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Growth mechanisms of carbon nanotrees with branched carbon nanofibers synthesized by plasma-enhanced chemical vapour deposition

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3

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Abstract

Y- and comb-type carbon nanotrees formed from branched carbon nanofibres grown by plasma-enhanced chemical vapour deposition were studied by transmission electron microscopy. Different growth mechanisms are proposed for the two types of nanotrees based on the observed and reconstituted dynamic transformations of the catalyst particles during synthesis. However, the splitting of the larger catalyst particles is required for both kinds of nanotrees, whatever the involved growth mechanism. The carbon nanotrees are well crystallized and connections of the branches are continuous, which may be interesting for future applications in nanoelectronic devices and also composite materials.

1. Introduction

The connection between carbon nanotubes (CNTs)/carbon nanofibres (CNFs) attracts great attention due to potential applications as building blocks in nanoelectronic devices as well as CNT-reinforced composites[1-3]. Zhou et al. first reported the growth of branched CNTs by arc discharge and L-, Y- and T-type connections of CNTs were observed [4]. Soon after, catalytic chemical vapour deposition (CCVD) [5-10], and template methods [11-13] were mainly used to grow branched CNTs. Furthermore, electron beam welding in a transmission electron microscope was found to be useful for in situ fabrication of CNT connections [14-16]. The arms of the branched CNTs are rather straight and the connections are predominantly Y-type, which can be hierarchically branched into nanotrees [13, 17]. The branching mechanism for CNTs synthesized inside porous anodic alumina (PAA) templates is easy to understand, since the PAA acts as a mould for CNT growth. For CNT connections by CCVD growth, however, there are two opposite growth mechanisms. Zilliet al. [18] and Luo et al. [9] ascribed the connections of CNTs to a catalyst-merging mechanism: the two encountering nanoparticle catalysts weld together and subsequently act as a unique catalyst for the second CNT branch. On the contrary, Li et al.[6] considered that the splitting of catalyst particles was at the origin of the Y-type CNTs. Teo et al.[19] proposed that the breaking up of large catalysts under the perturbation induced by changing the temperature was the reason for the branched CNTs, which is similar to the mechanism proposed by Li et al. [6]. Unfortunately, no more details were discussed about this mechanism.

In this letter, we report a Y- and comb-type carbon nanotree, synthesized by plasma-enhanced chemical vapour deposition (PECVD). Those nanotrees have their trunks composed of carbon nanorods and their branches are formed of parallel CNFs. The growth mechanisms for the connecting CNF branches are discussed based on transmission electron microscopy (TEM) observations. Detailed growth models for the Y- and comb-type nanotrees are also

proposed. We emphasise here that the growth of such nanotrees is observed in our PECVD growth experiments as long as the catalyst thin film thickness is larger than $\sim 20\text{-}25$ nm. Such large catalyst film thickness give rise to a corresponding large variety of particle sizes upon the thermal treatment applied to break-down the thin catalyst film into islands (see below).

2. Experimental details

The CNTs/CNFs were grown in a home-made dc-PECVD system, which comprises three independent electrodes. Two electrodes are used to generate the plasma and the third one (substrate holder) is negatively biased in order to extract the ions from the plasma. More details on the growth reactor can be found in Ref. [20]. We have used either Ni or Fe as metal catalysts for the growth experiments presented here. For experiments involving Ni, 30 nm thick layers were first evaporated on oxidized Si wafers and then loaded into the PECVD system to grow CNTs/CNFs at 650 °C for 85 minutes. For the experiments involving Fe, both α -Fe and iron carbides (essentially Fe_3C) happened to act as catalysts [21]. The starting material was a 20 nm thick Fe film and growth was also performed at 650 °C. The reactive gas source was composed of a mixture of water vapor (H_2O) and isopropyl alcohol ($\text{C}_2\text{H}_5\text{OH}$). A Philips CM30 microscope operated at 300 kV and a FEI Tecnai G² microscope operated at 200 kV were used to observe the structure and morphology of CNTs/CNFs, by using selected-area electron diffraction patterns (EDPs), conventional and high resolution electron microscopy (HREM) images.

