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Arc-grown Y-branched carbon nanotubes observed by scanning tunneling microscopy (STM)

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

Research Institute for Technical Physics and Materials Science, Nanostructures Laboratory, Konkoly Thege M. ut 29-33, MFA, P.O. Box 49, H-1525 Budapest, Hungary

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Abstract

Scanning tunneling microscopy (STM) observation of Y-branched carbon nanotubes produced by the arc-discharge method is reported. A drilled out graphite rod filled with a nickel/yttrium particle mixture was used as anode in the arc chamber under He atmosphere of 660-mbar pressure. Straight multi-wall nanotubes and asymmetrical Y-branches were found in a sample taken from the cathodic deposit. As measured by STM the Y-junctions have low apparent heights in the range of 1 nm. This may be an indication that these nanotubes have only few walls, or possibly they are single-walled. The asymmetrical Y-branches found in this experiment may be related to the additional use of metals or/and to changed temperature conditions on the cathode side due to the switch-off of the cathode water-cooling.

1. Introduction

Carbon nanotubes were intensely studied in the past decade for their promising properties. Soon after the discovery of straight carbon nanotubes [1], the possible existence of branched nanotubes was predicted [2–4]. These branched nanostructures may have potential applications as building elements in nanoelectronic devices [5–7]. According to theoretical models, the branching of a carbon nanotube may occur where non-hexagonal carbon rings are incorporated in the hexagonal network of the graphene sheet building up the carbon nanostructure [2–4]. Experimental observation of spontaneously branched multi-wall carbon nanotubes produced by the arc-discharge method was first reported in 1995 [8]. The experiment was carried out under specific conditions, using He atmosphere at 500 torr pressure and a hollow anode. Since then several groups reported the observation of branched nanotubes: single-wall Y-branched carbon nanotubes were found during room-temperature growth of carbon nanotubes on graphite substrates by decomposition of fullerene [9,10], and multi-wall Y-branched carbon nanotubes were grown in a procedure based on the pyrolysis of nickellocene [11]. Branched multi-wall carbon nanotubes were also grown

* Corresponding author. Fax: +1-36-1-392-2226.
E-mail address: biro@mfa.kfki.hu (L.P. Biró).

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forcedly, in alumina nanochannel templates by pyrolysis of acetylene [12]. Recently, Y-junction nanotubes were produced by the pyrolysis of ferrocene and cobaltocene with thiophene [13]. The methods mentioned above, except the arc-discharge method [8], are usually characterized by relatively low (650–1000 °C), or very low (room-temperature) growth temperature. When using high-temperature growth methods like arc-discharge or laser ablation under usual conditions, the branched nanotubes are not reported as being observed routinely. However, STM and scanning tunneling spectroscopy (STS) measurements on a Y-branched carbon nanotube produced by the arc-discharge method was recently reported [14].

In this Letter, we report the STM observation of few-walled Y-branched carbon nanotubes produced by the arc-discharge method. The Y-junctions were grown under specific conditions, using large amount of catalysts, and they were found on samples coming from the cathodic deposit. We show that Y-junctions may be produced by the arc-discharge technique in a reasonable proportion and they may exhibit a large variety of branching angles.

2. Experimental conditions

Carbon nanotube samples were produced employing the electric arc-discharge technique. 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 length. The rod was used as 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 article. Transmission electron microscopy shows that this material contains multi-walled carbon nanotubes (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 nanotube containing material taken from the cathodic deposit was ultrasonicated in 20 ml toluene for 60 min. After ultrasonication 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. Mechanically cut Pt/Ir tips were used.

3. Results and discussion

An asymmetrically branched carbon nanotube is shown in Fig. 1. Theoretical model structure of such an asymmetrical stem branching was proposed in [7]. The stem has an apparent height of $h_a = 0.92$ nm and the branches have smaller

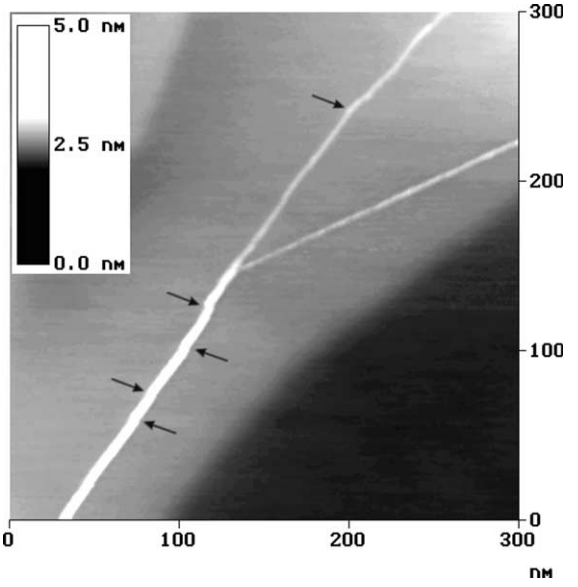

Fig. 1. STM image of an asymmetrically branched carbon nanotube, recorded in constant current mode. Tunneling conditions: $I_t = 300$ pA, $U_t = 0.5$ V. The positions indicated by arrows designate growth instabilities.

