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Room temperature growth of single-wall coiled carbon nanotubes and Y-branches

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Abstract

Straight carbon nanotubes, carbon nanotube "knees," Y-branches of carbon nanotubes and coiled carbon nanotubes were grown on a graphite substrate held at room temperature by the decomposition of fullerene under moderate heating (450 °C) in the presence of 200-nm Ni particles. The grown structures were investigated without any further manipulation by STM. The growth and the chemical stability of the carbon nanostructures containing nonhexagonal rings are discussed.

Keywords: Carbon nanotubes; Nanotube knees; Y-branching; Coiled carbon nanotubes; Haeckelite

1. Introduction

The discovery of straight carbon nanotubes [1]—constituted of perfectly rolled, defect-free graphitic layers—opened up a new path for rethinking the family of carbon based structures built up from sp^2 hybridized carbon. Quite soon, the idea of branched [2] and of helically coiled structures [3] emerged. Beyond their importance from the point of view of basic science, these new nanostructures are very interesting as possible building blocks of nanoelectronics—three-terminal devices and 2D networks—and from the point of view of nanoelectromechanical systems and nanoactuators.

A modification of straight carbon nanotubes predicted by Scuseria [4] and Chernozatonskii [5] in 1992, were the Y-branched nanotubes. The structure calculated by Scuseria is shown in Fig. 1. In this structure, the Y-branching is achieved by inserting only six heptagons in the hexagonal network at the branching point. The first experimental observation of spontaneously branched carbon nanotubes [6] was published in 1995. More recently, branched multiwall carbon nanostructures were forcedly grown using CVD in combination with an alumina template in which branched channels were produced by etching [7]. Spontaneous regular Y-branching of single-wall carbon nanotubes was observed [8] during the room temperature growth of carbon nanotubes on graphite, using a growth procedure based on the decomposition of C_{60} in the presence of transition metals [9]. Spontaneous Y-branching of multiwall carbon nanotubes grown by the pyrolysis of nickellocene was reported [10], too. Using the combination of pentagons and heptagons, various fully relaxed T junctions were calculated recently by molecular dynamic simulation [11].

Based on molecular dynamic simulations, single-wall coiled carbon nanotubes were predicted by Ihara et al. [3]. The coiling of the proposed structures originated from the regular insertion of pentagons and heptagons in the perfect hexagonal network. A year later, the first experimental observation of multiwall coiled carbon nanotubes produced by Co-catalyzed decomposition of acetylene was reported [12]. Coils with different pitch values were observed. In some cases, the neighboring coil elements seemed to be touching with an interspire distance close to the Van der Waals distance between the layers of graphite [13]. As shown by theoretical calculations, under certain conditions, due to interactions between neighboring coil element, the coiling may confer additional stability even to multiwall carbon nanotubes [14]. Despite the efforts to find single-wall carbon nanotube coils by high-resolution transmission electron microscopy (HRTEM), no conclusive evidence was found during TEM investigation of samples in which multiwall coils were found. Simulation shows [15] that in principle, single-wall coiled structures could be observable

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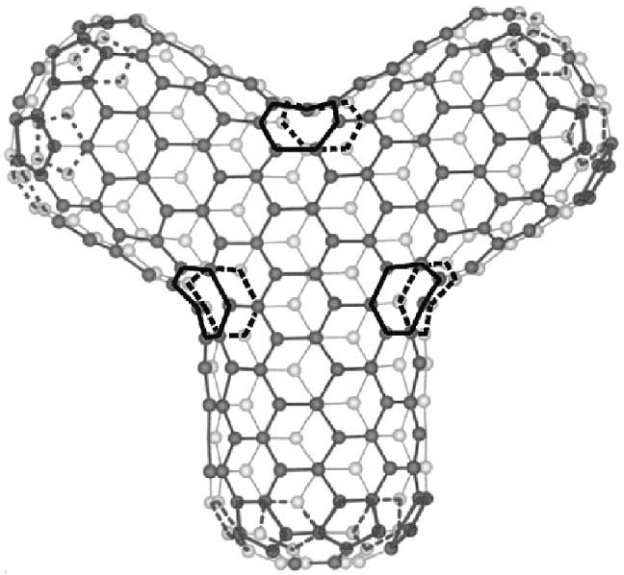

