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Growth of Y-shaped Carbon Nanofibers from Ethanol Flames

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Abstract Y-shaped carbon nanofibers as a multi-branched carbon nanostructure have potential applications in electronic devices. In this article, we report that several types of Y-shaped carbon nanofibers are obtained from ethanol flames. These Y-shaped carbon nanofibers have different morphologies. According to our experimental results, the growth mechanism of Y-shaped carbon nanofibers has been discussed and a possible growth model of Y-shaped carbon nanofibers has been proposed.

Keywords Y-shaped carbon nanofibers · Ethanol flames · Growth mechanism · Catalyst

Introduction

Since the first identification of carbon nanotubes (CNTs) [1], many different microstructure CNTs, such as single-walled CNTs [2, 3], double-walled CNTs [4], zigzag CNTs [5], bamboo-like CNTs [6–8], and Y-shaped CNTs [9–16], have been reported. Much research has been focused on Y-shaped CNTs for their potential applications in single-electron transistors because of their unique electrical properties [10] originating from their unique multi-branched structure. There are a lot of methods, such as catalytic arc discharge [17], template method [9, 14], welding technique [13], and chemical vapor depositions (CVD) [8, 11, 12, 15, 16] for synthesizing Y-shaped CNTs. It is obvious that the formation mechanism of Y-junction CNTs is different for different synthesis methods. For the template method, the formation of Y-shaped CNTs is due to the spatial confination of Y-shaped nano-channel of anodic aluminum oxide (AAO) templates. For the electron beam welding technique [13], two CNTs that were crossing and "touching" each other could form molecular junctions via cross-linking of dangling bonds by electron beam exposure at high temperatures. And then the molecular junctions can be tailored to form Y-junction by controlled electron irradiation. For CVD methods, the growth mechanism of Y-junction CNTs is more complicated due to spontaneity of formation of Y-junctions, but this question has been addressed by some authors [6, 15, 18].

Carbon nanofibers (CNFs) also have been attracted much attention because their properties are similar to that of CNTs. There are many reports on various microstructure CNFs, such as non-helical CNFs and helical CNFs. However, little research has been focused on Y-shaped CNFs. There are also few reports on the synthesis of Y-shaped CNFs. Recently, Sharon et al. reported that the Y-shaped CNFs were synthesized by chemical vapor deposition at 900 °C which employed camphor as carbon source and nickel nanofilms as catalyst [18]. The CNFs reported by Sharon et al. were multiple Y-shaped CNFs, but every branch on stem CNFs was relatively short, and only one type of Y-shaped CNFs was observed [18]. In their report, Sharon et al. considered that the formation of Y-junction branched CNFs was related to camphor (used as carbon

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source) which has two pentagonal and one hexagonal rings. So little extra effort is needed to form 5- and 7-membered rings and it has been possible to grow Y-junction branched CNFs easily with camphor [18].

In this article, we report the Y-shaped CNFs obtained from ethanol flames in low yield (<1%). It is interesting to find that there are several types of Y-shaped CNFs. The growth mechanism of Y-shaped CNFs also has been discussed.

Experimental Details

The Y-shaped CNFs were synthesized by ethanol catalytic combustion (ECC). The process of ECC is described as follows: copper plates were employed as substrates, nickel nitrate, nickel chloride, and iron nitrate as catalyst precursors, and ethanol as both carbon source and fuel to provide energy for CNF growth. Copper plates were ultrasonically washed in acetone for several minutes. Catalyst precursors were dissolved in absolute ethanol to form saturated precursor solutions. Then some drops of catalyst precursor solution were dripped to cleaned surface of copper plates. After dried naturally, the coated copper plate was inserted into ethanol flames. The substrates stayed in ethanol flames for about 10 min. At last, wool-like deposits were found on the surface of copper plate.

In our experiments, the flames of ethanol are diffusive. The height of stable flames was about 8 cm, but the part of flames over 5 cm was very unstable (the bottom position of the flames was defined as the reference position). The copper substrates for sampling were normally located at the position of 2 cm in height. The temperature at that position was 545 ± 10°C which was measured by thermocouple.

