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From straight carbon nanotubes to Y-branched and coiled carbon nanotubes

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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 by the decomposition of fullerene under moderate heating (450 °C) in the presence of transition metal particles. The grown structures were investigated without any further manipulation by STM. The observed coiled carbon nanotubes are tentatively identified with the theoretically predicted haeckelite. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Soon after the discovery of straight carbon nanotubes [1] — constituted of perfectly rolled, defect free graphitic layers — the idea of branched [2–4] and coiled [5] carbon nanostructures emerged. The branched nanotubes can constitute valuable building blocks for nanoelectronics [6,7] — for three-terminal devices and 2-D networks — while the nano-coils may be promising from the point of view of nano-electromechanical systems and nano-actuators [8].

There are two distinct ways to produce branched carbon nanostructures: by (i) 'forced' branching in templates with branched nano-channels [9]; and by (ii) spontaneous branching during growth [10–12]. The first procedure yields structures with non-equal angles between the branches, while the procedures from the second group usually yield structures with branches oriented at 120°, like the one shown in Fig. 1. However, the graphene layers in the Y-junctions grown using the method reported by Satishkumar [12], are oriented in a fishbone-like way, i.e. these layers are not parallel with the axes of the structure.

Multiwall coiled carbon nanotubes were first observed by transmission electron microscopy (TEM) [13]. Coils with different pitch values were observed, in some cases the neighboring coil elements are touching with an interspire distance close to the van der Waals distance between the layers of graphite [14].

Although sustained efforts were invested to find single wall carbon nanotube coils by high resolution transmission electron microscopy (HRTEM), up to now no conclusive evidence was found during TEM investigation of samples in which multiwall coils were found. The first experimental observation of tightly wound, single wall coiled carbon nanotubes was achieved by scanning tunneling microscopy (STM) [15]. In a sample in which multiwall coils were found — prepared using the procedure given by Amelinckx et al. [13] — several single wall coils of different pitches were found.

In the present work we report the observation of nanotube knees, Y-branched and coiled single wall carbon nanotubes grown on a graphite substrate, using a similar growth procedure as the one reported by Biró et al. [16] for straight carbon nanotubes. The relation of the observed carbon nanostructures with the theoretically predicted haeckelite-type structures [17] proposed recently is discussed.

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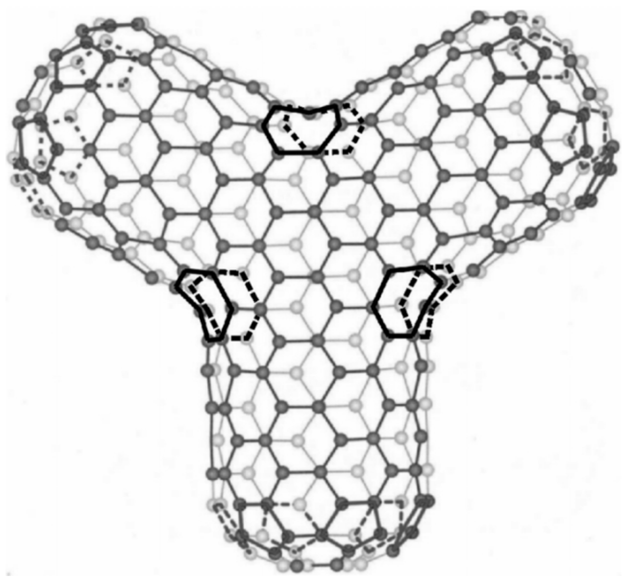

Fig. 1. Ball and stick model of the Y-branching of carbon nanotubes proposed by Scuseria [3]. Heavy line marks the six heptagons. (Used with permission from Scuseria.)

