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STM observation of asymmetrical Y-branched carbon nanotubes and nano-knees produced by the arc discharge method☆

Z. Osváth[a,*], A.A. Koós[a], Z.E. Horváth[a], J. Gyulai[a], A.M. Benito[b], M.T. Martínez[b], W. Maser[b], L.P. Biró[a]

[a] *Research Institute for Technical Physics and Materials Science, P.O. Box 49, H-1525 Budapest, Hungary*
[b] *Instituto de Carboquimica, CSIC, C/Miguel Luesma Castán 4, E-50015 Zaragoza, Spain*

Abstract

The scanning tunneling microscopy (STM) observation of arc-grown Y-branched carbon nanotubes and sharp nanotube bends (nano-knees) is reported. A drilled out graphite rod filled with a nickel/yttrium particle mixture was used as the anode in an arc chamber under He atmosphere of 660-mbar pressure. Straight multi-wall nanotubes, Y-branches and nano-knees were found in a sample taken from the cathodic deposit. The asymmetrical Y-branches and complex nano-knees found in this experiment may be related to the additional use of metals or/and to induced changes of the temperature distribution on the cathode side. It is suggested that complex nano-knees could be new examples for carbon quantum dots.

Keywords: Carbon nanotube; Y-branching; Nanotube bend; Nanotube knee; Quantum dot

1. Introduction

Carbon nanotube Y-junctions and knees can be regarded as possible building blocks in nanoscale electronic devices [1–3].

In the theoretical models of branched carbon nanotubes, the branching is caused by non-hexagonal carbon rings incorporated in the hexagonal atomic network of the carbon nanostructure [4–6]. Experimentally observed spontaneously branched nanotubes were first reported in 1995 [7]. In the past 3 years, other groups observed and reported branched carbon nanotubes. Single wall carbon nanotube (SWCNT) Y-junctions were found during room temperature growth of carbon nanotubes by the decomposition of fullerene [8,9]. Multi-wall carbon nanotube (MWCNT) Y-junctions were grown by the pyrolysis of nickellocene [10], and more recently by the pyrolysis of ferrocene and cobaltocene in the presence of thiophene [11]. Y-junction nanotubes were produced also by confining the nanotubes to grow within Y-shaped nanochannel templates [12].

Carbon nanotube knees can be formed by introducing topological defects (for example one or more pentagon–heptagon pairs) in the hexagonal atomic structure of the straight tubes [13,14]. As a result, a nanotube knee can be regarded as a connection of two carbon nanotubes with different chiralities. The possible electronic structure of such nanotube connections was investigated theoretically [15,16]. It was demonstrated that nanotube-knees can have rectifier properties [17].

In the present work we report the observation with scanning tunneling microscopy (STM) of nanotube knees and few-wall asymmetrical Y-branched carbon nanotubes produced by the electric arc method.

2. Experimental conditions

The nanotube samples were produced by the electric arc-discharge method. A graphite rod (100 mm in length and 6 mm in diameter) was concentrically drilled out (4 cm in length and 3.5 mm in diameter) and filled with a nickel/yttrium mixture resulting in an overall graphite/nickel/yttrium composition of 90/7/3 wt.% over the drilled-out

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* Corresponding author. Tel.: +36-1-392-2222x1157; fax: +36-1-392-2226.
E-mail address: osvath@mfa.kfki.hu (Z. Osváth).

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length. The rod was used as the anode and placed in front of a graphite cathode (10 mm in diameter). Subsequently, the filled part of the graphite rod was completely evaporated under a 660-mbar helium atmosphere within a time of 2 min applying a current of 100 A and a tension of 40 V. About 45 wt.% of the evaporated material resulted in the formation of a cathodic deposit. The black inner core of the deposit was taken out and used for the investigations presented in this paper. Transmission electron microscopy shows that this material contains MWCNTs with diameters typically around 10 nm. Additionally, graphitic nanoparticles (GNPs) and metal nanoparticles with sizes between 10 and 20 nm are found. For the STM investigations, 1 mg of material was ultrasonicated in 20-ml toluene for 60 min and droplets of the suspension were dispersed on freshly cleaved HOPG. The toluene was allowed to evaporate at room temperature. The sample was investigated by STM in constant current mode under ambient conditions. Tunneling currents of 0.3–0.5 nA and bias voltages in range of 200–700 mV were preferred. The STM tips were prepared by mechanically cutting from a Pt(90%)–Ir(10%) wire.