The as-synthesized deposits were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). During SEM and TEM characterization, some types of Y-shaped CNFs were found and characterized.

Results and Discussion

We obtained mass products of CNFs on substrates; however, the Y-shaped CNFs have a small portion. Figure 1 shows SEM images of as-synthesized deposits grown on copper plate by employing nickel chloride as catalyst precursors. From these images, we can find some Y-shaped CNFs in deposits (marked by Y-like black lines). According to SEM observations, the yield of Y-shaped CNFs versus other morphologies was estimated to be less than 1% because the Y-shaped CNFs were not difficult to be found during SEM observations.

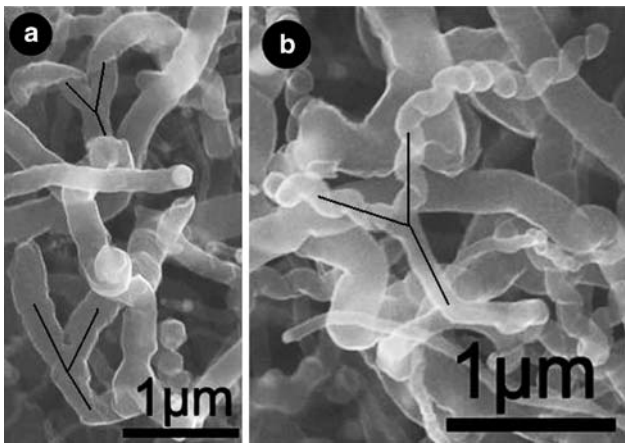

Fig. 1 SEM images of as-synthesized deposits on copper plate by employing nickel chloride as catalyst precursor

Figure 2 shows TEM images of Y-shaped CNFs synthesized by employing nickel nitrate as catalyst precursors. From Figs. 1 and 2, several types of CNFs can be identified; they are (i) Y-shaped CNFs with three non-helical CNF branches (shown in Fig. 1a), (ii) helical Y-shaped CNFs with three helical CNF branches (shown in Fig. 2a), (iii) helical Y-shaped CNFs with two junctions (shown in Fig. 2b), and (iv) hybrid Y-shaped CNFs with non-helical CNF branch (shown in Figs. 1b and 2c). The helical morphologies and hybrid morphologies of Y-shaped CNFs with helical and non-helical branch CNFs are outstanding characteristics that make our Y-shaped CNFs differ from previous reports [8–16].

Although the morphology of these Y-shaped CNFs is different, the diameter of branches of these Y-shaped CNFs is all about 100 nm and the angles between three branches are all close to 60° and 150°, respectively. These Y-shaped CNFs also have a relatively longer branch with the length of up to micrometer scale. This length is longer than the length of branches of CNFs synthesized by Sharon, where the length of branches was normally less than several hundred nanometers [18]. These TEM images also revealed that there were no catalyst particles located at the center of Y-junctions, which was important to understand the formation of Y-junctions.

Figure 3 shows a TEM image of that Y-shaped CNF synthesized by employing iron nitrate as catalyst precursors. Like the Y-junctions shown in Fig. 2, there also was no catalyst particle located at the center of this Y-junction. However, it is a great difference that there is a catalyst particle located at the tip of each branch, which is driving the growth of the Y-junction to form Y-shaped CNFs. This phenomenon is not reported in previous works [8–16]. For identifying the catalyst particle, we performed selected area electron diffraction (SAED) analysis for the samples. The SAED pattern (see Fig. S1) from a catalyst particle