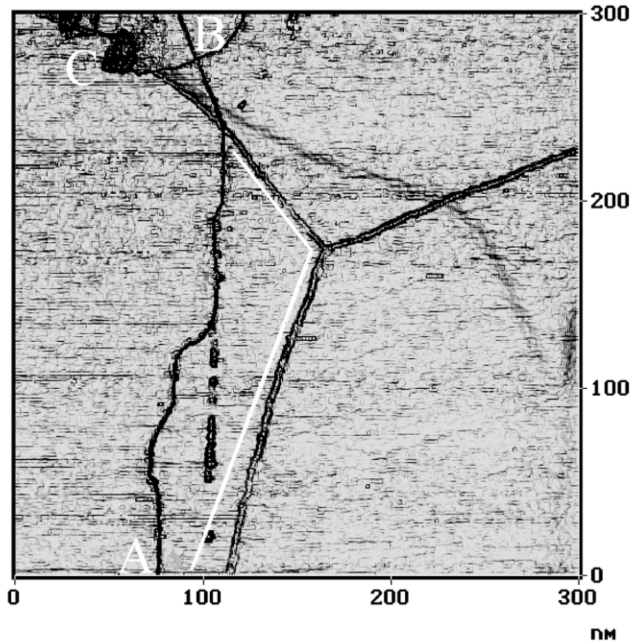

Fig. 3. Constant current topographic STM image in top view presentation with artificial illumination from top, showing a Y-branched carbon nanotube image ($I_t = 200$ pA, $U_t = 1$ V, PtIr tip). The undulated line from A to B is step edge, while the structure labeled C is an extended defect. The white lines make an angle of 121°.

2. Experimental results and discussion

The room temperature growth of nanotubes was carried out under similar conditions as reported earlier [16]. Nickel particles of 200 nm in size, or Ni and Co particles (Co particles of 60 nm) were mechanically mixed with C_{60}, or with C_{70} powder; a 1:2 metal to fullerene mass ratio was used. The mixture was loaded in a quartz ampoule placed in an electric furnace. The vacuum chamber was pumped down to a pressure of 2×10^{-6} mbar. During deposition the ampoule was heated at 450 °C. 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 a thickness monitor. During heating up to deposition temperature and cooling down, the substrate was protected by a shutter. In room temperature experiments — as measured by a thermocouple — the temperature of the substrate was not modified significantly during deposition. In other experiments the substrate was resistively heated during deposition, or after deposition, to perform an in situ annealing for removing the fullerenes that were not reacted. The thickness of the deposited layers was in the range of 3–10 nm of equivalent fullerene thickness, the deposition time ranged from 3 to 10 min.

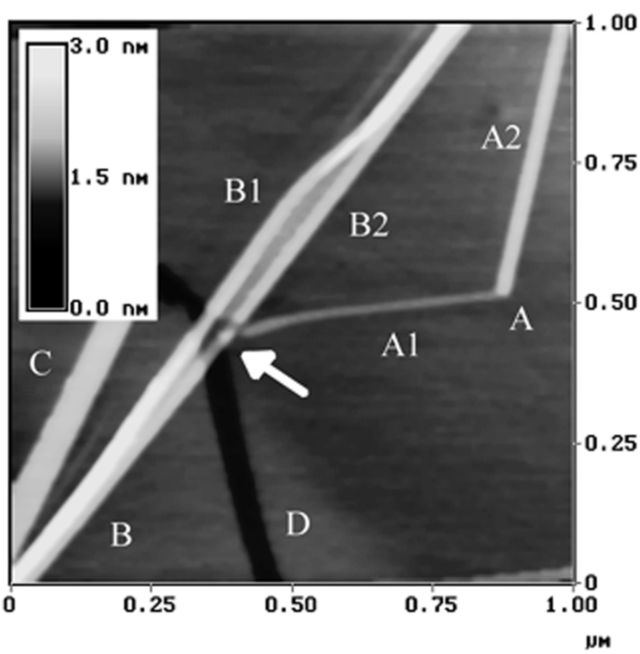

Fig. 2. Top view, constant current, topographic STM image ($I_t = 1$ nA, $U_t = 1$ V, PtIr tip) of carbon nanotubes grown by fullerene decomposition. The gray scale included in the image shows the extension in a direction perpendicular to the plane of the image: object C is a two atomic layer thick graphite stripe with a measured height of 0.7 nm.