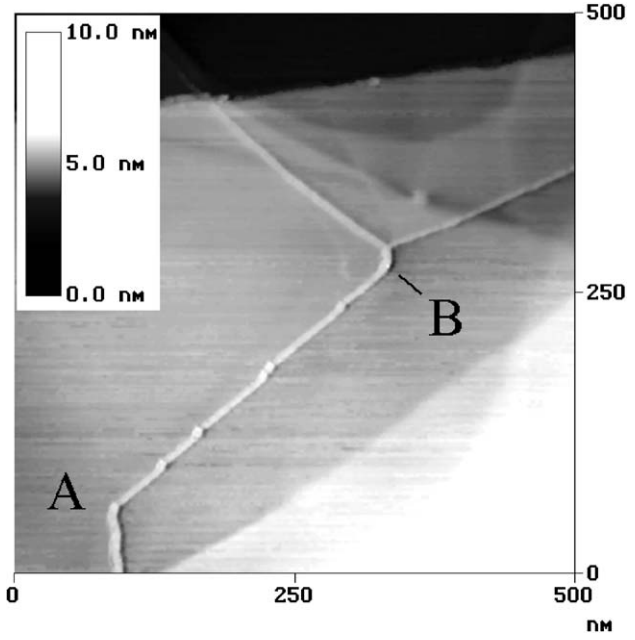

Fig. 1. Constant current topographic STM image, showing an Y-branched carbon nanotube, which exhibits two knees before branching. Tunneling conditions: $I_t = 500$ pA, $U_t = 0.2$ V.

3. Results and discussion

Scanning tunneling microscopy of a sample from the cathodic deposit shows straight (presumably multi-wall) nanotubes with apparent diameters between 2.8 and 20 nm. Moreover, STM also revealed Y-branched carbon nanotubes with few walls, with apparent heights around 1 nm. The finding of these nano-objects by STM is due to the particular imaging mechanism, i.e. a vertical resolution in the order of 10^{-2} nm, which allows the efficient search for single- and few-wall nanotubes in observation windows of 1 μm^2. Unlike the Y-junctions produced by decomposition of fullerene [8,9] or by the pyrolytic methods [10,11], these Y-branched structures are usually asymmetric.

An asymmetrically branched carbon nanotube is shown in Fig. 1. Here one can see two well-developed "knees" too: one in the left bottom part of the image (A) and the other right before the Y-branch (B). Between the two knees there are several growth instabilities which tend to produce modification of the growth direction. However, the nanotube continues to grow in the same direction till the knee labeled with B is reached. These defects do not induce any change in the nanotube diameter, only locally introduce an ascent in the height of around 0.2 nm, which is attributed to the changed local density of states (LDOS). This change in the LDOS may be attributed to atomic vacancies, which can appear during the nanotube growth. As recent calculations predict [18], a single vacancy—even when an idealized, single atom tip is assumed—can induce in the STM images of an SWNT a hillock-like feature with a lateral size around 1 nm, and a height up to 0.1 nm. One can mention that the nanotube parts confined between two of these local defects could behave as carbon quantum dots [19,20]. The number and kind of non-hexagonal rings at the branching point makes possible the branching and the nanotube then achieves a stable structure. The asymmetry of the Y-branches may be related to the specific growth conditions used here: the switch-off of the cathode water-cooling leads to changed temperature conditions and induces larger temperature fluctuations. This could facilitate the introduction of a higher number of pentagonal and heptagonal defects into the hexagonal network of the nanotubes. The fact that catalytic particles are additionally involved (normally not necessary for the growth of MWCNTs) also could contribute to further temperature fluctuations.

