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Controlled synthesis of pointed carbon nanotubes

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Abstract

To fully realize the potential for the many applications of carbon nanotubes, it is necessary to control their morphology at will. Here we describe the controlled synthesis, on the fibers of a carbon paper, of multi-walled carbon nanotubes having either a regular cylindrical morphology or a novel morphology consisting of nanometric cylindrical tubes terminated by pointed tips about 0.5–1 μm long. Reshaping of the Ni–Co catalyst particle during the growth process has been directly observed for both regular and pointed nanotubes. However, total liquefaction of the catalyst particle is only observed during the growth of pointed tubes. Regular tubes result from the spiral scrolling of a graphene sheet resulting in a herringbone texture, while the tip of the pointed tubes displays a concentric textural character. The change in growth mechanism seems to occur upon total liquefaction of the catalyst.

1. Introduction

Since the well-known paper by Iijima on carbon nanotubes [1], various novel carbon nanostructures have been observed, such as helically-shaped nanotubes [2], nanohorns [3], microtrees [4], nanopipettes [5] and nanocones [6]. Conical carbon nanomorphologies have attracted great interest due to their shape and potential applications as probes for scanning probe microscopy and field emitters [7–9]. Iijima et al. [7] observed the sharp tips of carbon nanotubes synthesized by arc discharge. Merkulov et al. [8] reported the synthesis of carbon nanocones (CNCs) by plasma enhanced chemical vapor deposition, while Zhang et al. [9] synthesized tubular graphitic cones (TGCs) by chemical vapor deposition (CVD). Both the CNCs and the TGCs present nanometer scale tips and base diameters in the micrometer range.

Recently, we applied a special CVD approach to grow multi-walled carbon nanotubes (MWCNTs) on highly porous carbon paper by Ohmically heating Ni–Co alloy nanoparticles used as catalytic sites for the growth of the nanotubes from ethylene feedstock [10–12]. As the heated carbon paper has very little thermal inertia, it has the advantage of precisely controlling the growth process as well as the morphology of the nanotubes by the ability to quickly reach the growth temperature and also to quench the growing nanotube back to room temperature in order to elucidate the first steps in its growth. In this paper, we report on a method to synthesize a new type of cylindrically-pointed tube consisting of a nanometric cylindrical base and a sharply pointed tip, whose morphology is completely different from those mentioned above.

2. Experimental

2.1. Catalyst preparation for nanotube growth

Details of the Ni–Co particle preparation have been described previously [11,12]. Briefly, the dipping solution to obtain the metal catalysts was prepared as follows: First, 2(4-chlorosulfonylphenyl) ethyl trichlorosilane 50 vol% in dichloromethane (Gelest Inc., PA, USA) was diluted

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by a solution of 6 vol% water in ethanol to give silane concentrations of 1 vol%. After stirring the silane solution for 2 h at room temperature, Co and Ni nitrates with a 1:1 molar ratio were added to the solution to give combined transition ion sulfonate concentrations of 0.6 M. After further stirring for 30 min, the carbon paper, which is used to support the nanotubes, was immersed in the solution for 10 s and wiped off with a filter paper. The important step in the synthesis of the nanotubes is the use of a commercially available silane which, upon hydrolysis, forms a sulfonic acid–silicate, permitting the exchange of H^+ for Co^{2+} and Ni^{2+} ions. These latter ions are the precursors of the Ni–Co particles. Prior to Co–Ni deposition, the carbon paper backings were pre-treated with methanol for 30 min, in order to improve the homogeneity of the Co–Ni particle sizes and their distributions on the carbon fibers comprising the backing.

2.2. Synthesis of nanotubes

Multi-walled carbon nanotubes were synthesized by heating the Ni–Co particles deposited on the fibers of the carbon paper in a specifically designed CVD reactor, whose overall conditions are those of a cold-wall reactor. This reactor takes advantage of the fact that the carbon paper (E-TEK, Division of DeNora with 81% porosity) is the most resistive part of the electrical circuit. It can therefore be Ohmically heated up to 850 °C, a temperature high enough to decompose the ethylene feedstock and grow the nanotubes. The temperature of the carbon paper was determined pyrometrically (Leeds and Northrup). All the tubes were grown in this reactor.

