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Scanning tunneling microscopy observation of tightly wound, single-wall coiled carbon nanotubes

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Abstract. – Scanning tunneling microscopy (STM) images of carbon nanotubes grown by the catalytic cracking of hydrocarbons, which exhibit a well-defined axial periodicity in the 1 nm range, are reported. The data are interpreted as tightly wound, single-wall, coiled carbon nanotubes with an interspire distance of 0.34 nm as the distance between graphene layers in graphite or the distance of single-wall carbon nanotubes in ropes.

Due to their fascinating electronic and mechanical properties, the carbon nanotubes have attracted a continuously growing interest from both fundamental and technological points of view [1,2]. Among the several techniques available for the synthesis of carbon nanotubes [1,2], the catalytic vapor deposition method is known to produce a controllable fraction of multi-wall nanotubes wound into beautifully regular coils [3]. Transmission electron microscopy has revealed that some coils are so tightly wound that the separation between the adjacent spires is reduced to the 0.34 nm interlayer spacing of bulk graphite [4]. Here we report on STM observations of nanotubes grown by the catalytic method which appear to be tightly wound, *single-wall* nanotube coils. These helical structures have an outer diameter of about 2 nm and show a pronounced longitudinal periodicity of 1 to 1.2 nm. The analysis of the STM data indicates that these tiny, molecular-size coils are made from graphene tubules having the smallest diameter experimentally observed for nanotubes, namely around 0.7 nm [5].

While the growth mechanisms of the carbon nanotubes still remain unclear, different production techniques have been established. Among these techniques, a few have been optimized for the synthesis of single-wall nanotubes [6, 7] which are made of one single rolled sheet of graphene. The nanotubes examined in this report were synthesized by catalytic thermal decomposition of acetylene by Co nanoparticles supported on silica [8]. Most of the carbon fibers produced by this method are straight or slightly curved multi-wall nanotubes, but a certain fraction of them happen to be coiled nanotubes with regular pitch [3]. All the observations of coiled nanotubes reported so far were obtained by transmission electron microscopy (TEM) and electron diffraction, which revealed them as helical multi-wall structures presenting a large variety of pitch values [3, 4, 9]. These TEM observations enabled to propose possible growth modes [3] and atomic structures [4] of coiled nanotubes which are thought to represent the nanoscopic-size cores of larger coil-shaped filament previously observed in the process of catalytic decomposition of hydrocarbons [10]. In the present work, we report on STM observation of graphitic structures having an apparent outer diameter of the order of 2 nm, and showing a regular axial periodicity of 1.1 nm, typically, with a peak-to-valley distance of about 0.6 nm. These objects are believed to be coiled nanotubes a factor of ten smaller than those observed by TEM. Single-wall, coiled-carbon nanotubes with comparable pitch and diameter values have been predicted on the basis of molecular-dynamic calculations [11] shortly after the discovery of carbon nanotubes by Iijima [12].

The present STM data are interpreted as being the signature of coiled *single-wall* nanotubes (CSWNT) made from a tube of diameter of about 0.6 to 0.7 nm wound at a spire separation of 0.34 nm, which is the distance between straight single-wall tubules in bundles known as ropes [6,7]. The present CSWNT could reveal novel electronic, magnetic and optical properties related to their highly chiral structures [13]. In addition, their existence may throw some additional light on the processes of catalytic synthesis of multi-wall coiled nanotubes.

The coiled nanotubes were found in the same batch as the one that produced rafts of straight carbon nanotubes described earlier [14], where bundles of single-wall nanotubes with diameter in the range 0.9–1.1 nm were found. The STM samples were prepared as reported previously: the powder material containing the nanotubes was ultrasonicated in toluene after chemical removal of the catalyst. No oxidation which could have destroyed the pentagonal defects was performed. The suspension was placed on freshly cleaved HOPG and the toluene was evaporated at room temperature. STM imaging was carried out in ambient atmosphere using mechanically prepared PtIr tips. The tunneling current used was of the order of 0.5 nA, the tunneling voltages varied from 0.5 to 0.8 V, and typical scan frequencies used were around 1 Hz.

