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Growth and Formation Mechanism of Branched Carbon Nanotubes by Pyrolysis of Iron(II) Phthalocyanine

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Abstract: In this letter, a route for synthesizing vertically aligned multi-walled carbon nanotubes (MWCNTs) with branched nanotubes in large area was reported. The branched MWCNTs up to about 30% can be generated by the pyrolysis of iron(II) phthalocyanine in presence of thiol under Ar/H_2 at 800∼900℃. The growth mechanism of the branched nanotubes was proposed and the possible reason that thiol enhanced branched nanotubes growth is discussed. The as-prepared samples provide a suitable candidate to investigate the special electrical or thermal properties of CNTs with branched structures further.

Keywords: Carbon nanotube; Chemical vapour deposition; Branched; Growth mechanism

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Introduction

Since the discovery of carbon nanotubes (CNTs) by Iijima in 1991, various CNTs with straight, curved, bamboo-like, planar-spiral, or helical shapes have been identified experimentally either by a carbon-arc-discharge method or by a catalytic pyrolysis of hydrocarbon [1,2]. In addition, other nanoscaled carbonaceous materials including carbon polyhedral [2], graphite onions [3], carbon nanochain [4], carbon "sea urchins" [6], carbon bead with protruding cones [6], fullerene "crop circle" [7], cubic carbon nano-cage [8] and nanohorn [9] have also been reported. Particularly after earlier experimental observation of branched CNT or "Y" junction CNTs [10], controllable fabrication of branched single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs) or "Y" junction CNTs were fabricated via template-based chemical vapour deposition (CVD) method [11] as well as pyrolysis of organometallic precursors [12-17]. Theoretical calculations and experimental measurements show that the "Y" junction has interesting electrical properties and potential applications in nanoscaled transistor and amplifiers [18, 19]. The evidence for a dramatic electrical switching behaviour in "Y" junction CNTs has been observed and it is possible as logical gate or other nanoelectronics proposed applications [20]. However "Y" junction CNTs prepared by common templated approaches consist of larger diameter stems with two smaller branches with an acute angle between them resembling "tuning forks" and usually have low graphitisation. Various metal-catalysed CVD methods are usually less controllable for the structures of the Y-junction. It is of particular interest to control the fabrication of the architectures of branched CNTs for the investigation of their properties, especially electrical and thermo-conducting properties [17, 21-23].

We have developed a feasible method to generate free-standing aligned CNT arrays in large scale by pyrolysis of iron(II) phthalocyanine (designated as FePc) which is used as either catalyst and carbon source during 800∼1100℃ under H_2/Ar atmosphere [24]. It was

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found that a certain percentage branched CNTs can be found in the aligned nanotubes sample when the pyrolysis temperature is over 1000℃, which prompted us to enhance the percentage of the branched CNTs. Here we reported an approach to generate the branched CNTs more efficiently by introducing thiol into the pyrolysis process of FePc at 800∼900℃. Various structures of the branched CNTs were observed and the possible growth mechanism of the branched nanotubes is discussed.

Experimental

Large area aligned CNT arrays on substrate were generated by pyrolysis of iron (II) phthalocyanine (FePc), which is used as catalyst and carbon source, at 800∼1100℃ under H_2/Ar atmosphere. The detailed experiment processes was reported in our previous paper [19]. Similar process was applied to fabricate branched aligned CNT arrays in which 2∼5 wt% thiol (octadecanethiol) was added in FePc as a source. Samples were characterized by scanning electron microscopic (SEM, XL-30 FEG SEM, Philips, at 5 kV), EDX attached onto SEM and transition electron microscopy (TEM, JEOL 2010).