During the STM examination we also found several sharp nanotube bends (nanotube knees). A multi-wall carbon nanotube knee of 30° can be seen in Fig. 2a. Both nanotube arms of the knee have a length around 320 nm and the apparent heights are 7 nm in case of the nanotube arm in the lower part of the figure and 7.7 nm in case of the upper nanotube arm. The ends of the nanotube arms do not appear very well defined in the image. This is because they were not strongly fixed to the substrate and the STM tip shifts them during scanning. A higher magnification with a closer region of the nano-knee is presented in Fig. 2b. Here one can see that the nano-knee exhibits a complex bending. Going from the lower left corner of the image, on the convex part of the knee first occurs a bend of 19° to left (A) and after 35 nm s, a well-defined curvature of 51° to right (B), resulting to an overall knee of 30°. The bending in A is attributed to heptagon rings while the curvature in B is ascribed to pentagons incorporated in the system. On the concave part of the knee there is only one well-defined bend

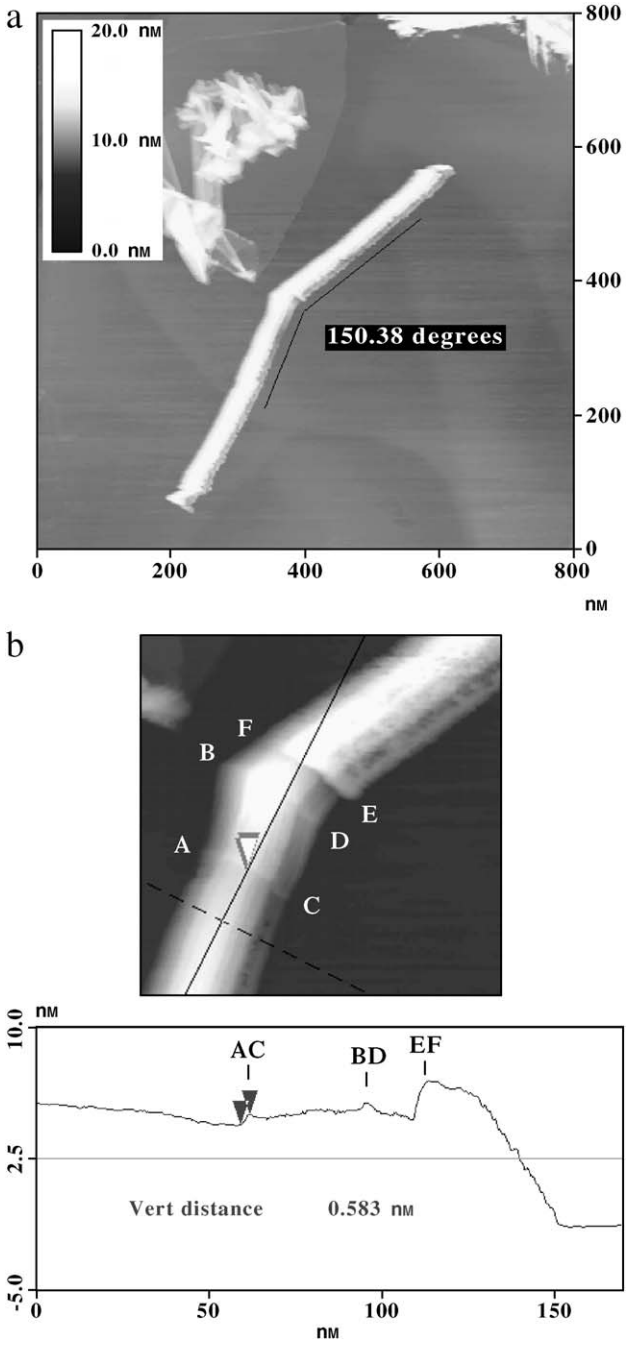

Fig. 2. (a) Topographic STM image of a multi-walled carbon nanotube knee of 150°. The image was recorded in constant current mode, using a bias voltage of 0.7 V and the tunneling current was set to 300 pA; (b) Higher magnification of the knee region: small collar-like modifications in the tube diameter at sections AC and BD. At section EF a sudden thickening occurs due to the addition of new graphitic layers.

of 30° to right (the point labeled with D). One can observe that in C (which is equivalent to A) there is no significant deviation from the growing direction, which means the hexagonal structure was not altered in that region. It is worth pointing out that the apparent tube diameter at sections BD and AC is 52 and 45 nm, respectively, and that AC is parallel with BD. In this way the ABCD spatial formation can be regarded as a semi-conic-like structure [21] with the base plane at BD.

Another aspect that attracted our attention is the fact that along the sections AC and BD there is a small increase in the measured heights, i.e. 0.5 nm along AC and 0.3 nm in case of BD (see cross-sectional line in Fig. 2b). We attribute these small "collar-like" modifications in the diameter of the tube to local modifications in the electronic structure due to the defects (non-hexagonal rings) that produced the bending of the nanotube. As shown in Ref. [1], heptagons and pentagons can induce additional electronic states near the Fermi energy.