The STM image displayed in fig. 1(a) shows objects which we believe are CSWNTs. An atomic model of such a coil is shown in fig. 1(b). Such a contorted structure is made possible with sp^2 carbons by the introduction of strategically placed ring defects (pentagons, heptagons ...) in the curved honeycomb network. In the STM image, the objects B and C present a regular pattern of maxima and minima along their axis. The simultaneous presence of the object A, which does not show any periodic features along its axis, is a proof that the observed periodicity of B and C is not an imaging artifact. Moreover, object C shows the same camel-back structure as the one found earlier on a multi-wall coiled nanotube having a much larger pitch [15]. Objects B and C bear some resemblance with the bead-like structures obtained after strong irradiation of single-wall nanotubes with a high-energy electron beam [16], but they are much more regular and straight. Apart from the ultrasonication, our samples did not receive any treatment and all the nanotubes observed in other regions were found to be well graphitized. Unfortunately, we did not succeed in finding CSWNTs similar to objects B and C by transmission electron microscopy, which should have confirmed the present interpretation of the STM data. The TEM observation of isolated single-wall carbon nanotubes itself is a demanding task. It is highly recommended that the sample, *i.e.* the nanotube to be examined is not supported in the region of interest by anything, not even by the usual thin layer of amorphous carbon which is commonly used for covering TEM grids intended for routine TEM investigations. The details of the TEM image formation mechanism of carbon nanotubes are discussed by Iijima in his first paper on carbon nanotubes [12]. If the thickness of the amorphous carbon layer is comparable to, or larger than the "effective" thickness of the tube, *i.e.*, the total thickness of the nanotube, which could be considered as being parallel with the electron beam of the TEM (denoted by V in ref. [12]), then no contrast will be seen in the image. The case of a coiled single-wall carbon nanotube is much less favorable for TEM observation than that of straight SWNT. In some occasions zig-zag structures which could be coiled carbon nanotubes with a few walls have been observed, but

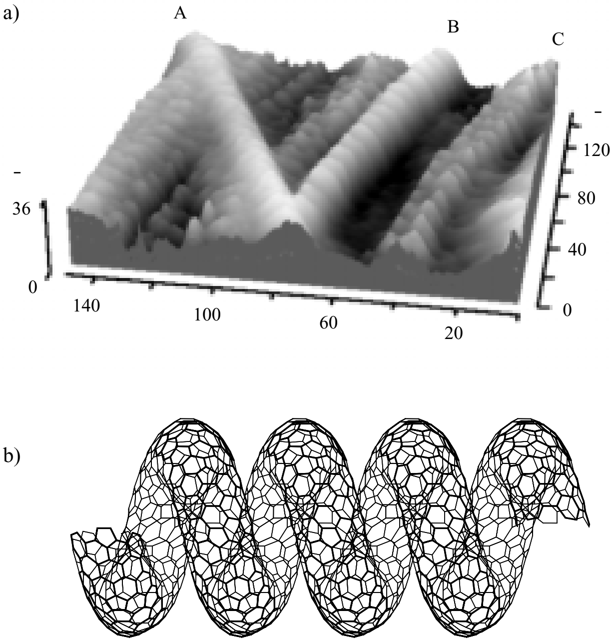

Fig. 1 – (a) 3D view of a constant-current STM image showing an assembly of several carbon nanotubes on HOPG. The assumption that the objects B and C are single-wall coiled nanotubes provides a straightforward interpretation of their regular, periodic structures along their axis. (b) Atomic model of a CSWNT made from segments of (6, 6) and (10, 0) nanotubes (0.8 nm diameter). A unit cell of the helix is composed of 440 atoms, and contains 5 octagons on the inner side of the spires and 10 pentagons on the outer side. The external diameter of the structure is 2.3 nm and the pitch is 1.17 nm.