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 range of 1 Hz were preferred.

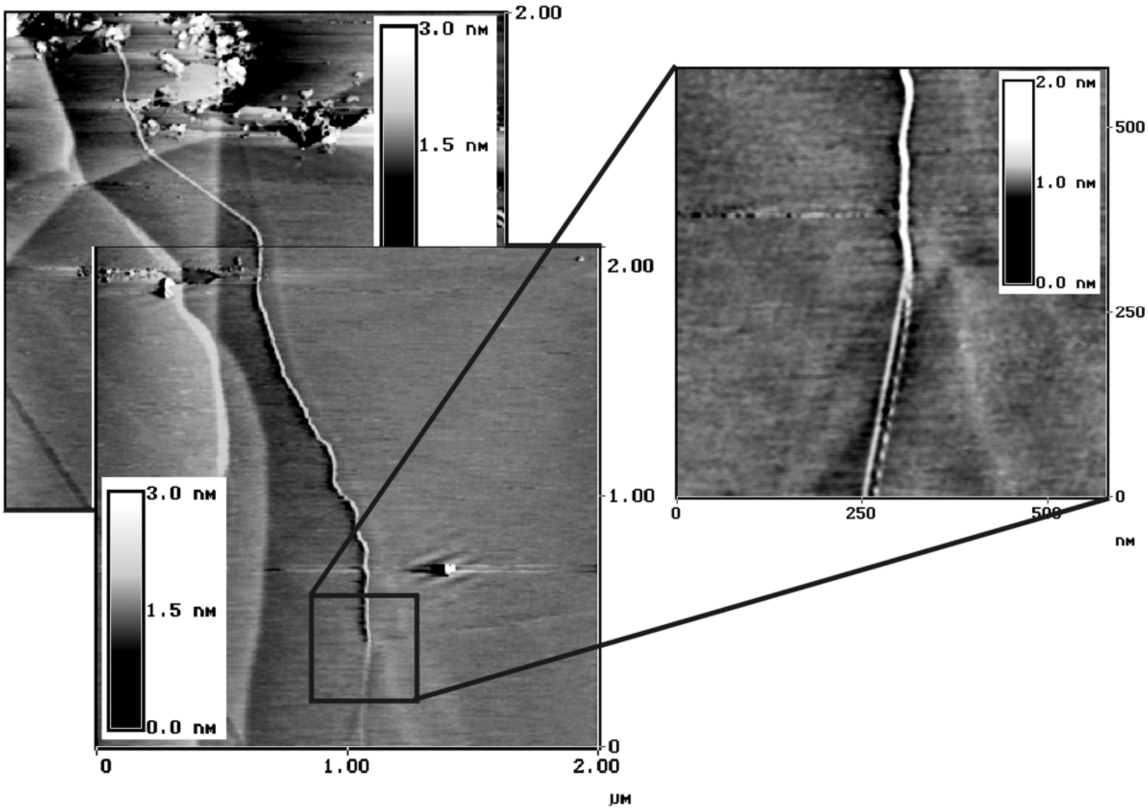

Fig. 4. Constant current topographic images mounted together showing a carbon nanotube making knees and random curvatures produced by defects, branching into a straight and a coiled tube. The detail shown on the left-hand side is a higher magnification image taken of the box indicated in the composed image. In each image, the gray scales indicate the corresponding extension in a direction perpendicular to the plane of the image.