3. Results and discussion

Figure 1 shows bright-field TEM images of carbon nanotrees grown from Ni catalysts. The Ni nanoparticles are located at the tips of the CNFs indicating a tip-growth mode. Figure 1a is a typical nanotree with two branches. The parallel CNFs are connected to a short carbon

trunk (a kind of carbon nanorod - CNR) to form a Y-type junction. Three well oriented CNF branches are also found to connect together (Fig. 1b), similar to the observed branched CNTs caused by the perturbation during dc-PECVD growth [19]. We can understand the occurrence of parallel CNF branches because dc-PECVD is well-known to induce the growth of well oriented CNTs/CNFs [22]. Interestingly, we notice that the branches of CNFs can be inclined, at least temporarily, with respect to the axis of the trunks. For example, the left CNF in Fig. 1c is inclined by $\sim 16^\circ$ and the second trunk in Fig. 1d is inclined by $\sim 37^\circ$. We note however that after some time, the growth direction tends to become again parallel to the axis of the trunk. The common feature for the inclined CNFs is the fact that the graphene layers at their lower part, where branching occurs, are non-homogeneously distributed. For instance in Fig. 1c, there are many more layers of graphene at the lower left part of the left branch than at its right part, as seen clearly in the enlarged image in Fig. 1g. Moreover, because the graphene layers at the upper surface of the second trunk are under direct ion bombardment from the plasma, they will tend to be unstable. Consequently, the elongated Ni nanoparticles (nanorods), pushed by the graphene layers underneath, have the opportunity to be exposed to the plasma at the upper surface of the second trunk, where only few (if any) graphene layers are present (this is indicated by an arrow in Fig. 1g). Due to the stress applied by the continuing growth of graphene layers in between the already existing ones and the catalyst nanorods (see e.g. ref. [23]), those exposed Ni nanorods can be further stretched and broken into several smaller ones as the growth time is increasing [20], and they can behave as “second generation” catalysts for the growth of new CNFs, as shown in Fig. 1d.

The enlarged TEM images shown in the lower row of Fig. 1 demonstrate that the residual Ni nanoparticles at the connecting area of the branches are linked to the hollowed part of the CNF branches. It is worth noticing that the continuous Ni nanorod encapsulated in the CNFs at the joint in Fig. 1g (highlighted by yellow dashed lines), connects the two

branches. Several grain boundaries are observed when the triangle particle at the bottom is tilted to [110] orientation, suggesting that the stretched Ni nanorod consists of crystalline grains exhibiting different orientations, a situation we already observed in the past [20]. Furthermore, the elongated Ni nanorod shared by two branches is extruded towards the catalyst at the tip of the right-hand side CNF through the cavity of the tube, which is an indication that the two branches of CNFs were grown from the splitting of a former large nanoparticle. The polycrystalline character of the continuous Ni nanorod is beneficial to the splitting operation [20].

Let us note at this stage that the phase of the catalyst, be it made of Ni, Fe or Fe-carbide, cannot be liquid during growth. The melting points of these metals or compounds are indeed well above 1100 °C, whatever their carbon content, while the growth temperature used here is 650 °C. We have annealed such particles and their CNFs in situ in the TEM [24, 25]: at 650°C, their shape may very significantly change but quite surprisingly, during the change, their structure and orientation may undergo only little evolution [25]. Moreover, a possible decrease of the melting temperatures due to the small size of the particles cannot enter into play, as the particles have sizes well above 10 nm. Thus, the catalytic growth mechanism at play here is of the type VSS (Vapour Solid Solid). As a consequence the structure we observe after growth and cooling of the sample is most probably a good image of that at 650 °C during growth.