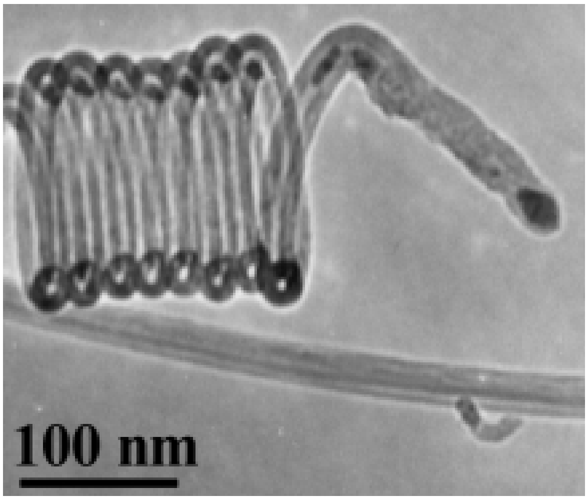

Fig. 2 – TEM image of a multi-wall tightly wound coiled carbon nanotube with a wall thickness of 28 graphene layers.

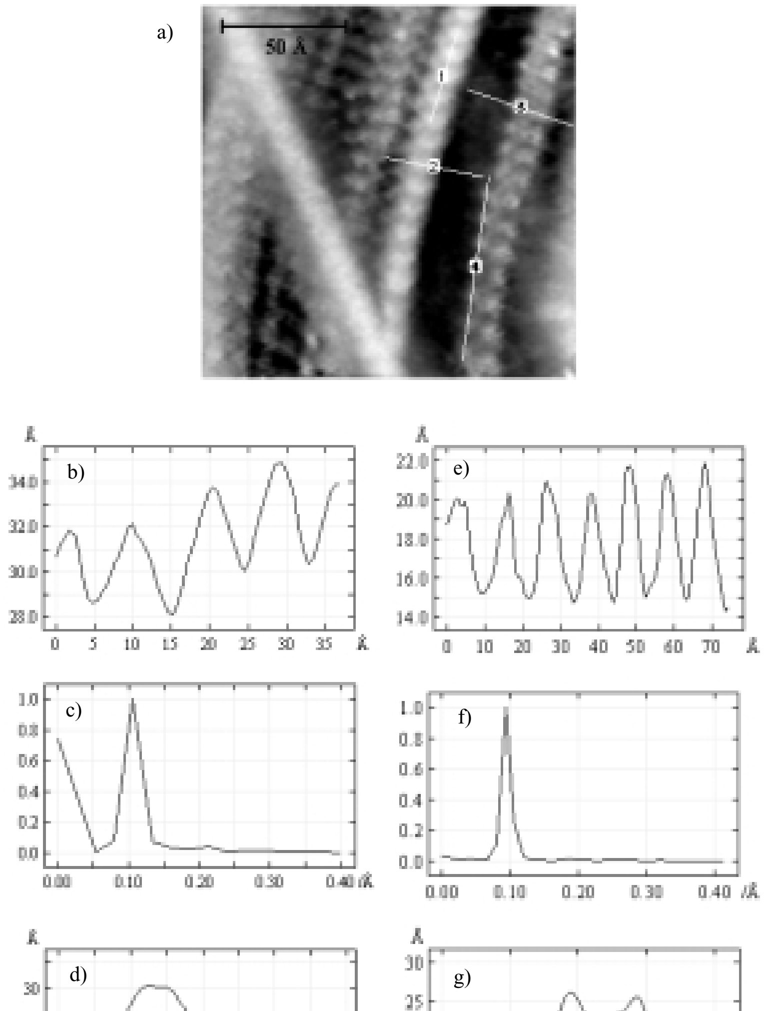

Fig. 3 – (a) 2D representation of the STM image shown in fig. 1(a). Topographical profiles of the objects B and C: line cuts 1 (b), 2 (d), 4 (e), and 3 (g). Normalized Fourier spectra of the longitudinal profiles along line cuts 1 (c) and 4 (f).

these structures were extremely unstable under the irradiation by the electron beam. It was not possible to set the proper conditions for taking images, or to carry out examination at high magnification. The TEM image of a coil with the wall composed of 28 layers is shown in fig. 2. One may judge what would be visible from a coil composed of one single layer.