Results and discussion

Figure 1(a) and 1(b) shows typical SEM images of aligned CNTs. It can be seen that catalytic metal particles exist both on bottom and top indicated by white arrows in Fig. 1(b), which is different from other CNTs prepared using metal catalysts. The inset in Fig. 1(a) shows the corresponding TEM image (bottom side). It was noted when pyrolysis temperature is over 1000℃ (1000∼1150℃), small amount of CNTs (about 5%) were branched and have bamboo-like structure. The bottom parts of the branched CNTs are normally irregular and the diameter is much large than that produced at 800∼900℃. Figure 1c and 1d are the typical SEM and TEM images of the branched MWCNTs arrays (as indicated by white arrows) produced by the pyrolysis of FePc at over 1000℃. This result encouraged us to enhance the yield of the branched CNTs.

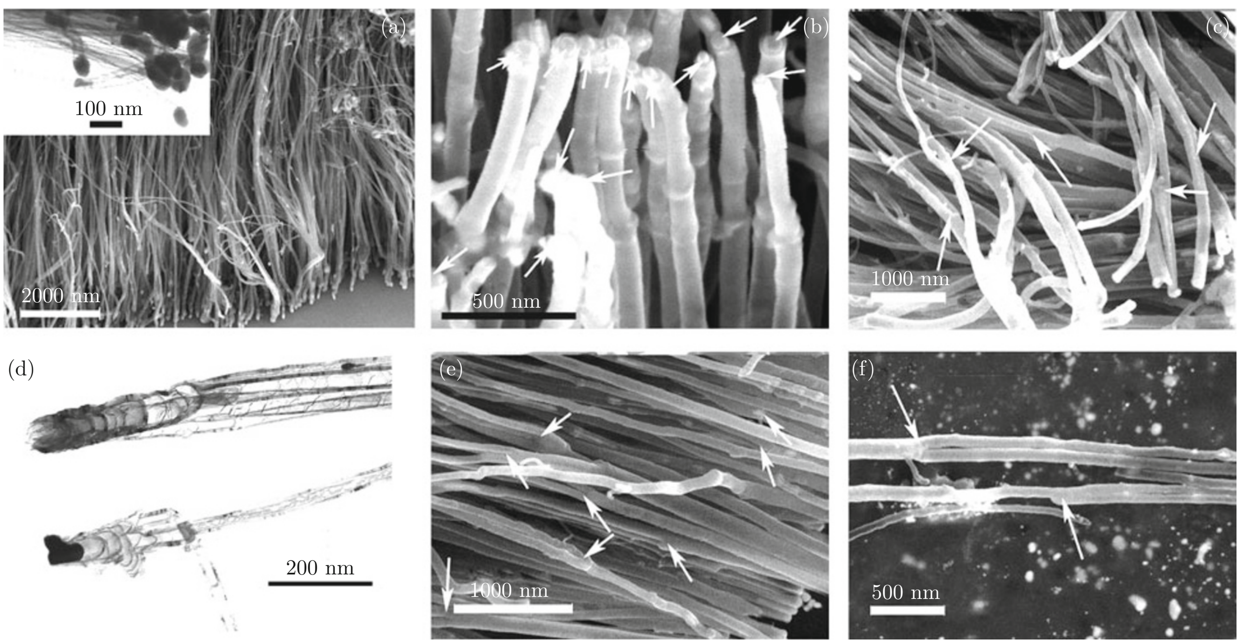


Fig. 1 Typical SEM and TEM images of the aligned branched carbon nanotubes produced by pyrolysis of FePc with presence of thiol: (a,b) at 850℃; (c,d) at 1100℃; (e,f) at 850℃. The branched CNTs were indicated by arrows.

As we know that thiol is one of the molecules which can be usually used to adjust the growth activity and the structure of CNTs [25, 26]. In this experiment, 2∼5% (wt%) thiol (e.g. octadecanethiol) was introduced into the reactor where thiol and FePc were simply mixed and the pyrolysis temperature was 800∼900℃. It was very interesting that the yield of the branched nanotubes increased dramatically up to about 30%. The diameter of the nanotubes became smaller and more uniform than that produced over 1000℃. Figure 1e and 1f represent the typical SEM images of the branched (as indicated by arrows) aligned CNTs arrays and individual CNTs produced by pyrolysis of FePc in the presence of thiol. More detailed TEM observations showed that various branched nanotubes with different structural architectures were also produced in the samples as shown in Fig. 2(a)-2(k).