More interestingly, a carbon nanotree with parallel branches was found to form a comb-type nanostructure (Fig. 1d), which has often been reported for ZnO nanostructures [26, 27], but to the best of our knowledge, has not been observed in CNTs/CNFs. Eight discrete CNFs with Ni nanoparticle catalysts on their tips form the comb-like structure over the trunk, with the two extreme ones, No. 1 and 8, being longer as well as larger in diameter. This suggests that the starting time for nucleation and growth of the short CNFs was delayed compared to

the CNFs grown directly from the first trunk. One possible explanation is that it takes some time to form the second generation catalysts, since the Ni nanorods have to be broken into separated smaller particles capable to seed the growth of new CNFs (Fig. 1h) and this can only happen while the second trunk of Fig. 1d is growing. The local lack of carbon resource could be a second explanation, because the short CNFs are surrounded by long and thick ones “pumping” the growth nutrients and exhausting the plasma atmosphere around them. Actually, both explanations are likely to hold. Compared to the previous method which used a second catalyst deposition and a second growth step to form branched CNTs [10], the branched CNFs obtained here from the splitting of large catalysts can be synthesized in one step only, which is an advantage.

Some characteristics of the carbon nanotree shown in Fig.1d were studied by HREM imaging. The nanotree is well crystallized, as typically shown in Fig. 2. Figure 2a is an enlarged view of No. 4 and 5 CNFs from the white rectangle of Fig. 1d, which helps situate the various portions which we observed under HREM imaging. Figure 2b, taken at the root of the thin CNF (see circle on Fig. 2a), shows several orientations for the graphene layers (red and green dashed lines), as well as a meandering hollow core which suggests that the initial growth period was quite difficult, probably because of the concomitant growth of the large fiber (No. 5), on the right-hand side. As can be observed in the volume between the red and bottom green dashed lines, the graphene layers are first roughly parallel to the axis of the second trunk (see Fig. 1d for the labelling), which indicates that nucleation of the CNF occurred by the already known mechanism, by which carbon is expelled from the supersaturated metal particle at its lower part, forming several layers of graphene which are parallel to the substrate. Then, because of reshaping of the metal particle, usually in the pear-like configuration, graphene precipitation starts to occur on the side walls of the particle leading to the characteristic bamboo-like structure for the CNF. This is highlighted by the

green dashed lines on both sides of the hollow part of the fibre and we can observe the good continuity of the graphene layers between the carbon trunk and the CNF branches. It is interesting to note that the graphene layers of the side surface at the base of the CNF are highly curved (which is highlighted by the green dashed lines) in contrast with the more straight ones observed in the higher part of the image. This indicates that the catalyst metal particle was totally re-organized during growth of the CNF and went from an oblong, pebble-like shape (the latter resulting from the stretching imposed by the graphene layers during growth of the second trunk) to a pear-like shape. The meandering aspect of the CNF at the initial state implies that the alternate change of growth directions of the catalyst (consequently, for CNF too) is easier than a straight growth. Figure 2c is the HREM image from the upper part of No. 4 CNF. Both the number of graphene layers at both sides of the catalyst and the angles of the layers to the axis of the tube are different because of the asymmetric shape of the catalyst. The HREM image from the trunk in Fig. 2d shows well crystallized characteristics of a graphite-like solid. However, the graphene layers seem to be slanted at some angle with respect to axis of the trunk. The phase of the nanoparticles at the tip of the CNF branches is confirmed to be Ni by EDPs. Twins in Ni nanoparticles at the tip of the branched CNTs are also found, as demonstrated in Fig. 2e, consistent with previous reports [20, 28].

