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Y-branching of single walled carbon nanotubes

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Abstract. Y-branching was observed by scanning tunnelling microscopy (STM) in single wall carbon nanotubes grown by thermal decomposition of C_{60} fullerene in the presence of transition metals. These novel carbon nanostructures may play an important role in carbon-based nanoelectronics.

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Carbon nanotubes (CNTs) are one of the most promising materials for the fabrication of nanotechnological devices in the future. Considerable research efforts are focused on the investigation of their structure, as well as their mechanical and electric properties [1, 2]. Various procedures have been developed for the production of CNTs, such as: arc discharge [3], laser vaporization [4], or catalytic decomposition of hydrocarbons [5]. A new production method based on the thermal decomposition of C_{60} in the presence of transition metals was presented recently [6, 7]. One of the major advantages of this method is the low amount of soot by-products produced. The electronic properties of CNTs, which were measured in recent years by scanning tunnelling spectroscopy (STS) [8, 9], confirmed earlier theoretical predictions [10] which attributed the metallic or semiconducting electronic properties of CNTs to the way in which the graphene sheet is wrapped to form the nanotube. This makes the CNTs promising materials for nanoelectronic applications. The feasibility of carbon nanotube-based 2-terminal nanoelectronic devices has been reported and their functionality was experimentally proved [11].

In the present letter, we report the first STM observation of Y-shaped single-wall CNTs (SWCNTs), which could constitute the basis of 3-terminal nanoelectronic devices. The branching of SWCNTs was first predicted in 1991 by Macky and Terrones [12] in a complicated super-fullerene structure. They constructed a joint of 3 perpendicular SWCNTs, inserting 5- and 7-atom rings into the joint. The geometric considerations were supported by energetic calculations. In 1992, Scuseria [13] proposed a Y-shaped branching of SWCNTs by inserting rings of 7-C atoms into the joint. The resulting structure is a three-pointed star-like feature, with 120° angles between the branches and with dangling bonds at the end of the branches, providing sites for further growth. A similar branching was proposed by Chernazatonskii [14] in the same year. In 1995, Zhou and Seraphin [15] presented HRTEM images of multi-walled CNTs showing an L-shaped joint of tubes with different diameters, and a Y-shaped branching, where two of the branches are very short. To the knowledge of the authors, no experimental observation of Y-branching of SWCNTs has been reported as yet.

The Y-shaped nanotubes where produced by means of thermal decomposition of fullerene in the presence of different transition metals in a similar way to methods reported elsewhere [6, 7]. Hoechst "gold grade" fullerene and the powder of one of the transition metals: Ti ($< 45\,\mu$m), Cr ($< 75\,\mu$m), Fe ($< 45\,\mu$m), Co ($< 150\,\mu$m, $< 3\,\mu$m), or Ni ($< 150\,\mu$m, 200 nm) (the grain sizes are given in brackets), were mechanically mixed (fullerene to metal ratio 1:2) and heated to 450 °C in a quartz cartridge under vacuum at a pressure of 2×10^{-6}mbar. The evaporated material was condensed on a piece of freshly cleaved highly oriented pyrolithic graphite (HOPG). Following deposition, the HOPG was investigated by STM. We found different structures, such as fragments of graphitic layers the shape of which – given their deep "fjord-like" features oriented parallel to the cleavage plane – suggest growth during deposition rather than formation by cleaving the HOPG, "raft"-like aggregates [7], which can be attributed to stacks of nanotubes, as well as thick or thin linear objects, which can be attributed to multi- or single-walled nanotubes according to their height and diameter [19]. In this work we report on the observation of linear objects connected in Y-like fashion, which we attribute to branched CNTs. The objects described here were not observed on HOPG samples with-

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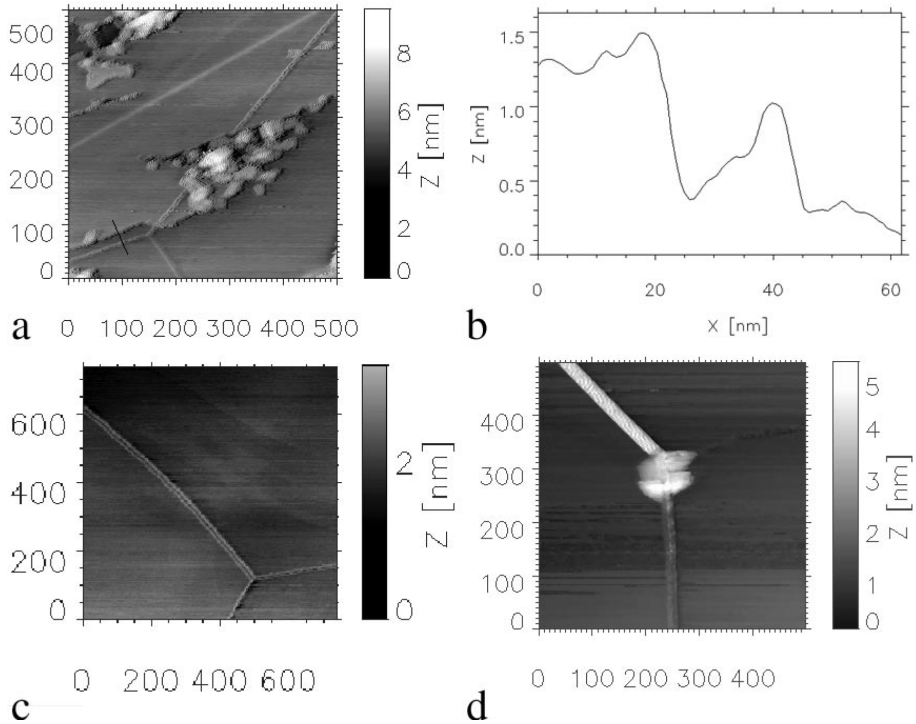