Typical topographical line cuts taken on objects B and C (fig. 1) are shown in fig. 3. The Fourier spectrum (c) of the profile (b) along the axis of coil B (line cut 1 shown in fig. 3a) reveals a well-defined longitudinal periodicity (helical pitch) of 0.94 nm. The peak-to-valley distance measured on this line cut is 0.4–0.5 nm. As shown by the profile (d) along the line cut 2, object B does not have a camel-back structure. The apparent diameter of coil C, as measured from the STM image, is 2 nm. The distance between the camel-back peaks in a series of topographical profiles like the one along the line cut 3 shown in (g) is 0.9–1.5 nm. The depth of the depression separating the two humps varies between 0.3 and 0.5 nm. The fluctuations of all these values may result from local variations of the electrical contacts of the coil with the underlying substrate. According to the Fourier spectrum (f) of the profile (e) traced along line cut 4 parallel to the axis and passing by one row of maxima, the pitch of the helix is found to be 1.07 nm. The peak-to-valley distance along this line cut is around 0.6 nm.

Ge and Sattler [17] reported the observation by STM of a superstructure arising from the misorientation of the two outer layers of a multi-wall carbon nanotube. This structure is clearly different from what we have measured: i) it shows up in atomic resolution images, ii) it does not look like a "necklace of pearls" (fig. 1a, the central object), but it rather looks like local maxima distributed helicoidally along a cylinder. Ge and Sattler reported a zig-zag angle with respect to the tube axis of 120°. In our case, as can be seen from fig. 3a, the orientation of the maxima is almost normal to the tube axis, and within "one turn" the local maximum is continuous. No such pattern can be generated by Moiré-like effects. As proposed by Sattler and Ge, the production of a Moiré-like superstructure is due to the rotation of the axes with respect to each other of the graphene sheets which are rolled to produce the outer wall of the nanotube and that immediately below it. This effect is well known in STM images HOPG (see [18] and references therein). The typical vertical amplitude of the Moiré-like superstructure is of the order of 0.1 nm. Our line cuts (fig. 3b and e) clearly show that the vertical amplitude of the oscillations is of the order of 0.5 nm.

There are not too many ways to build a double-wall carbon nanotube which has the maxima of the Moiré-like pattern arranged strictly along the tube axis. These maxima are produced in the regions where locally the two lattices overlap with a small difference. To achieve the alignment of the maxima along the tube axis, the outer and the inner tubes have to have the same absolute values of chiral angles —as measured from the zig-zag axis which should be parallel with the tube axis— but one of the layers has to be left handed while the other right handed. It is unlikely that several double-wall carbon nanotubes are produced in the same time, at the same place, which all have the same particular arrangement of the two layers that gives the alignment of the Moiré-like maxima along the axis of the tube. The Moiré-like effect may show up only in multi-wall carbon nanotubes. A three-wall nanotube is much too thick to be imaged by STM as an object with the apparent diameter of 2 nm. Therefore, we think that the observed periodicity cannot be produced by Moiré-like effects.

Several coils found in the same region of the sample were characterized in a similar way. Changing the scan angle did not modify the observed periodicity. The data are summarized in table I, which lists five different values of the pitch. The apparent outer diameters are all around 2–2.5 nm, with one exception for the coils having the 1.11 nm pitch. One may not exclude that some coils were partly embedded in the surrounding material. In that case the pitch could be correctly determined on the topmost part of the object, but the measurement of the apparent diameter would be underestimated as compared to free-standing coils.