Table 1
Apparent heights of the observed Y-branched nanotubes; length and angle of the branches correlated to the stem

No.	Stem height (nm)	Branch heights (nm)		Stem-branch angles (°)		Branch lengths (nm)	
1 (Fig. 1)	0.92	0.24	0.22	0	28	>900	394
2	0.6	0.2	0.22	40	64	>150	>100
3 (Fig. 2)	0.5	0.3	0.25	50	74	>500	>650
4	0.38	0.3	0.2	15	20	42	100
5	0.3	0.2	0.2	47	74	>200	>200
6	0.27	0.15	0.15	46	80	>800	>500

heights of $h_{a1} = 0.24$ and $h_{a2} = 0.22$ nm, respectively (see also Table 1, No. 1). One can see several defects along the Y-branched nanotube (marked with arrows). These defects introduce a slight change in the growth direction, but no change in the apparent height. In the case of an asymmetric junction like the one in Fig. 1, one can assume that the nanotube was growing from the lower left corner of the image towards the branching point (it is unlikely that by accident the two branches join to produce the stem). The positions indicated by arrows designate growth instabilities, i.e., regions where the growing nanotube tried to achieve a stable structure. This was finally achieved at the branching point, where the number and kind of non-hexagonal rings was sufficient to make possible the branching. The presence of growth instabilities indicates that defects, most likely non-hexagonal rings are incorporated in the growing structure. However, only particular combinations of such defects [3,4,7] are suitable to induce the Y-branching. Once such a configuration is achieved, the branching may take place even given that the overall energy of the two narrower branches is larger than that of the stem. This assumption is strengthened by another branched nanotube seen in Fig. 2. 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). As shown in theoretical model structures [15–19], such knees can grow if one or more pentagon–heptagon pairs are incorporated in the graphitic network. Between the two knees there are several less well-formed knees 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

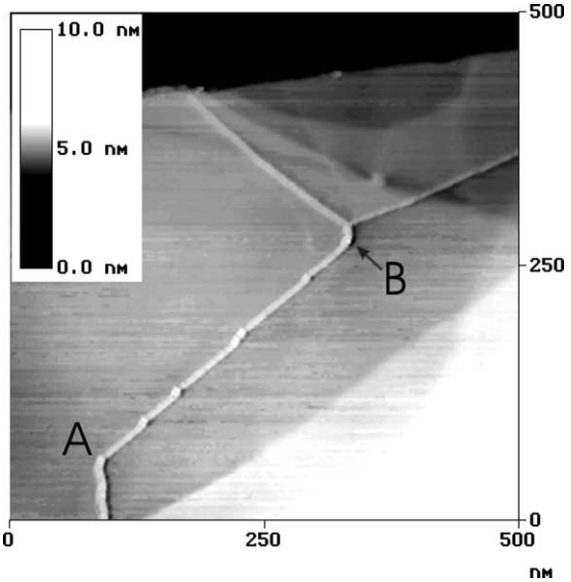

Fig. 2. Constant current topographic STM image ($I_t = 500$ pA, $U_t = 0.2$ V), showing an Y-branched carbon nanotube, which exhibits two knees before branching (labeled with A and B, respectively).

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 [20], a single vacancy, even when an idealized, single atom tip is assumed, can induce in the STM images of a single-wall carbon nanotube (SWCNT) a hillock-like feature with a lateral size around 1 nm, and the height up to 0.1 nm. The protrusions in the STM images can be also

attributed to defects such as pentagon–heptagon pairs, slightly separated from each other, which may also produce peaks in the LDOS [21,22].

Generally, the carbon nanotubes collected from the cathodic deposit of the arc-discharge chamber are multi-walled [23,24]. However, Lin et al. [25] reported on short SWCNTs produced in a dc arc chamber, collected from the cathodic deposit. They used a composite anode made of graphite and copper, and have correlated the formation of single-wall nanotubes to the presence of copper.

Our STM investigation of a sample from the cathodic deposit shows multi-wall nanotubes with apparent diameters between 2.8 and 20 nm. Furthermore, STM also revealed Y-branched nanotubes with a few walls whose characteristics are given in Table 1. The finding of these nano-objects by STM is attributed to the particular imaging mechanism. In STM one may have a vertical resolution in the order of 0.1 Å, in combination with a horizontal image of micron^2 size, which allows the efficient search for single- and few-wall nanotubes. Taking into account that by only topographic STM measurements it is not straightforward to distinguish sharply between SWCNTs and few-wall tubes, we cannot exclude that some of the structures measured with STM are SWCNT Y-junctions.

The Y-branched nanotubes reported here are asymmetrical, while the majority of branched nanotubes produced by the decomposition of C_{60} [9,10] or by the pyrolysis of nickellocene [11] are symmetrical. The asymmetry of the Y-branches may be related to the specific growth conditions used here: the switch-off of the cathode water-cooling changes temperature conditions and induces larger temperature fluctuations, facilitating the introduction of a higher number of pentagonal and heptagonal defects into the hexagonal network of the nanotubes. The catalytic particles additionally involved here (normally not necessary for the growth of MWCNTs) also could contribute to temperature fluctuations. Furthermore, an asymmetric branching indicates that the stem of the tube was growing towards the branching point, while a symmetric branching may occur when the growth starts from the branching point [26]. This may have further important implications in the application of Y-branched structures, because (as pointed in [7]) structural symmetry plays important role on the transport properties of the carbon nanotube Y-junctions.

4. Conclusions

The STM observation of Y-branched carbon nanotubes grown by the arc-discharge method is reported. The Y-branches were found in a sample taken from the cathodic deposit. As Table 1 shows, the branching of nanotubes are asymmetrical, while most of Y-junctions produced by other methods (except those based on alumina template [12], i.e., 'forced growth') are symmetrical. We conclude that the type of Y-junctions depend on the specific conditions used for the growth of carbon nanotubes. The asymmetrical Y-branches being found in this experiment may be related to the additional use of metals (which normally is not required for the growth of MWCNTs in an arc-discharge process) or/and to changed temperature conditions on the cathode side due to the switch-off of the cathode water-cooling. The effect of metals and the temperature provoking growth instabilities, which lead to the formation of Y-branches are currently being studied in more detail.

Acknowledgements

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