Fig. 2 shows several nano-objects grown from the decomposition products of C_{70}. After deposition, without breaking vacuum, the sample was annealed at 515 °C for 25 min. The two carbon nanotubes labeled B1 and B2 grew side by side, except the region marked by a white arrow. There, they cross a cleavage defect seen as a dark feature (labeled D). A nanotube 'knee', labeled A, is formed when two tubes of different diameters grow together. Structures of this kind were found by TEM in samples of multiwall carbon nanotubes [18], their possible electronic structure was investigated theoretically [19,20]. The two tubes composing object A have different diameters, as one can deduce from the apparent height values measured by STM, $h_{A1}=0.27$ nm and $h_{A2}=0.70$ nm, respectively. These values cannot be directly converted to geometric diameters because of differences in electronic structure and due to the existence of two tunneling gaps: STM tip/nanotube; and nanotube/substrate [21,22]. The diameter ratio of approximately 3 may originate from one tube being metallic while the other tube is semiconducting. It is worth pointing out that the tube A1 seems to have started growth in the region where B2 crosses the cleavage defect. It is frequently observed that surface defects influence or initiate the growth of carbon nanotubes under the conditions used in the present work.

As proposed earlier in theoretical model structures [18–20,23], a knee, like object A, can be built by incorporating one or more pentagon–heptagon pairs in the graphitic network. More complex structures, like T- or Y-junctions can be constructed too, using a larger number of heptagons, with or without pentagons [2–4,6,7]. The spontaneous and free branching of single wall carbon nanotubes grown by fullerene decomposition on graphite, yields Y-like single wall structures, like the ones already reported by Nagy et al. [11] and Biró et al. [24]. This branching may be related to the three axes, oriented at 120°, for which the interaction energy of a carbon nanotube and of the graphite support is minimal [25,26]. In Fig. 3, a branching is shown in top view presentation. This Y-junction was grown by the decomposition of C_{70}. The growth by fullerrene decomposition usually yields Y-branches with angles of 120°. A possible structure for such a branching is shown in Fig. 1. The apparent heights of all three branches are in the range of 0.2 nm.

When a larger number of defects is inserted in the hexagonal network building up the carbon nanotubes,