Fig. 1a–d. Y-branching of nanotubes in samples produced by the catalytic decomposition of C_{60} in the presence of transition metal powders. **a** 200-nm Powder of Ni. Clusters of amorphous C or C_{60} are covering parts of one of the branches. **b** Line cut across the line in **a**. The height of the branch is approximately 6 Å, comparable to that of single-walled carbon nanotubes, the height of the graphite step is 10 Å. **c** Powder $< 45\,\mu$m of Ti. **d** Metallic powder $< 45\,\mu$m of Fe. A cluster of amorphous carbon or C_{60} is sitting in the middle of the joint of the branching. All scales are in nanometres

out deposit or with fullerene deposits made from a quartz evaporator.

Figure 1 shows three topographic images of such Y-shaped objects measured on different samples. The sample in Fig. 1a was prepared with fullerenes decomposed in the presence of nickel (200 nm). The joint of the nanotubes is in the vicinity of a step of the HOPG. On the right side of the image clusters of amorphous carbon or C_{60} are covering one of the branches. The line cuts, like the one shown in the image, reveal that the heights of the branches are between 4 and 7 Å. The values are close to values obtained for single-walled nanotubes under similar conditions (in the range of 6 Å). The value of the measured height is below the geometrical value because of the presence of two tunnelling gaps: STM tip/nanotube, and nanotube/HOPG [16]. A second cause of this discrepancy lies in the differences in the electronic structure of the nanotube and that of HOPG [17, 18]. The step height in Fig. 1a is approximately 10 Å, three times the inter-planar distance in HOPG, as measured in a direction normal to the cleavage plane. The irregularity on the left side of the CNT line cut is an effect of tip-sample convolution, showing that the active tip has a non-symmetric shape. Figure 1c. shows the branching of a CNT on the sample produced by fullerene decomposition in the presence of titanium. The joint is clearly visible, but the upper left branch appears to be doubled, possibly caused by a double tip. In the case of an object with branches oriented at 120°, two equivalent tips situated close to each other will produce doubling of only one of the branches. At the other two branches the two tips are oriented in such a way that they will start imaging the object almost simultaneously. This may show up in the image as alteration of the apparent width and height of the object.

The CNT heights measured on line cuts for the branch in the upper left corner and at the bottom of the image are between 6 and 8 Å and are typical for SWCNTs. The height of the tube to the right side was measured to be only 3 Å. The discrepancy in the height values for the other two branches, as pointed out earlier, could come from multiple tip effects, or may be an indication of a different electronic structure. When measured at low tunnelling bias (below 1 V) the different densities of state in the vicinity of the Fermi level for metallic and semiconductor CNTs could produce such differences in the height values measured by STM.

In Fig. 1d a sample was measured which was produced using a mixture of fullerenes and < 45-μm iron powder. A cluster of amorphous carbon or fullerene covers the joint of the Y-shaped branches. Although it cannot be completely excluded, it is very unlikely that metal particles with sizes comparable to the object covering the joint are transported from the oven to the substrate. The branches are oriented at 120° angles to each other. Line cuts taken on the tubes towards the bottom and the right side of the image again give heights of between 4 and 8 Å. The upper left tube has a height of approximately 20 Å. This large diameter, which could be due to a multi-wall tube or a bundle of single-wall tubes, is not resolved by the tip. Our earlier work [7] shows that the growth procedure based on the decomposition of fullerene frequently yields rafts of nanotubes.

In contrast to the method used in [7], we used pure transition metal powders as decomposition agents in the present work instead of a complicated alloy of transition metals, such as stainless steel. When fullerene was decomposed by stainless steel we did not observed Y-shaped structures, only rafts of CNTs, or individual tubes, while for three different metals, Ni, Ti, and Fe, Y-shaped structures were found together with rafts of nanotubes, or individual tubes. On the basis of our data it is not easy to formulate a possible growth mechanism for the Y-shaped nanotubes. Two distinct families of scenarios may be considered: i) formation of the Y-nucleus in the oven, and ii) formation of the Y-nucleus on the HOPG substrate. Mass spectrometric data [7] showed that fullerene fragments are fused together in the oven. The observation of Y-branching only when using pure transition metals in the oven may indicate that the Y-nuclei are produced in the oven. On the other hand, Y-branching may originate from the strong templating effect characteristic of the HOPG substrate [7]. When deposited from suspensions in organic solvents CNTs tend to align themselves along the three axes of the basal plane of HOPG [16, 20], which are oriented at 120° to one another. This is an indication that this particular arrangement corresponds to a minimum in the energy of the system. Taking into account that in our experiments the growth takes place at room temperature it is reasonable to suppose that those defects which may cause Y-branching are the more stable ones.

The Y-branching described in this letter is different from the Y-shaped nanotube structures grown using nanotemplates made of nanochannel alumina, with channels branched in Y [21]. There the branching is a mechanical constraint imposed by the template, while in our work it is an inherent effect of the structure of the single-wall carbon nano-object as predicted by earlier theoretical works [12–14].

In summary, we have found Y-like branching of SWCNTs in samples produced by decomposition of fullerenes in the presence of metallic powders. Our measurements are the first experimental confirmation of Y-shaped branching of SWCNTs predicted theoretically [12–14]. This novel class of carbon nanostructures may constitute the basis for 3-terminal carbon nanoelectronics.

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