Fig. 1. Ball and stick model of the Y-branching of carbon nanotubes proposed by Scuseria [4]. Heavy line marks the six heptagons. (used with permission from Scuseria).

by HRTEM. The lack of success in finding these objects by HRTEM may be tentatively attributed to the mechanical instability of the free-standing coil-like objects under e-beam irradiation. The first experimental observation of tightly wound, single-wall coiled carbon nanotubes was achieved by scanning tunneling microscopy (STM) [16]. In a sample prepared using the procedure given in Ref. [13], several coils of different pitches were found, the STM imaging of some of these coils was possible only in point contact regime, indicating semiconducting behavior in accordance with theoretical calculations [17].

In the present work, we report the observation of Y-branched and coiled single-wall carbon nanotubes grown on a graphite substrate at room temperature using a similar growth procedure as the one reported in Ref. [9], and the observation of a single-wall coiled nanotube intercoiling with itself similar to the multiwall one reported in Ref. [12], Fig. 1d.

2. Experimental results and discussion

The room temperature growth of nanotubes was carried out under similar conditions as reported earlier [8,9]. Nickel particles 200 nm in size were mechanically mixed with C_{60} powder. A 1:2 metal to fullerene mass ratio was used. The mixture was loaded in a quartz ampoule. After loading, the ampoule was placed in an electric furnace in a vacuum system. The vacuum chamber was pumped down to a pressure of 2×10^{-6} mbar. During deposition, the ampoule was heated at 450 °C. The thickness of the layer deposited on the substrate was monitored by a quartz thickness monitor. The flux of material emerging from the ampoule was directed onto a highly oriented pyrolitic graphite (HOPG) substrate at a distance of 30 cm situated near the thickness monitor. During heating up to deposition temperature and cooling down, the HOPG substrate was protected by a shutter. As measured by a thermocouple, the temperature of the substrate was not modified significantly during deposition. The thickness of the deposited layers was in the range of 3–10 nm of equivalent fullerene thickness, the duration of the deposition ranged from 3 to 10 min. Carbon nanotubes were produced only when using HOPG substrate. On Au or mica, a mixture of amorphous carbon with fullerene was deposited [9].

After deposition, the HOPG substrates were examined by STM under ambient conditions. Commercially available mechanically cut PtIr tips were used. Constant current topographical images were acquired using typical tunneling currents $I_t = 500$ pA and tunneling bias $U_t = 1$ V. Usually, low scan frequencies in the rage of 1 Hz were preferred. In some cases, after STM examination, a thin surface layer of the HOPG was cleaved, placed in alcohol or acetone and ultrasonicated. Droplets of the suspension prepared in this way were placed on amorphous carbon covered grids and investigated by transmission electron microscopy (TEM).

The sample in which the single-wall carbon nanotube intercoiling with itself was observed was prepared by the catalytic procedure and subjected to two cycles of wet oxidation [18]. Carbon nanotubes were synthesized by the catalytic decomposition of acetylene as carbon source at 700 °C over supported cobalt-containing catalysts; 2.5% Co on faujasite type zeolites was used [19]. Separation of nanotubes and catalyst particles was carried out by repeated dissolution of the support in hydrofluoric acid and filtering. The zeolite-free nanotube samples were subjected to $KMnO_4/H_2SO_4$ aqueous oxidation procedure [20] in order to remove the amorphous carbon and graphitic particles. This oxidation procedure is known to attack selectively the amorphous carbon and the defect containing regions of the graphitic network.

Fig. 2 shows two thin carbon nanotubes grown from the decomposition products of fullerene. One may remark that the angle between the two tubes is of 60°. This is a frequently observed arrangement which follows from the templating effect of the HOPG [9], i.e., the orientations for which the underlying graphitik network and graphene sheet of the nanotube are in registry are more favorable energetically. The thicker tube, with an apparent height of 0.9 nm, clearly originates from a wider structure in the left hand side of the image. This structure is formed on a surface defect of the HOPG, seen as a darker structure marked by an arrow. Although it is not a generally respected rule, it is a frequent observation that carbon nanotubes start growing from surface defects, or change structure after crossing defects, or cleavage steps. The thinner tube in Fig. 2 has an apparent height of 0.4 nm, while the vertical distance to the higher step to the lower one (along line AB) is 0.73

nm, i.e., corresponding to two atomic layers. The apparent height of 0.4 nm indicates a single-wall tube. The geometric dimension values of carbon nanotubes measured by STM are affected by two effects: by the geometric convolution leading to widening in the horizontal plane, and by the reduction of the measured height due to the existence of two tunneling gaps in the system (STM tip–nanotube and nanotube–substrate) [21,22].