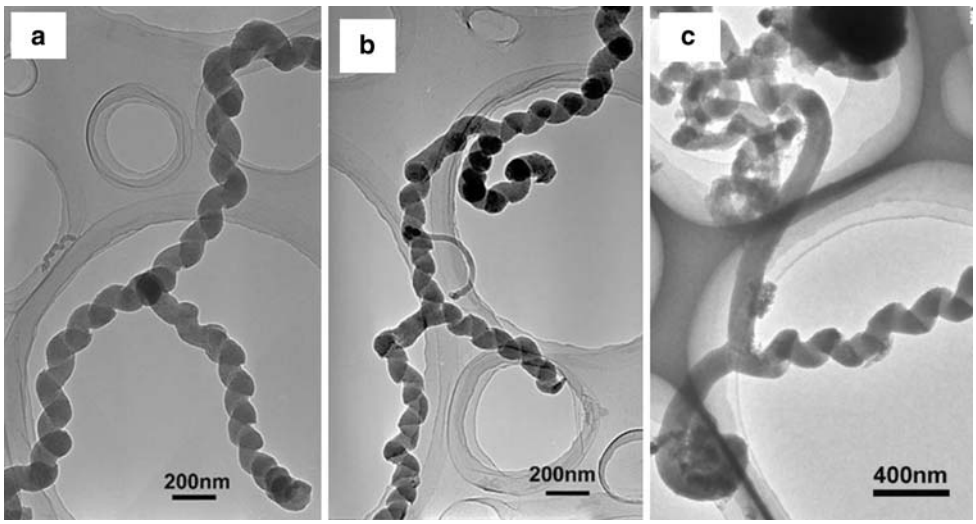

Fig. 2 TEM images of Y-shaped CNFs by employing nickel nitrate as catalyst precursor

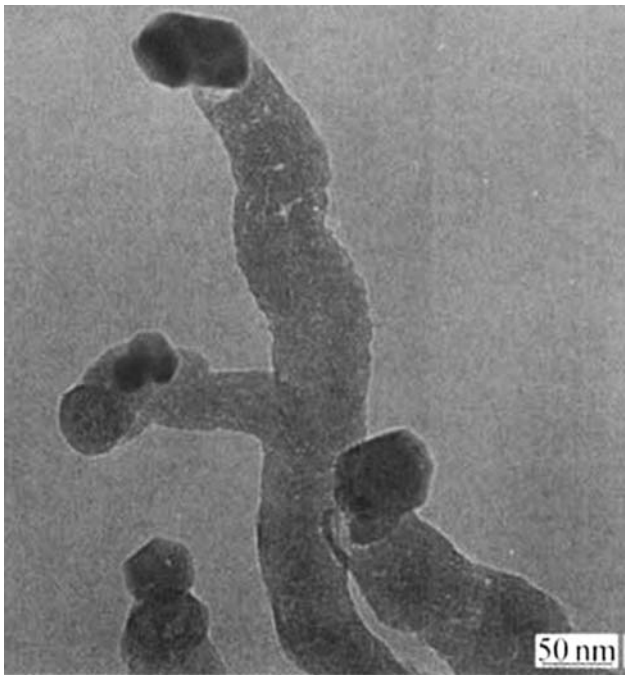

Fig. 3 TEM images of Y-shaped CNFs by employing iron nitrate as catalyst precursor

attached at the tip of a CNFs indicates that the catalyst is γ-Fe and not carbon nano/microspheres.

The growth mechanism of CNFs and CNTs is similar, where the carbon source is catalytically decomposed to carbon atoms; these carbon atoms are dissolved into catalysts and diffused through catalysts, and then precipitated to form CNFs/CNTs after saturation. For Y-shaped CNFs, their growth mechanism is also similar to that of Y-shaped CNTs which have been proposed by some authors. Su et al. [6] proposed that the formation of Y-junction CNTs was the result of changes in growth direction. They proposed that, first, carbon atoms dissolved into metal catalysts were precipitated to form initial CNTs, then because some of the synthesis conditions change, the initial CNT ceased extending, and a new CNT of a different orientation started to grow. As a result, the two CNTs formed a knee-like kink and the catalyst particle located at the kink. If the direction of precipitation of carbon atoms changed for a second time, a third tube from a two-branch junction with the catalyst particle moved away from the junction, resulting in the formation of Y-junction CNTs. These Y-junction CNTs do not include a metal catalyst particle at the center of the Y-junction. However, it was interesting that the Y-junction with a triangle-shaped catalyst particle at the center of the junction was observed by Li et al. [15] early. They proposed that the growth of the Y-junctions was derived by the pear-shaped particles and the triangle particle seated at the center of the Y-junction resulted from the split of the pear-shaped catalyst particles probably due to the thermal fluctuations during growth and left behind during the growth of the tubes.