2.2.1. Growth of regular tubes and pointed tubes

The preparation procedure of the Ni–Co catalyst is the same for the synthesis of regular and pointed carbon nanotubes, except for the rate at which the temperature of the carbon paper loaded with Ni–Co catalyst is raised to 850 °C. The effect of the heating rate on the tube morphology will be discussed in Section 3. A mixture of the following gases (Ar:H_2:ethylene; 90:5:5 vol%, respectively) was introduced into the reactor for 5 min before increasing the temperature. In both cases, the temperature was maintained at 850 °C for 10 min after the growth phase to anneal defects in the resulting MWCNT structures. Finally, the system was cooled under an Ar atmosphere.

2.2.2. Growth of second generation tubes for studies of growth initiation

In order to follow carbon nanotube growth initiation by transmission electron microscopy (TEM), a second generation of nanotubes can also be grown on first generation tubes by a similar procedure. Prior to Ni–Co deposition to grow this second generation of tubes, the first generation tubes were first pre-treated in 70% HNO_3 at room temperature for 4 h. Ni–Co particles were deposited on the first generation tubes using the same silane derivative as that used to obtain Ni–Co particles on the carbon fibers. In both cases, the composition of the solution was the same: 93% ethanol, 6% water, 1% silane, in which 0.3 M cobalt nitrate and 0.3 M nickel nitrate were dissolved. However, the growth of the second generation tubes was carried out for 10 min in 90% Ar, 5% H_2, and 5% CH_4 at 900 °C, a higher temperature than that used for first generation tubes (850 °C) to avoid the formation of amorphous carbon on the first generation tubes [13].

2.3. Characterization of the nanotubes and nanoparticles

The nanotubes and the Ni–Co nanoparticles produced were characterized using a Hitachi H-9000 NAR high-resolution transmission electron microscope (HRTEM) operated at 300 kV and an S-4700 Hitachi scanning electron microscope with a field-emission gun operated at 15 kV. The samples for HRTEM observation were directly cut from the carbon paper. Composition analyses were carried out in the HRTEM microscope by X-ray energy-dispersive spectrometry.

3. Results and discussion

Two very different morphologies of carbon nanotubes may be grown in our reactor by the decomposition of ethylene on Ni–Co catalyst particles deposited on the fibers of the carbon paper. The two morphologies are illustrated in Fig. 1a. In this figure, the regular multi-walled nanotube has a uniform diameter from one end to the other, while the pointed tube has a cylindrical base and a very sharp tip (up to 1 μm long). We have found that the formation of pointed tubes is associated with three important factors: (1) a fast heating of the catalytic particles under ethylene; (2) a small initial Ni–Co nanoparticle; and (3) the presence of sulfur in the Ni–Co catalytic particle. When all the factors are simultaneously present, up to 85% of the tubes produced have the pointed structure as shown in Fig. 2a and b.

In order to elucidate the effects of the heating rate on the morphology of carbon nanotubes, we carried out controlled experiments at three heating rates. These experiments show that: (i) a very fast heating (less than 1 s to reach the growth temperature, ~850 °C) leads to pointed tubes without a cylindrical base (the tubes are sharp from the beginning, as shown in Fig. 1b); (ii) fast heating (between 1 and 3 s) results in pointed tubes having a cylindrical base as shown in Figs. 1a and 2b; and (iii) slow heat-