On the left-hand side of the surface defect seen in Fig. 2, one may notice several short nanotubes, some of which seem to be branched like a Y. A more clearly visible example of Y-branching is shown in 3D presentation in Fig. 3. The angles of 120° between the branches and the same diameter values on all sides of the Y part of the structure shown in the image indicate an atomic arrangement like the one in Fig. 1. After crossing the cleavage step at the point labeled by C, the upward-oriented branch of the Y changes orientation by 30°, producing in this way a 150° "knee." Similar, multiwall knee structures were observed by TEM in a carbon nanotube sample grown by the arc method [15]. Such a knee is produced when a pentagon and a heptagon are introduced in the hexagonal network [15,23]. Although this may seem to be a "half Y-branch," there are some differences to be pointed out:

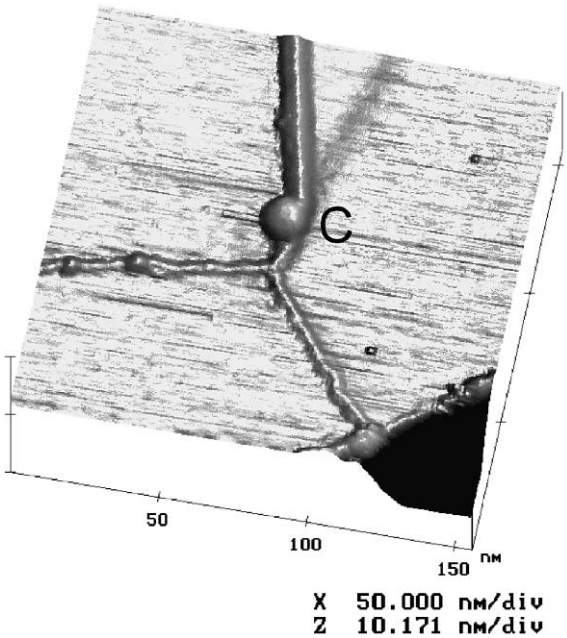

Fig. 3. Constant current topographic STM image in 3D presentation showing a Y-branched carbon nanotube, which continues with a 150° knee (I_t = 250 pA, U_t = 400 mV, PtIr tip).

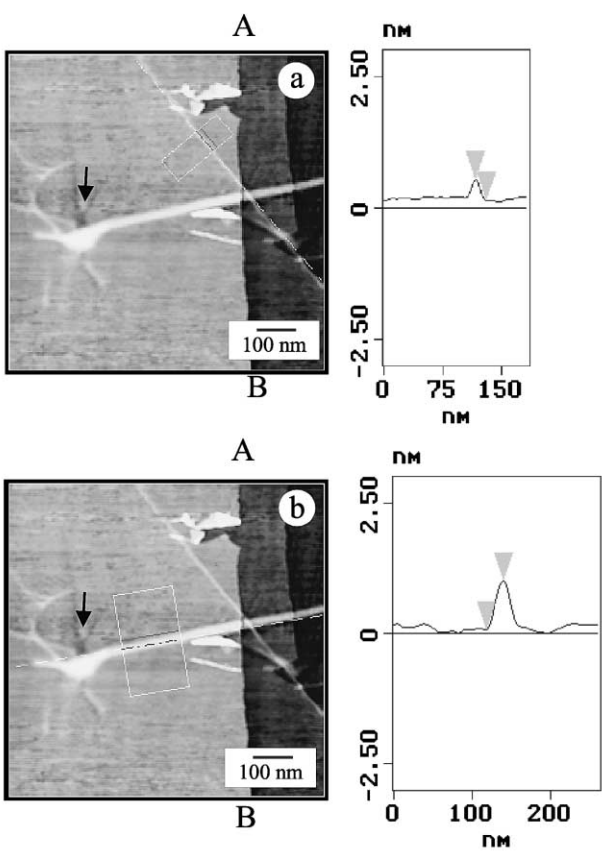

Fig. 2. Top view, constant current, topographic STM (I_t = 300 pA, U_t = 1 V, PtIr tip) image of carbon nanotubes grown by fullerene decomposition. The first step crossed by the two long tubes oriented at 60° is two atomic layers thick.

