Synthesis of Y-junction Carbon Nanotubes from Graphite Composites by Arc-discharge

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Abstract

Y-junction carbon nanotubes were synthesized by arc discharge method from composite anode made of graphite powder, coal tar and alloy catalysts consisting of Fe, Ni, Co and S element. The synthesis of Y-junction carbon nanotubes was carried out in a mixture gas of 200 Torr Ar and 100 Torr H_2. The as-synthesized Y-junction carbon nanotubes were examined by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy dispersive X-ray analysis (EDX). The results show that the Y-junction carbon nanotubes with short branches are long multi-wall carbon nanotubes with walls more than 20 nm in thickness and high graphitic degree. It can be found that the length of most branches is less than 5 micrometers and the angle between the stem and branches is in the range of 60-150^o. The EDX analysis reveals that the catalysts located at the Y-junction are alloys consisting of Fe, Ni, Co and S element. A growth process is proposed to explain how the YCNTs are formed.

Introduction

Y-junction carbon nanotube (YCNT) with structure composed of three joining CNTs was studied widely because of its potential ability to bring novel mechanical, electrical, thermal and hydrogen storage properties to nanodevices. Many theoretical studies have been done in exploring the atomic structure and possible electrical properties of YCNT. It has been suggested that Y-junction can be created with an equal number of five- and seven-membered rings and this junction could be the building block of nanoscale electronic device made entirely of carbon. Recently, many methods about synthesis of YCNTs have been reported. YCNTs with the average diameter about 200nm have been synthesized within porous anodic aluminum oxide template. N.Gothard et al. had reported a simple process for growing controlled branching YCNTs in bulk. Identical carbon nanotube Y junctions have been successfully synthesized by pyrolysis of methane over cobalt supported on magnesium oxide. Through electron beam welding to form Y-shaped molecular junction crossing, single-walled carbon nanotubes can be joined. Single walled Y-junction carbon nanotubes can also be catalytically synthesized by thermal CVD using Mo-doped Fe particles as catalysts. However, few papers reported synthesis of YCNTs by arc-discharge method. In this study, arc-discharge method was successfully applied to synthesize large scale YCNTs.

Experimental

In this experiment, an alloy was used as catalyst and it was prepared as follows: a mixture of 16.7 at.%Fe, 16.7 at.%Ni, 16.7 at.%Co, and 50 at.%S was calcined at temperature of 873 K for 1 hour, then the as-prepared sinter was ground into catalyst powder in mortar. Coal tar was employed as binder mixed with catalyst powder and graphite powder in a ratio of 5.3 and 52.6 wt.% to get a paste. The paste was pressed into a stainless steel tube to form green graphite composite rods with a diameter of *ca.* 10 mm. For making the electrode rods the green composite rods need be carbonized at temperature of 1173 K for 2 hours under flowing N_2. A graphite column 30 mm in diameter and 15 mm in highness was used as cathode, and the arc-discharge was carried out under the current of 80-100 A in atmosphere of 200 Torr Ar and 100 Torr H_2. In arcing process the gap of two electrodes was kept within 2-3 mm. For each run, five centimeter anode was consumed and *ca.* 150 mg sponginess production can be collected around the cathode.

The as-grown product was characterized by scanning electron microscope (SEM, JEOL 5600LV), transmission electron microscope, high resolution transmission electron microscope and energy

dispersive X-ray (TEM, HRTEM and EDX, Philips Tecnai G^2 20).

Results and discussion

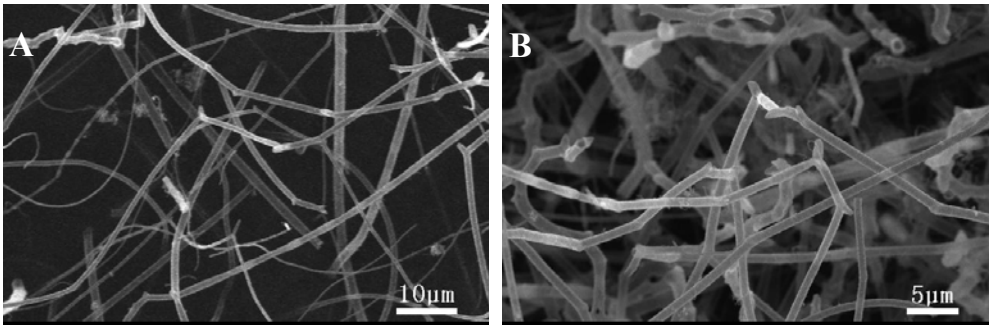

Figure 1. SEM images of YCNTs

From Figure.1 (A) and (B) it can be found that most CNTs were YCNTs with different diameters, and almost each YCNT has a main long stem and short branches with length less than 5 micrometers.