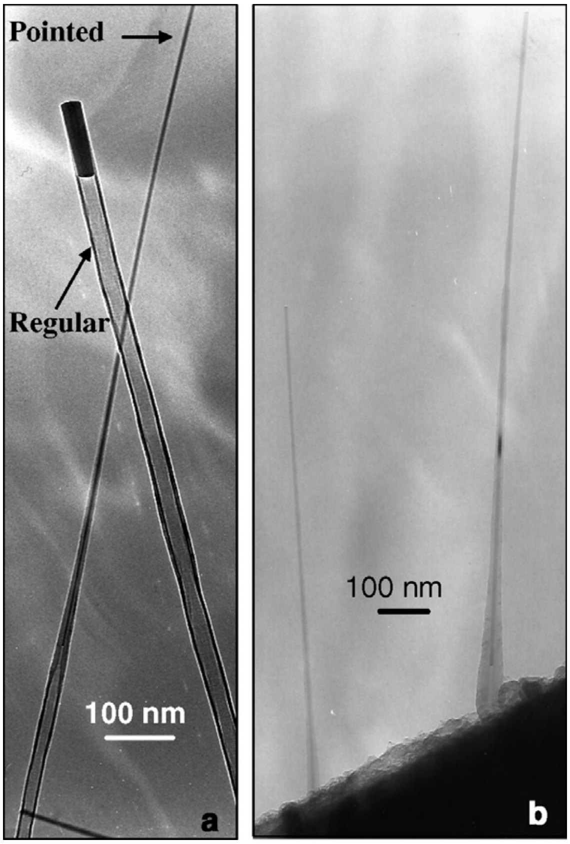

Fig. 1. TEM images of: (a) pointed and regular MWCNTs grown on carbon fibers by a specifically-designed CVD device; (b) pointed nanotube without cylindrical base.

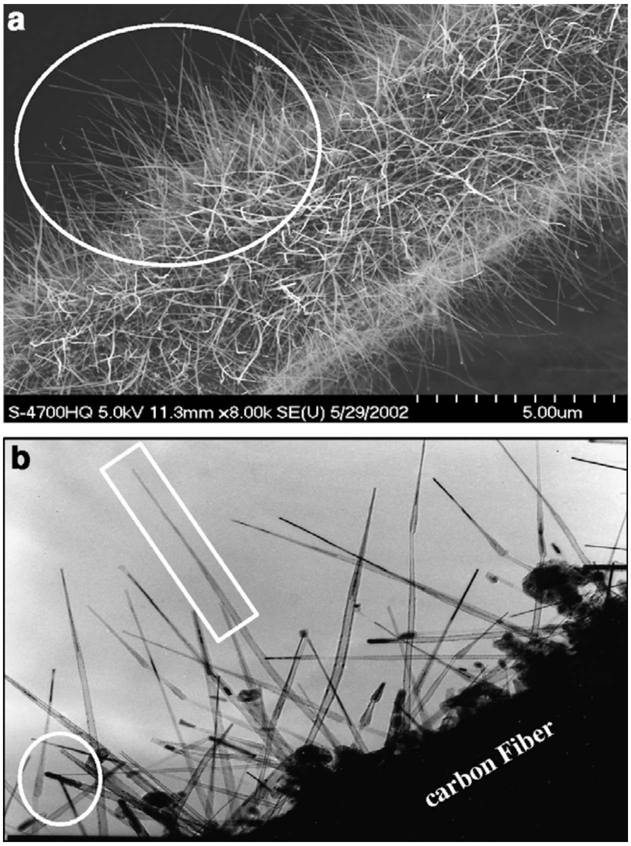

Fig. 2. (a) SEM and (b) TEM images of pointed nanotubes grown on a carbon fiber.

ing (>5 s) gives rise to regular cylindrical tubes without any pointed structure (Fig. 1a).

The main difference between regular and pointed tubes is the geometry of the catalyst particles at the tips of the tubes. These suggest that the morphological characteristics of the resultant tubes, either pointed or regular, are directly related to the change in shape of the catalyst particle during tube growth, as reported elsewhere [14–16]. It is also observed that the volume of the Ni–Co catalyst particle in a pointed tube is always smaller than that in a regular tube. For comparison, if the catalysts for pointed nanotubes and those for regular tubes were shaped into spheres, they would typically have diameters of 25–40 nm in the case of the pointed tubes and diameters of 50–65 nm for the regular tubes. Fast heating produces relatively smaller catalytic particles due to the very short time allowed for the reduction and aggregation of metal atoms into active catalytic particles. The size of these particles reacting with carbon is of prime importance in establishing whether they become either totally liquid at the growth temperature or only liquid at the surface of a solid core [17].