In our experiments, the Y-shaped CNFs obtained from ethanol flames also have no catalyst particles located at the center of the Y-junction. So the growth mode [16] proposed by Su et al. can be employed to explain the formation of some Y-shaped CNFs (shown in Fig. 1). First, carbon atoms produced from the decomposition of ethanol molecules were adsorbed on a catalyst particle. They diffused along the surface and/or in the interior of the catalyst particle. After saturation, carbon atoms emanated from catalyst particle to form CNFs. Second, carbon atoms accumulated at a different location on the surface of the catalyst particle due to some fluctuations. As a result, the original nanofiber ceased growth and a new nanofiber of different orientation started to grow. By now, the catalyst particle was locating at the junction. Lastly, the catalyst particle left the junction due to some perturbations and catalyzed the growth of the third branch by tip-growth

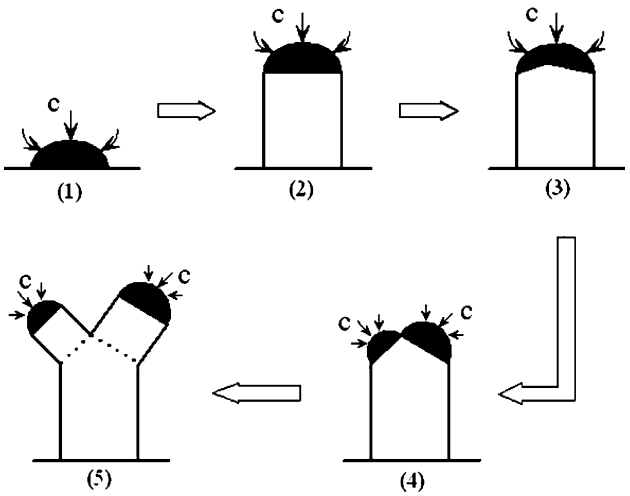

Fig. 4 Growth model of Y-shaped CNFs

mechanism [19] to form Y-shape CNFs without a catalyst particle located at the center of Y-junctions.

Another different situation is observed in our experiment. There is a catalyst particle located at the tip of the two branches of Y-shaped CNFs (see Fig. 3). It is obvious that the growth model proposed by Su et al. and Li et al. cannot be employed to explain it. For CVD method to grow Y-junction without assistance of template, it is believed that the formation of Y-junctions is related to fluctuation of growth conditions [6, 15], such as reaction temperature, concentration distribution of carbon atoms in the catalyst particles, and so on, although the formation mechanism of Y-junction is not fully understood presently.

Based on this unique observation, the growth of the present Y-junction CNF is to be the result of split of a catalyst particle (Fig. 4). First, a CNF grew by means of tip-growth mechanism [19] at the initial growth stage; that is, the catalyst particle moved with the growth of CNFs (see Fig. 4(1) and (2)), then the carbon atoms rapidly accumulated at two regions on the surface of the catalyst particle due to fluctuation of growth conditions, such as carbon concentration or growth temperature. This rapid carbon atom accumulation leads to the splitting of catalyst particle into two sections (see Fig. 4(3) and (4)). These two catalyst sections continued to catalyze the growth of CNFs respectively by means of tip-growth mechanism [19] (see Fig. 4(5)). At last, with the growth of branch CNFs, the Y-shaped CNF formed.

There are also some questions needed to be addressed, such as why the Y-junction presented here has helical branch and how to improve the content of Y-shaped CNFs in deposits. These questions are under investigation by our group.

Conclusion

In summary, the Y-shaped CNFs were obtained from ethanol flames. The formation of Y-shaped CNFs was ascribed to the fluctuation of growth conditions. Sometimes these fluctuations lead to the growth of CNFs of different orientation at different location on the surface of the catalyst particles and the formation of the Y-shaped CNFs. Sometimes these fluctuations lead to the split of a catalyst particle into two catalyst sections during the growth of CNFs. Then the two catalysts continue to catalyze the growth of CNFs respectively and the Y-shaped CNFs is formed at last.

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