The branched CNF structure caused by the splitting of catalysts is also observed from samples using iron as a growth catalyst. Figure 3a shows a bunch of CNFs grown using iron (or iron carbide [21]) as catalyst and sharing the same root. Here again, it is clear that the catalyst nanorod on the left-hand side originates from the breakage of the one in the middle, because the hollowed part of the left-hand side CNF is directly connected with the protuberance at the bottom left-hand side of the middle catalyst, as seen more clearly in the enlarged image in Fig. 3b. Note that for the CNFs shown on Fig. 3, growth has proceeded

from iron carbide (and not Fe) catalyst nanoparticles, as indicated by the bamboo-type structure with regularly-spaced graphene walls inside the hollow core of the CNFs (for the differences of shape between Fe- and iron carbide-catalysed nanofibres, see ref.[21]).

The schematic diagrams of Fig. 4 give brief explanations on the whole process of generating branched CNFs. It includes two kinds of situations: (1) the branched CNFs have parallel axis and are perpendicular to the substrate; (2) some of the axes are inclined to the substrate over a certain length. We consider that in all situations the splitting of the catalyst particles is responsible for the branched structure. However, whether the branches are parallel or inclined with respect to the direction perpendicular to the substrate (i.e., the electric field direction during growth) depends on the original shape of the catalyst particles, which determines how graphene layers nucleate at the initial stage of growth. Let us discuss the first situation where the branched CNFs have parallel axis, perpendicular to the substrate; this is summarized on the first row in Fig. 4. The PECVD growth process has superiority in growing well aligned CNTs and this has been discussed at length in the literature [22]. Therefore, we focus on the explanation of generating connections of CNFs rather than parallel branches. To begin with, polycrystalline nanoparticles form on the surface of the unreactive substrate (as verified before [20-22]). These nanoparticles originate from the fragmentation and re-arrangement of the metal catalyst film, due to surface and interface energy minimization. Because of the symmetric shape of the catalyst particle, graphene layers then start to grow homogeneously at the bottom part of the catalyst nanoparticle [22], fuelled by surface/bulk carbon diffusion (Fig. 4a and b). Next, the large polycrystalline catalyst particle is elongated along the growth direction and changed to a pear-like shape (Fig. 4b), due to the compressive stress from the graphene walls of the CNF, as well as the electrostatic force originating from the dcPECVD process[21, 22, 29]. At some stage, the large catalyst starts to break into smaller ones, because of the increasing stress from thicker graphene layers at the base of the

particle (Fig. 4c). Splitting is probably initiated at grain boundaries where the metal-metal bonds are weaker and carbon saturation at the grain boundaries further weakens them.

Once splitting has started, the particle adopts a more oblong shape (Fig. 4d), again because of the asymmetric stretching, due to the large difference in graphene layer numbers between its top and bottom parts. This is due to both delayed nucleation on the top part and direct exposure to the ion flux from the plasma of the top graphene layers, rendering them instable (Fig. 4d). Subsequently, the metal keeps stretching and parallel CNFs, each catalysed by smaller metal particles, start to grow along the direction of the electric field and perpendicular to the substrate. This happens not only because of the electrostatic force [22, 29], but also because of the homogeneous and uniform precipitation of the graphene layers around the side surface of the second generation catalysts. However, the catalyst can still be continuous from one CNF to the other because of its deformation and elongation during growth (Fig. 4e). As growth proceeds, the catalyst gets broken into several smaller particles, probably because the metal stretching rate is lower than the CNF growth rate (Fig. 4f). Finally, the branched CNFs with their axis parallel to each other are formed. They share the same graphite nanorod at the base to form a Y-type CNF junction.

The second situation to be discussed is when the axes of CNFs/CNRs are inclined rather than perpendicular to the substrate, at least during a certain growth time, e.g. Fig. 1c, d. This situation is not often observed, but worth discussing because it produces a comb-type carbon nanotree with several parallel branches. We ascribe this phenomenon to the presence of more efficient nucleation sites for graphene on one side of the catalyst particle (see the lower row in Fig. 4). First, the initial catalyst has an asymmetric shape, where one side has more active nucleation sites, e.g. atomic steps, than the other side (Fig. 4g). Second, the graphene layers prefer to nucleate at the active sites, with the layers parallel to the side surface of the catalysts, but inclined with respect to the substrate (left-hand side in Fig. 4h & i). Third, the thicker