Fast heating and a small catalyst alone are not sufficient to produce pointed tubes on Ni–Co catalysts. The presence of sulfur in the catalyst is also essential to grow clean pointed (and regular) tubes. To confirm the role of sulfur in the silane for producing pointed tubes, controlled experiments were carried out with Ni–Co catalyst particles dispersed by a similar silane without sulfur. The silane without sulfur was: *N*-[(3-trimethoxysilyl)propyl]ethylenediamine triacetic acid (50% in water) [$C_{14}H_{25}Na_3O_9Si$]. In this case, no pointed tubes were obtained and the density of the regular tubes was also reduced. The role of sulfur (at a ppm level) has been reported to improve the reactivity and the selectivity of catalysts [18] and to promote the growth of carbon nanotubes [19,20]. This effect is considered to be related to both an enhancement of carbon deposition during the growth of the nanotubes [18,21] and a decrease in the melting point of the catalyst particles [22].

To further elucidate the growth mechanism of both the pointed and regular tubes, it is essential to understand how the nanometer catalyst particles initiate the growth of the tubes. In order to follow by TEM the first steps of a nanotube growth, we developed a method using first generation nanotubes as supports to grow a second generation of nanotubes [13]; this was necessary since the first generation of nanotubes are transparent to TEM while the carbon fibers of the paper are not.

Fig. 3 shows TEM micrographs of the regular or pointed nanotubes at the early stages during the growth process. The beginning of the growth is depicted in

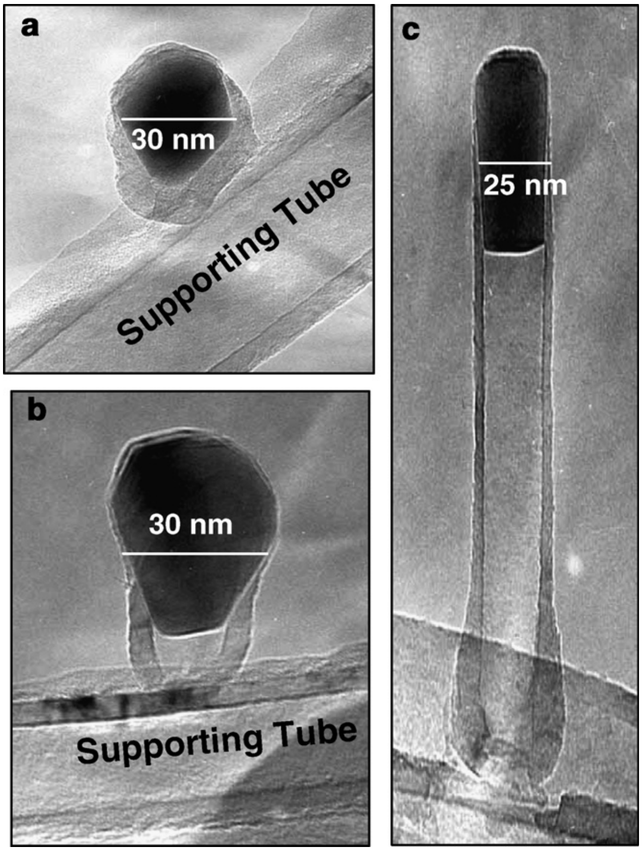

Fig. 3. Microstructure of the initiation of the pointed or regular tubes. (a) Partially melted Co–Ni catalytic nanoparticle with carbon layers accumulated near the solid side of the particle. (b) The catalytic particle lifts off the substrate and the tube begins to form. (c) The length of the tube increases and the catalytic particle becomes cork-shaped. *Note:* all micrographs are from different growth sequences.