(i) on the two sides of the knee, the diameter of the nanotubes is different, while at the Y-branching, the tube diameter is the same for all three branches as shown in Fig. 1; (ii) the bending in the knee model is produced by a pentagon–heptagon pair, while in the case of the Y model, the branching is produced only by heptagons. This second difference is worth pointing out because it can influence the electronic properties of the junction as showed by theoretical calculation for two T junctions, one with, the other without pentagons [11]. Another factor that is influenced by the kind of non-six-membered rings in the region of the junction is the stress to which the C–C bonds are subjected [11], which may influence the resistance of the structure to chemical etching. Multiwall knees are also produced during the growth of carbon nanotubes from fullerene fragments, Fig. 4. shows the TEM image of a multiwall knee observed in the TEM sample prepared by cleaving the HOPG on which the deposition took place and ultrasonication.

Coiled carbon nanotubes, nanoobjects resembling the "telephone cables" of our macroscopic world, are really surprising structures. The proposed models, are all based on the very regular incorporation of pentagon–heptagon pairs in the hexagonal network. In a certain sense, these coil models can be viewed as being composed of a sequence of short knees with the same diameter on both sides of the knee. The coil in Fig. 5a was observed in an as-grown sample prepared by fullerene decomposition, while the two tubes intercoiling (or the tube intercoiling with itself) in Fig. 5b was found in a catalytically grown sample subjected to two steps of wet oxidation. Judging

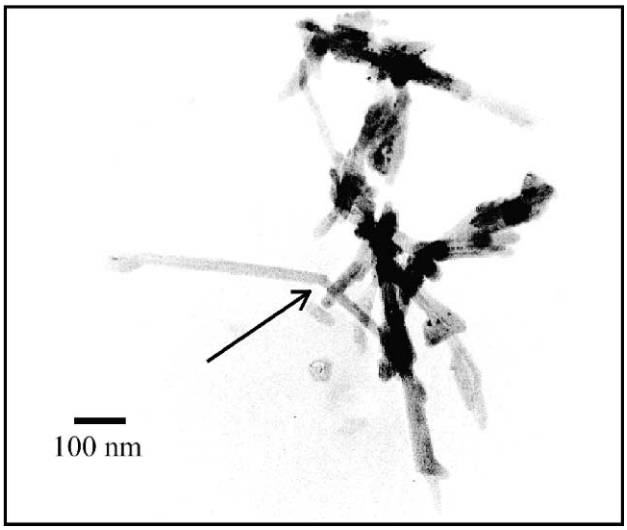

Fig. 4. TEM image of multiwall carbon nanotubes grown on HOPG from the decomposition products of C_{60}. A nanotube "knee" is marked by an arrow.

from their apparent height, both structures are single-wall structures. The pitch value for the coil in Fig. 5a is 3.5 nm. After deducting the value of the graphite interlayer distance, this yields a maximum possible value of 3.2 nm for the tube diameter. The maximum possible tube diameter calculated from the distance between the intercoiled tubes seen in Fig. 5b is 3 nm, while the pitch is 11.2 nm. The value of the apparent height of 0.4 nm indicates a single-wall tube. The fact that the intercoiled tubes survived two steps of oxidation shows that despite the large number of nonhexagonal rings they must contain, none of the tubes was attacked by the chemical etching. This gives rise to the question: is it justified to regard the heptagons and pentagons as *defects* causing the coiling of an otherwise straight carbon nanotube?

The observation of similar coils in samples produced by fullerene decomposition, like the ones observed in catalytically produced samples, shows that coiled carbon nanotubes are not an exotic product characteristic only for the catalytic procedure, but a new kind of carbon nanostructure produced irrespectively of the growth method chosen, if some particular growth conditions are achieved. One of the likely conditions may be the low growth temperature: 700 °C, for the catalytic procedure, and room temperature for the fullerene decomposition procedure, as compared with the two other widely used procedures, the arc and the laser ablation growth with characteristic growth temperature over 2000 °C. At lower temperatures, the mobility of carbon atoms is low. This is clearly demonstrated by the observation of amorphous deposit when Au or mica substrates are used instead of HOPG in fullerene decomposition growth, or by the higher number of defects found in the catalytic nanotubes, as compared with the ones grown by high temperature procedures. Under such conditions, pentagonal or heptagonal rings may be more easily quenched in the growing nucleus. If a haeckelite-type structure [24] is formed, built of heptagons and pentagons as regular building blocks, not as defects, this structure may be stable enough [24], and may grow as a coil. Moreover, recent theoretical calculations showed that one may construct only from pentagons and heptagons, "self-coiling" structures, i.e., structures in which the bond strain is best relaxed when it takes the shape of a torus [25].

