed into bundles is due to the interferences between the form factor of the two walls of each tube (see equation above).

Discussion of growth mechanism

According to our structural analysis, it is tempting to propose that small bundles with uniform tube composition are grown all together from single catalyst particles. This hypothesis seems to be in contradiction with previous reports about the same type of samples that suppose the bundles to be formed after or maybe during the growth of isolated tubes. We think that this type of individual growth mechanism is involved in the formation of bundles with different types of tubes (diameter and number of layers) that gather due to van der Waals forces (Fig. 2(a)). Moreover, this post-synthesis mechanism can explain the presence of larger double-walled nanotubes located in the external layers of bundles, where they are grown individually and stick to the bundle after or during their formation (Fig 2(b)). However, it seems very difficult to visualise that individual double-walled nanotubes growing from different particles (with different shapes, sizes and growth temperature) lead to the formation of identical tubes and that afterwards, in the post-synthesis process, the tubes pack together to form a perfect hexagonal lattice.

Other studies also conclude to the possible existence of a “collective” growth of bundles from single catalyst particles, whatever the production methods. There is also a debate concerning the size of the particles involved. Some reports claim that catalyst particles below ca. 5 nm produce nanotubes while larger particles are encapsulated. In agreement with our hypothesis, other results reported that the bundles emerge from nanoparticles of around 15 nm of size, never exceeding 40 nm.

Rings of double-walled carbon nanotube bundles

Real space evidence

We report on the observation of perfect rings of double-walled carbon nanotubes similar to the rings of single-walled nanotubes observed previously. While examining the same sample by TEM, we regularly observed circular bundles of nanotubes. Their concentration agrees with that given for SWNT rings (between 0.01 and 0.1%) in laser ablation material. Fig. 5(a) shows the structure of a ring that looks like a perfect torus. However, TEM images sometimes exhibit the two ends of the bundle constituting the ring. The structure is therefore a coil, not a torus, in agreement with the case of SWNT rings. Fig. 5(b) is particularly interesting because it shows the cross section of the observed end of the coil that clearly reveals a hexagonal lattice of DWNTs (Fig. 5(b)).
estimate that this coiled bundle is composed of about 120 nanotubes of uniform external diameter. The measured lattice parameter is 1.85 nm, slightly larger than that generally reported for ropes of SWNTs (1.7 nm).\textsuperscript{29, 30} This indicates that the DWNTs have an external diameter around 1.5 nm.

Reciprocal space evidence

In spite of the small quantity of rings and the entanglement of other nanotube structures in the sample, it was possible to perform SAED experiments on isolated DWNT rings. A typical experimental ED pattern of a ring having its rotational axis parallel to the electron beam is shown in Fig. 5(c), where it is compared to simulations generated by the kinematic theory of diffraction\textsuperscript{14} (Fig. 5(d) and (e)). As already explained in the case of a straight bundle, most of the diffracted intensity is concentrated along the equatorial line, perpendicular to the tube axis. Here, the tube axis direction changes continuously around the ring, and therefore the EL of the ring rotates continuously around the 000 central beam. Top view TEM images of the rings generally display different lattice fringes that change continuously around the ring due to a twist of the bundle. Because the bundle is twisted, only those sections of the ring where the hexagonal lattice of the bundle is under Bragg conditions are diffraction spots observed along the corresponding ELS.

This explains why spots are preferentially observed along some radial directions only. The most intense spots are concentrated around curved polygons. The part of the experimental pattern in Fig. 5(c) is best reproduced by the simulation when assuming that the bundle is twisted by 60° over one eighth of the ring circumference, leading to the eight-fold symmetry of the diffraction figure (Fig. 5(d)). The same orientation of the hexagonal lattice is recovered after one-height of a turn around the ring and therefore after a complete turn of 360°. There is no reason to have a real phase coherence after 360°, because the structure is not a torus, but experimentally phase clashes are not observed. The dark annular zone indicated by the double-headed arrow in Fig. 5(c) and (d) is present when simulating the ED pattern with SWNTs (Fig. 5(e)). This is because of destructive interferences between the form factor of the two walls of the DWNTs, as explained in the case of straight bundles. These patterns indicate unambiguously that the ring is indeed composed of DWNTs.\textsuperscript{31}

Conclusion

We have highlighted experimental facts showing that the double-walled carbon nanotubes can be coherently packed within small bundles with uniform diameters and helicity. These bundles do not comprise all of the observed sample. Isolated tubes, bundles with different kinds of tubes, or larger bundles of DWNTs resulting from the coalescence of smaller ones due to van der Waals forces are most often observed. However, the present observation of a uniformity of the tube diameter and helicity is a strong indication of the growth mechanism of these bundles from single catalyst particles.

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References