Fig. 3a, where well defined angles of the solid crystalline Co–Ni catalyst are only seen on the lower half of the particle. Carbon layers accumulate there and are in contact with the supporting tube. The upper half of the particle seems already partially melted. Fig. 3b shows a later stage of the growth where the catalyst is lifted from the surface. The particle deforms and elongates upon superficial melting, ending up as the typical conical cork-shaped catalyst always found at the tip of regular tubes (Fig. 3c). Depending on the initial amount of metal and the growth conditions, subsequent growth will end up producing either a regular tube as in Fig. 1a or a pointed tube as in Fig. 1a or b. It will be shown that for pointed tubes, the smaller catalytic particles undergo a transition from initially partially melted (like in Fig. 3c) to totally liquid in the time leading to the thin catalyst particle present at the tip of the pointed tubes. It will also be shown that the complete liquefaction of the catalyst also results in a drastic change in the growth procedure, leading to the particular shape of the pointed tubes.

Fig. 4 depicts a typical pointed tube. Details about regions A, B, and C of Fig. 4 are given in Figs. 5–7, respectively. In the morphological details given in Fig. 5a, it is important to notice that the walls of the tubes are initially of constant thickness during all the time that the catalytic particle remains cork-shaped like in Fig. 3c. A close observation of the tube base in Fig. 5a and b shows that both *external* and *internal* lattice fringes of the tube wall terminate at more or less regular intervals since the lattice fringes are inclinated at an angle similar to that of the conical cork-shaped catalyst. The presence of the lattice fringe terminations suggest that the cylindrical bodies of both pointed and regular tubes have a scrolled structure [23,24]. As a scrolled graphene sheet may lead to either a herringbone or a concentric texture, the entire cylindrical nanotube seems, in the present case, to be obtained by the spiral scrolling of a single graphene sheet having a width equivalent to the length of the cork-shaped catalyst, producing new spirals inside the previous one. The herringbone texture seen in Fig. 5b is a consequence of the angle displayed by the conical cork-shaped catalyst which generates the graphene layer. The resulting tube is mechanically much stronger than a nanofiber, which presents a nested cone herringbone texture [25]. For the latter arrangement, each cone interacts with its neighbors only by van de Waals forces and the fiber is relatively weak. This is not the case here since a tape applied to the MWCNTs may be peeled off without removing any of the carbon nanotubes.

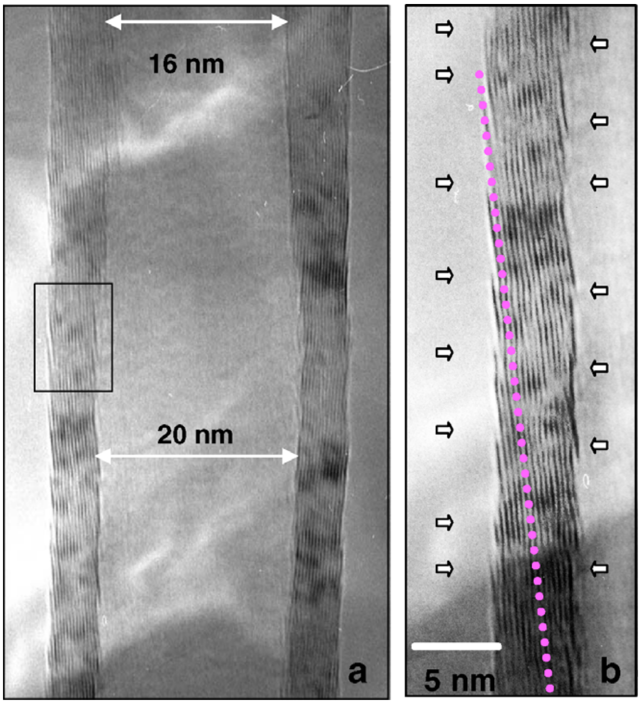

Fig. 5. (a) HRTEM image of the tube of Fig. 4 at location A showing that the internal hollow decreases in the growth direction by adding graphene layers on the inside; (b) close up showing the interruption (white arrows) of the *external* and *internal* lattice fringes of the nanotube wall. Note that the lattice fringes are at an angle with respect to the growth direction (dotted line).