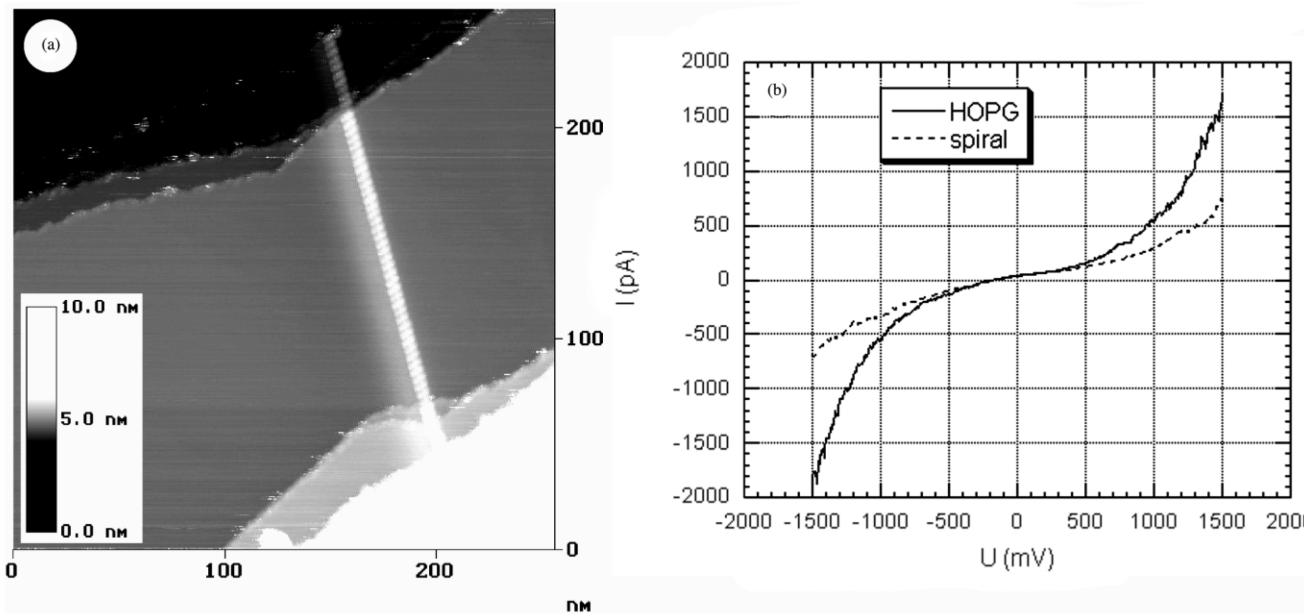

Fig. 5. Coiled carbon nanotube crossing several cleavage steps on graphite. (a) Top view, constant current, topographic STM images of carbon nanotube coil (I_t=300 pA, U_t=400 mV, PtIr tip); (b) STS spectrum showing the different electronic structures of the coil and of the HOPG substrate.

randomly curved tubes are obtained, like in the upper half of Fig. 4. This figure shows a carbon nanotube grown by C_{60} decomposition, which originates from a region of extended defects. After a number of knees — without diameter change — the tube starts meandering, and finally it branches into a straight tube (left) and into a coiled tube (right). The measured height values are as follows: 0.83 nm for the tube before branching; 0.33 nm for the straight tube after the branching; and 0.3 nm for the coil. The spires of the coiled tube in Fig. 4 do not 'touch' at the van der Waals distance corresponding for graphene layers. A coil with touching spires is shown in Fig. 5a. This coil traverses several cleavage steps, it was measured over a length of 1.8 μm. The scanning tunneling spectroscopy (STS) performed on the coil and on the HOPG far from the coil, Fig. 5b, indicates a much larger gap value — of the order of 1.5 eV — for the coil than for HOPG.

Earlier experimental [27] and theoretical [27,28] work has showed periodic 'stripe-like' features in atomic resolution STM images of single wall carbon nanotubes. These features have a much shorter horizontal periodicity — comparable to the distance of neighboring atomic positions — and much smaller corrugation amplitude, typically on the 0.1-nm scale as compared with the coils reported in the present work.

The structural models for regularly coiled carbon nanotubes are based on the regular incorporation of pentagon–heptagon pairs in the hexagonal network [5,15,18]. According to these models, the coil may be regarded as the succession of numerous short identical knees with the same tube diameter on both sides of the knee. However, the mechanism by which these defect pairs are inserted regularly, has not been clarified yet. On the other hand, if one does not regard the pentagonal and hexagonal rings as defects, but as regular building blocks, then their very precise positioning is an inherent property of the structure. Such structures, named haeckelites, constituted from pentagons, hexagons and heptagons, or only from pentagons and heptagons have been proposed recently [17]. According to theoretical calculations, the stability of tubular structures built from haeckelite is situated between that of regular carbon nanotubes and that of C_{60} [17]. In particular, a layered structure built only from pentagons and heptagons has a fairly good stability (0.307 eV/atom above graphene) as compared to fullerene (0.419 eV/atom above graphene) [17]. The coiling of tubular structures resulted from such haeckelite layers may be attributed to the relaxation of bond strain, as shown by recent calculations [29]. In this way the formation of carbon nanotube coils has a structural origin and the coils may be regarded as the first experimental evidence for the existence of haeckelite structures.

The production of numerous defect-based structures during the growth of carbon nanostructures on HOPG from the decomposition products of fullerenes is partly attributed to the low growth temperature, ranging down to room temperature. Under these conditions, the C atoms and clusters have low mobility, which may enhance the quenching in of the pentagonal and heptagonal rings in the growing structure. When a stable haeckelite nucleus is formed, this will continue to grow as a coiled structure.

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 non-hexagonal rings is attributed partly to the templating effect of the HOPG and partly to the growth at room temperature, which enhances the probability of quenching-in for non-hexagonal rings.

It is proposed that coiled carbon nanotubes may be regarded as being built from a theoretically predicted material, the haeckelite, in which pentagons, hexagons and heptagons are equally considered as regular building elements.

Acknowledgments

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