The lower limit of the diameter of a straight single-wall nanotube sets up when the binding energy of the network can no longer accommodate the strain energy due to the curvature [19]. For the armchair type, this limit is 0.7 nm, while it can be reduced to 0.5 nm in the case of the zig-zag geometry [20]. In a tightly wound coil, there is an additional van der Waals attraction between adjacent spires, which may yield a further energetic gain stabilizing small

TABLE I – *Geometrical parameters of single-wall coiled nanotubes determined by STM. The pitch was determined by Fourier analysis of topographical line cuts along the coil axis. When possible, the apparent diameter was measured on line cuts parallel to the spires.*

Pitch P (nm)	Tube diameter d (nm)	Number of observations	Overall diameter D (nm)	Remarks
1.25	0.87	4	2.4	Camel back (1) Regular (3)
1.11	0.65	3	1.35	Regular
1.07	0.70	1	2.2	Camel back
1.00	0.65	4	2.7	Regular
0.94	0.58	4	2.2 (one measurement)	Regular

tube diameters. Even before the first experimental observations of multi-wall coiled nanotubes, the elastic properties and the thermal stability of helical coiled cages of graphitic carbon were investigated by molecular dynamics [11]. Recent elasticity calculations [21] have shown that some coiled nanotubes are more stable than the straight ones.

The structures observed experimentally here have their geometrical parameters (see table I) reasonably close to the ones optimized by molecular-dynamics calculations [11], *i.e.* to coiled structures with pitch in the 0.8–1.4 nm range which were found to be energetically stable. The relation between the pitch (P), the tube diameter (d) and the outer diameter (D) of the helix is $P = (d + c_0)/\sqrt{1 - (d + c_0)^2/[\pi(D - d)]^2}$, where c_0 is the distance between successive loops. Taking $c_0 = 0.34\,\text{nm}$ leads to the following sequence of tube diameters: 0.58, 0.65, 0.70, and 0.87 nm. The first two values are close to the tube diameter (0.6 nm) of the C_{540} helix of ref. [11], which has a short pitch (0.85 nm) but a rather large outer diameter (4.1 nm). The last two values are close to the tube diameter (0.8 nm) of the C_{360} helix [11], the overall diameter of which is 2.3 nm. It is reasonably close to the apparent diameter of the coils measured by STM, taking into account the convolution effect between the STM tip and the imaged objects. The pitch of the C_{360} helix is 1.3 nm, slightly larger than the values of table I. Due to the large variety of possible nanotubes, we cannot identify unambiguously any of the observed structures with those calculated in ref. [11].

When the STM scans that part of the coil between two successive contact points with the substrate, the current tunneling from the tip bifurcates in two complementary paths (x and $L - x$) along the loop (total length L) before flowing into the substrate. Assuming constant section Ω and resistivity ρ for the tube, the total conductance of one single loop reads as $G = [R_\text{T} + \rho x(L - x)/\Omega L]^{-1}$, where R_T is the tunneling resistance. Provided that the tube resistance is high *vs.* R_T, the total conductance G shall decrease by a factor of two when the STM tip reaches the summit of the loop, during a cross-sectional scan. Therefore, in the case of high-resistance semiconductor tubes, one may encounter the situation where a dip will develop in the STM current above the topmost regions of the coil, leading to a characteristic camel-back profile in the corresponding line cut. However, current variations by one half can, by no means, account for the observed total height variations of 0.3 to 0.5 nm so that it is likely that a mechanical deformation of the coil occurring during the tip displacement is responsible for the camel-back structure. This latter explanation is supported by AFM measurements performed on coiled carbon nanotubes [22], and by recent theoretical arguments [23] which predict an additional energy barrier of the order of 10 eV between the carbon nanotube and a metallic contact at van der Waals distance. This additional barrier if added to the value of tunneling barrier can make the STM tip descend till it comes into mechanical contact with the coil.

In summary, several carbon nanotubes showing a regular longitudinal periodicity of 1–1.2 nm in their STM images have been observed. These data are best interpreted in terms of coiled graphitic structures, which are known to be produced by catalytic decomposition of hydrocarbon molecules. The geometrical parameters listed in table I identify these helical objects to tightly wound, single-wall coiled carbon nanotubes.

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