As one can see in Fig. 2b, there is a sudden increase of around 1.8 nm in the measured nanotube height at the site labeled with EF. Additionally, we measured the surface roughness of the nanotube beyond EF (top part of image), and compared it to the surface roughness of section ABCD and the lower nanotube arm. It turned out that the roughness beyond EF increased with around 65%. These results suggest that a few concentric grafitic layers suddenly added during growth to the outer nanotube walls at EF, forming a somewhat thicker tube. This assumption is justified by the fact that the apparent height of the upper nanotube arm is larger by 0.7 nm than the lower nanotube arm. Furthermore, the outermost nanotube walls can have different chiralities, and thus different electronic properties [22]. Accordingly, the ragged surface of the thicker tube is probably due to its electronic structure, which may differ from the other parts discussed above. It has to be emphasized that the external tube produced by the addition of new layers at EF has a

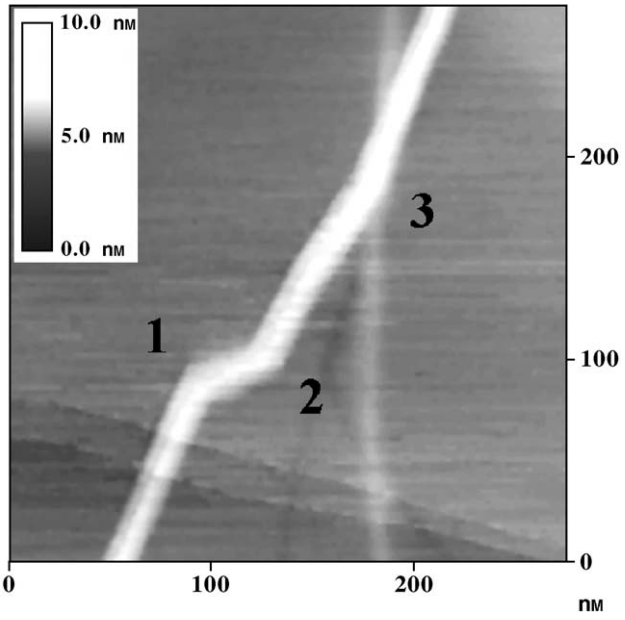

Fig. 3. Topographic STM image (constant current mode, $I_t = 300$ pA, $U_t = 0.7$ V) of a carbon nanotube which presents two similar bending: one of 50° at the point 1, and another one of 48° in the opposite direction at the point 2, respectively. At point 3, one can observe also a small angle knee of 13°.

somewhat larger diameter that it would be required to form a compact MWNT. As a consequence the van der Waals interaction attracts the inner tube to one side of the outer tube; this gives the sudden, asymmetric change in the shape of the nano-object at EF.

Another complex nanotube bending due to the incorporation of heptagon–pentagon pairs is presented in Fig. 3. The nanotube exhibits two similar bends: one of 50° at point 1, and another turning of 48° in the opposite direction at point 2, respectively. At point 3, one can observe also a small angle knee of 13°. One can note that the apparent nanotube diameter of 1.8 nm did not change during bending and the distance between points 1 and 2 is around 30 nm. We consider that this kind of nano-structures (the region between 1 and 2) could be examples for carbon nanotube quantum dots [19,20]. As shown in Ref. [19], the spatial confinement and number of discrete energy levels of a carbon quantum dot depends on the distance between the topological defects (heptagon–pentagon pairs) of the system, and this may open a way of engineering miniature building blocks for the future nano-electronics.

4. Conclusions

We reported the STM observation of Y-branched carbon nanotubes and nanotube-knees produced by the electric arc-discharge method. The apparent heights of the branched nanotubes suggest that some of them could be single-walled Y-branches. The incorporation of topological defects (vacancies and non-hexagonal rings), producing growth instabilities, asymmetrical Y-branches, and complex nano-knees, may be related to the changed temperature conditions on the cathode side due to the switch-off of the water-cooling, or/and to the effect of additional metals used in the experiment. It is suggested that nano-knees, which exhibit complex bending like the one in Fig. 3, could be new examples for carbon quantum dots.

Acknowledgements

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