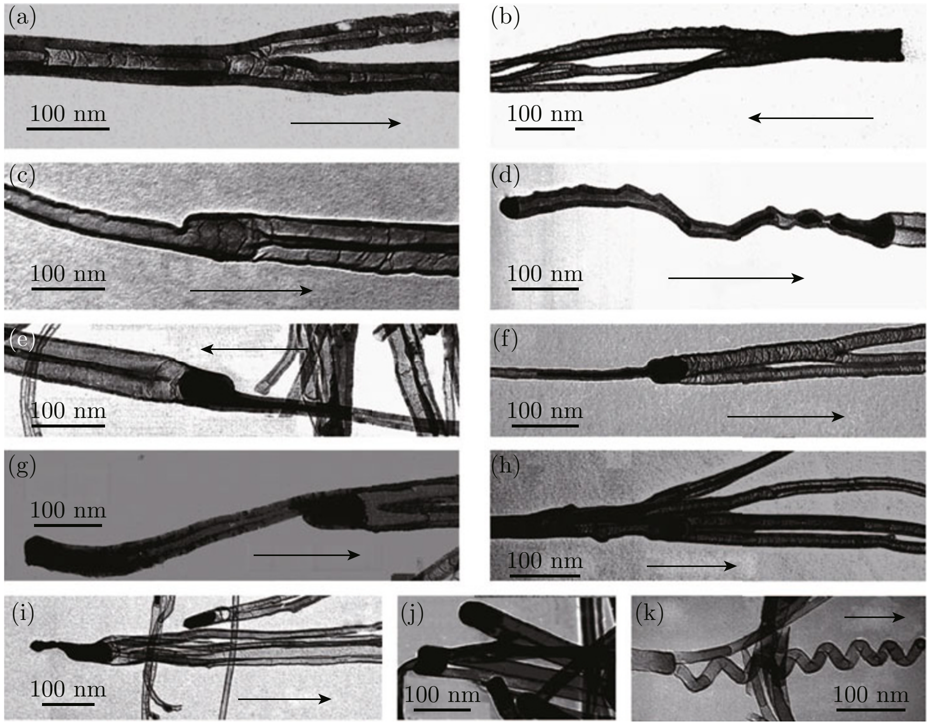
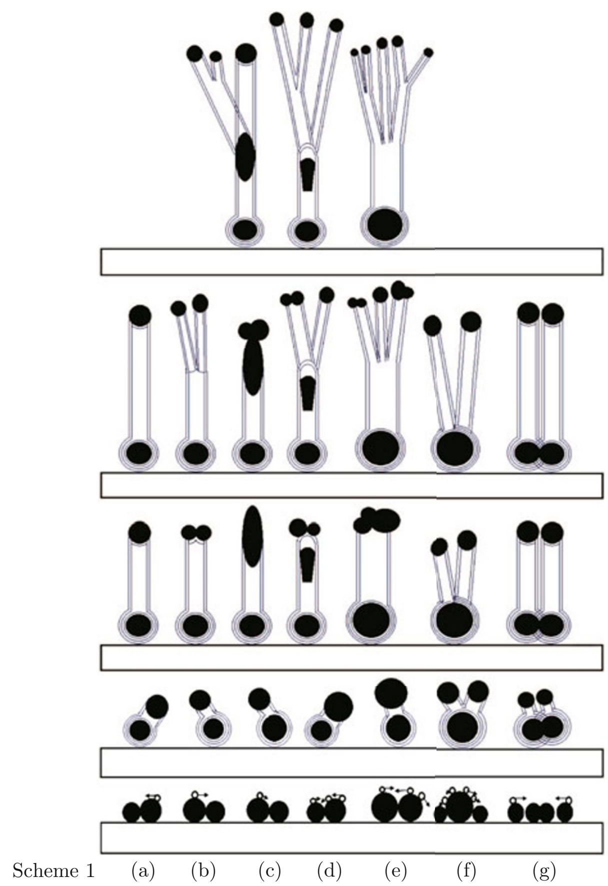


Fig. 2 TEM images of various branched CNTs produced by pyrolysis of FePc with existence of thiol at 850℃. Arrows represent the growth direction of CNTs.