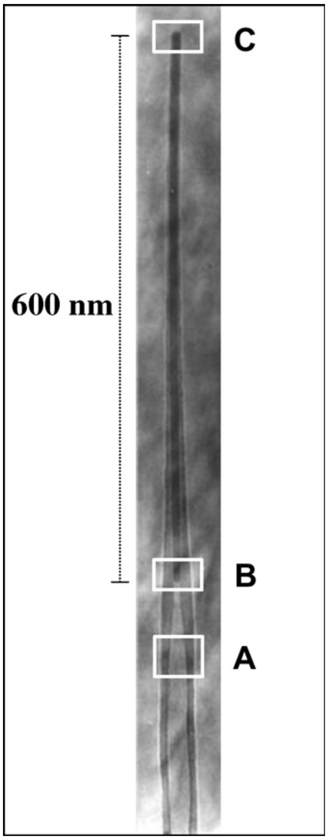

Fig. 4. TEM image of a typical pointed tube with three identified locations: A, B, and C.

Complete melting of the catalyst must start in region B of the tube that is depicted in Fig. 4. In this transition region, depicted in more detail in Fig. 6a and b, lattice fringes of the tube wall only terminate on the *outside* of the tube as the catalyst growth rate drastically increases and the lattice fringes of the tube wall now become aligned along the growth direction. Fig. 7 depicts the end of the

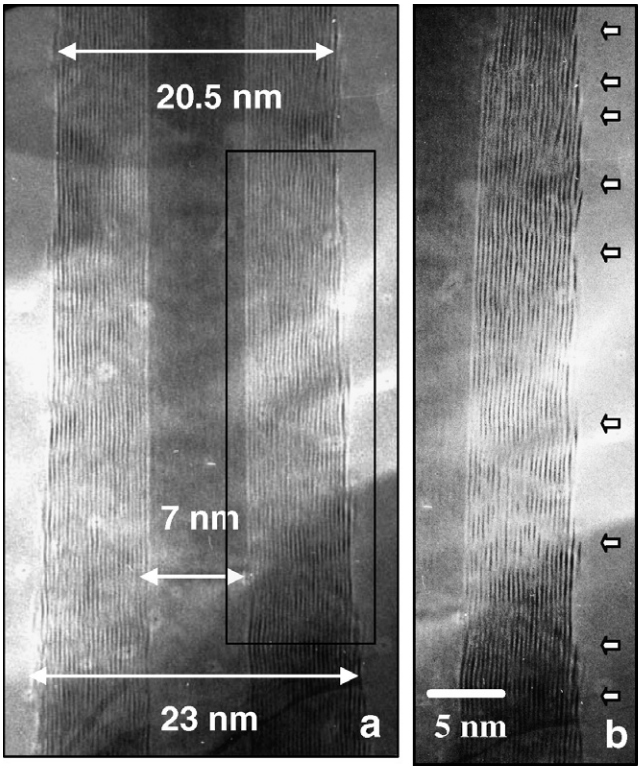

Fig. 6. (a) HRTEM image of the tube of Fig. 4 at location B showing the transition between regions A and C of the tube; (b) close up showing the interruption of the *external* lattice fringes only (white arrows) of the nanotube wall.