graphene layers impose the growth direction, due to their higher strength compared to the side with fewer graphene layers. At the same time, the catalyst is stretched by the compression of the graphene layers around it, which increases with the growth time. However, because one side is covered with fewer graphene layers, growth has also tendency to extend laterally (Fig. 4i). Fourth, as growth proceeds, the rather large catalysts are broken into smaller ones, just as explained in the previous paragraph, and line up on the surface of the second trunk (Fig. 4j). Each catalyst at the surface of the inclined nanorod can act as a secondary catalyst for growing the second generation CNFs. Finally, a comb-type nanotree with parallel CNF branches is generated (Fig. 4k).

Compared with the interconnected branches of the carbon nanotrees grown inside templates [13], the single carbon nanotree in our case grows alone, which highly simplifies the fabrication process for applications as building blocks in nanoelectronic devices. Meanwhile, the branched structures are relatively easy to synthesize in our case because we only need to deposit catalysts on the substrate and then load it into the PECVD reactor for growth. The drawback of our method, however, is that we cannot yet precisely control which catalyst will grow the branched CNFs and some more experiments with calibrated catalyst sizes are on-going to overcome this disadvantage.

4. Conclusion

Carbon nanotrees with branched CNFs were synthesized by PECVD and their structures were analysed by TEM. The junctions are mainly classified as two types. (1) Y-type connection, where the two branched CNFs are connected to a short graphite nanorod supporting them. (2) Comb-type carbon nanotrees, where a second generation of CNFs nucleate on the inclined carbon nanorods to form a comb-like nanotree, where several parallel CNFs are lined up. The breaking up of large catalyst particles into smaller ones is found to be the major step in the

branching mechanism, which is opposite to the catalyst-merging mechanism. The growth axis of some branches is significantly inclined with respect to the substrate normal. We propose that this tilt is related to the asymmetry of the catalyst particles in terms of nucleation sites. The carbon nanotrees are well crystallized and connections of the branches are continuous, which could be applied in the future to nanoelectronic devices and also composite materials.

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Figure captions

Figure 1. First row: bright field TEM images of branched carbon nanotrees taken at low magnifications. (a) Y-type nanotree with parallel CNF branches; (b) Carbon nanotree with three branches; (c) Y-type nanotree with one inclined CNF branch; (d) Comb-type nanotree with eight parallel CNF branches. Second row (e-h): enlarged TEM images of the branching regions of carbon nanotrees from the first row. The triangle particle at the lower part in (g) is tilted to $[110]_{\text{Ni}}$ direction, as inserted.

Figure 2. (a) Bright-field TEM image of No. 4 & 5 CNF, from the white rectangle in Fig. 1d. (b) HREM image of the area connected to second trunk and one CNF grown on it (corresponding to the lower white circle of (a)). The orientation of the graphene layers at the lower part of the CNF is highlighted by green dashed lines, whereas the orientation of the graphene layers at the surface of the second trunk is highlighted by the red dashed line. (c) HREM image of the head of the smallest CNF (No. 4). The angles of the graphene layers at the left and right-hand sides of the catalyst with respect to the axis of the tube are 23° and 7° , respectively. (d) HREM image of the second carbon trunk, suggesting well crystallized graphene layers. (e) $[110]$ electron diffraction pattern of one Ni catalyst at the tip of CNT showing a $\{111\}$ twin.

Figure 3. Branched CNFs catalysed by Fe/iron carbide. (a) Low magnification image; (b) enlarged image showing the branching area of CNFs.

Figure 4. Schematic diagram of the process of generating branched carbon nanotrees. First row (a-f): The different steps of the formation of a Y-type connection with parallel CNF branches. Second row (g-k): The different steps of the formation of a Comb-type connection.

The splitting of the large particles is found to be the primary reason for the formation of branched CNFs.