As reported in our early paper [27], growth of aligned CNTs by pyrolysis of FePc involves two metal nanoparticles. As shown in Scheme 1(a) [19], small iron particles at the bottom act catalysts for nucleation of nanotubes, whereas, large iron particles at the top is responsible for growth. However, in most cases the metal particles at the top will drop down upon sonication in acetone for TEM specimen preparation. Therefore in TEM observation images it is usually shown open tip.

Based on the detailed SEM and TEM observation (see Fig. 2), the possible mechanism of formation of various branched CNTs are described in Scheme 1(b)-(g). Like straight CNTs (Scheme 1(a)), two metal particles are hypothetically involved in branched CNTs growth (Scheme 1(b)). The small bottom particles are responsible for nucleation of CNTs and the large particles are for the growth of the nanotubes. As shown in Scheme 1(a), the nanotubes have bamboo-like structures and the inner tube is subdivided by a few graphitic layers. It is believed that the particles on tip of the nanotubes are actually in liquid-like states at high temperature, and carbon sources can diffuse between metal particles. So the particles on tip of nanotubes will easily split into two or more small particles and therefore result in growth of branched nanotubes. Since the split particles are smaller than original ones, the diameter of branched nanotubes is correspondingly smaller than that of original ones. The schematic diagram is shown in Scheme 1(b). This phenomenon was experimentally confirmed by SEM (Fig. 1(f)) and TEM (Fig. 2(a) and 2(b))



Scheme 1 Schematic illustration of growth mechanism of the branched carbon nanotubes.

observations.

In another case, the diameter of branched nanotubes is similar or even larger than that of original ones (see Fig. 2(c)). This phenomenon would be understood as follows: during CNTs growth processes, FePc is decomposed continuously and formed Fe atoms are deposited on Fe particles at the top of CNTs. The Fe particles grow larger and result in large-diameter CNTs. It was also observed some Fe particles located inside of nanotubes and "Y" junction of branched nanotubes (Fig. 2(d) and 2(e)). These inside particles may act as nucleation centres, which is similar to those of normal CNTs as described in Scheme 1(c). These particles are generated from the FePc decomposition as shown in Fig. 2(f) and described in Scheme 1(d). If the metal particle is large enough, the branched nanotubes will be branched further (Fig. 2(g)). Most of branched situation is either from middle (Fig. 2(h)) or from bottom (Fig. 2(i)) of nanotubes, which is described in Scheme 1(e) and 1(f). This will lead to tree-like structures (Fig. 2(h) and 2(i)). It is also very interesting to observe two nanotubes joint together at bottom of nanotubes due to high density of metal particles on the substrate (Fig. 2(j), Scheme 1(g) and 1(h)). A nanotube with helical structures was also observed occasionally (Fig. 2(k)).

The reason why thiol can increase the content of branched nanotubes is that sulphur in thiol may reduce the melting point of iron (Fe: 1535℃, FeS: 1193℃) during the pyrolysis process. This will result in the enlargement of iron particles which is responsible for nanotube growth. It is obvious that the metal particle size in bottom as well as the diameter of produced nanotubes is larger with the existence of thiol than those without thiol. As discussed above, since larger particles is responsible for nanotube growth there is more chance to split into smaller ones and therefore benefit branched nanotubes growth.

Conclusion

In summary, we have presented a way to generate aligned branched CNTs with high content up to 30% by pyrolyzing FePc with the existence of thiol at 800∼900℃. Various branched nanotubes with different structural features were observed and the possible growth mechanism was proposed. The synthesis of branched CNTs provides a candidate to investigate the special corresponding properties, especially electrical and thermo-conductive properties with this kind of nanostructures.

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