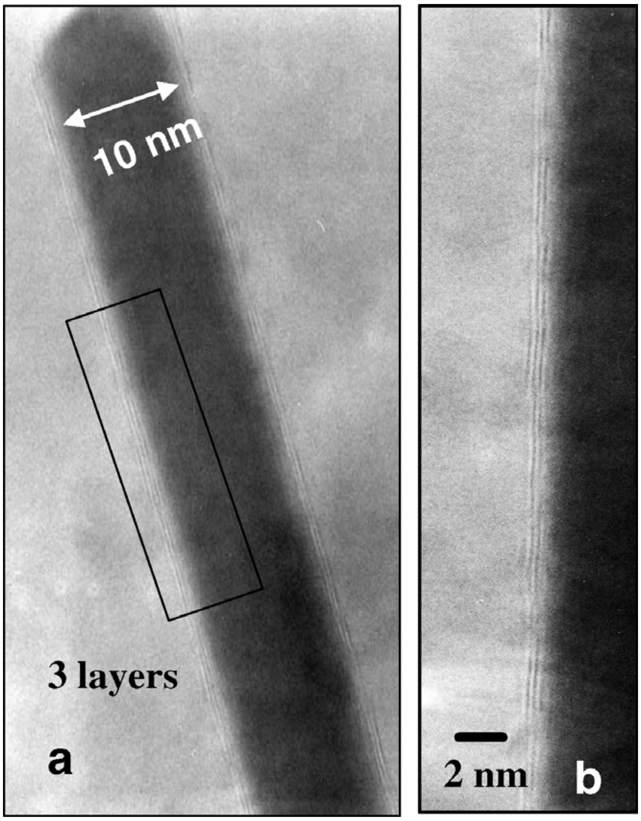

Fig. 7. (a) HRTEM image of the tube of Fig. 4 at location C showing the tip covered with three graphitic layers; (b) close up on the three layers of the nanotube wall.

tube where only three carbon layers remain around the needle shaped catalyst. No terminations of the lattice fringes are visible on either the inside or the outside of the tube wall.

Therefore, the particularity of the pointed nanotubes described in this work resides in the combination of the herringbone and concentric character of the MWCNTs in the same morphology. At point A (Fig. 4), the MWCNTs display a herringbone textural character, while it is concentric at point C. Part B represents a transition region having a concentric textural character towards the inner side of the tube, while keeping the herringbone character on the outside. The growth mechanism that characterizes these pointed tubes changes from a herringbone texture to a concentric one as soon as the catalyst becomes completely liquid upon heat intake by the metal as the temperature rapidly increases, within 1–3 s, from room temperature to 850 °C. As the growth of MWCNTs involves the decomposition of hydrocarbon gas, the diffusion of carbon in the catalytic particle followed by carbon precipitation at its surface [25], it is expected that all these steps will be accelerated by the total liquefaction of the catalyst.

Results from Ref. [26] suggest that the growth rate of carbon nanotubes is of the order of 0.2 μm/s near 700 °C with a Fe–Mo catalyst and ethylene as carbon feedstock. Using the growth rate values at 600, 650, and 700 °C reported in the above paper and assuming an Arrhenius type behavior for the change of the growth rate with the temperature, a growth rate of ∼0.65 μm/s would be obtained at 850 °C, the temperature used here to obtain pointed tubes. Since the tips are of the order of 0.5–1 μm long (see Figs. 1, 4–6), this would suggest that the critical heating time would be of the order of 1 s at 850 °C. This is what we found experimentally. Complete liquefaction only occurs when the volume of the catalyst is small. For larger catalytic particles and/or slower increase of the temperature, the catalyst will remain cork-shaped and MWCNTs with a herringbone texture will be obtained.

4. Conclusions

We have shown in this work that it is possible to control the morphology of MWCNTs grown on Ohmically heated carbon paper, by simply controlling the growth conditions. Nanotubes with pointed tips of the order of 0.5–1 μm long on the top of a cylindrical body are obtained by a fast heating (between 1 and 3 s) of small (below 40 nm diameter) Ni–Co nanoparticles containing some sulfur. It is the silane used to generate Ni–Co nanoparticles which is the source of the sulfur content of the catalyst particles. The cylindrical body of the tube seems to be obtained by the spiral scrolling of a single graphene sheet having a width equivalent to the length of the cork-shaped catalyst. The growth mechanism changes, however, as soon as the metal particle used as catalyst totally liquefies. A fine metal tip covered with a few concentric single-walled layers is then observed. Less rapid heating or catalytic particles of larger size do not develop the pointed tip and the MWCNT remains cylindrical. Experiments are now underway to investigate particular applications of these two types of morphologies.

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