The fact that the carbon nanotubes, Y-branches and coils were produced directly on the HOPG substrate on which the STM examination was carried out excludes any artifact arising from sample handling and preparation like

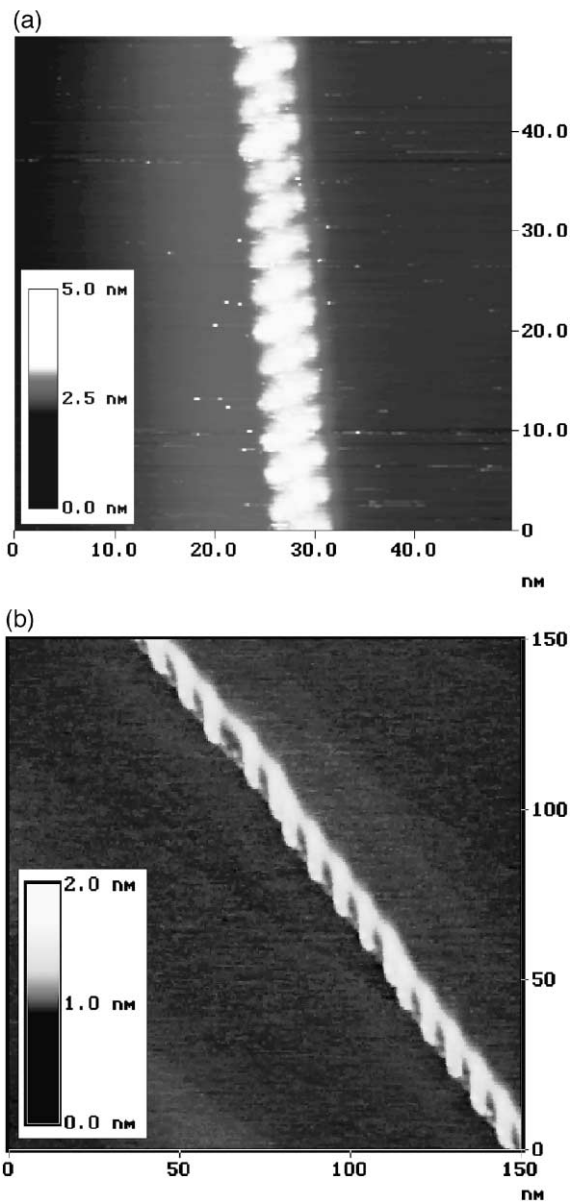

Fig. 5. Top view, constant current, topographic STM images of carbon nanotube coils: (a) tightly wound coil grown by fullerene decomposition ($I_t = 300$ pA, $U_t = 400$ mV, PtIr tip); (b) intercoiled tubes grown catalytically and subjected to several steps of chemical treatment ($I_t = 150$ pA, $U_t = 1$ V, PtIr tip).

it was proposed for the production mechanism of the nanotube "crop-circles" [26].

3. Conclusions

Novel carbon nanostructures, knees, Y-branched carbon nanotubes and coiled carbon nanotubes were produced directly on the HOPG substrate and examined by STM without any further manipulation. The formation of the carbon nanostructures containing nonhexagonal rings is attributed partly to the templating effect of the HOPG, partly to the growth at room temperature, which enhances the probability of quenching-in for nonhexagonal rings.

Similar coiled nanotubes were found after several steps of chemical treatment in a catalytically grown carbon nanotube sample. This observation suggests that in the coiled structures, the pentagons and heptagons do not play the role of defects, but that of regular building blocks. Coiled carbon nanotubes may be regarded as being built from a theoretically predicted material, the haeckelite [24], in which pentagons, hexagons and heptagons are equally considered as regular building elements.

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