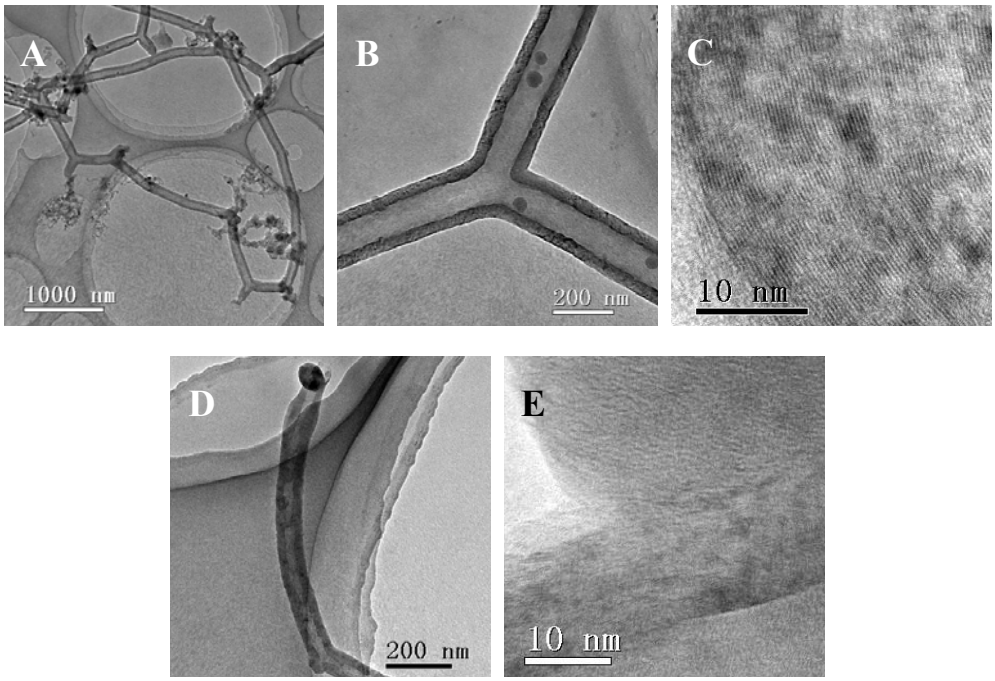

Figure 2. (A) TEM image of YCNT; (B) TEM image of Y-junction; (C) HRTEM image of Y-junction wall shown in Figure 2. (A); (D) TEM image of one Y-junction with catalyst particle on the top; (E) HRTEM image of a nano amorphous carbon sphere joined with the wall of CNT.

The YCNT has many branches, as shown in Figure 2. (A), and the inner diameter of stem was in the range of 100-200 nm. It can also be found in Figure 2. (A) that the angle between branch and long stem was bigger than 60° and no more than 150°. Figure 2. (B) shows Y-junction with thickness wall and one of the three angles between arms is close to 90° while the other two angles are both about 135°. The HRTEM image shown in Figure 2. (C) indicates that the well graphene structure of wall has gradual bends around the Y-junction which can arise due to the five- and seven-membered carbon rings in the graphene sheets. Figure 2. (D) shows a particle on the tip of one as-synthesized YCNT which suggests stem grew by tip-growth model. In the product there are some nano-sized spheres with the diameters *ca.* 50 nm. Figure 2. (E) shows that the nano-sized sphere is an amorphous one. Because it melts with wall of YCNTs, one can consider that it should be an amorphous carbon sphere which looks

similar to that reported by Walt et al.. It can be deduce that some carbon clusters formed into a little drop of liquid carbon at high temperature. However, the drop did not transform into graphite particle because of the abrupt decrease of temperature.

Some Y-junction was filled with catalyst particle, as shown in Figure 3. (A), and the HRTEM shows that it was a crystal one with big distance between some crystal faces. Figure 3. (B) shows the EDX spectra of the Y-junction shown in Figure 3. (A). Besides the Cu of grid and C of nanotube the signals of elements include Fe, Co, Ni and S were detected, which indicates that the component of catalyst particle did not change before and after arc evaporating process.

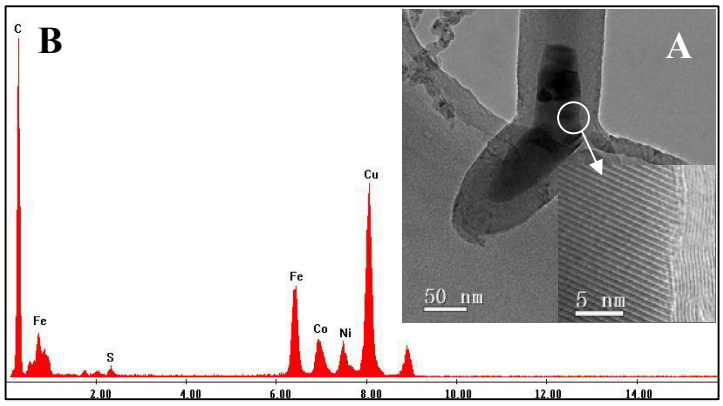

Figure 3. (A) TEM image of one Y-junction filled with catalyst particle and HRTEM image of the particle; (B) EDX spectrum of the Y-junction shown in Figure 3. (A).

The hydrogen in the mixture atmosphere may be one of factors for the product growing on the round of cathode. As a "quencher" for the carbon vapor in arc-discharge method, the hydrogen has two properties, which have been noted that hydrogen is the lightest element with the highest thermal conductivity (0.152 W/mK at 300 K) and it can reacts with carbon to form strong covalent C-H bonds. Thus, temperature condition for CNT growth should have been achieved at the round of cathode in the experiment. Additionally, the hydrogen atom can selectively etch amorphous carbon and prevent the CNT end from closing.

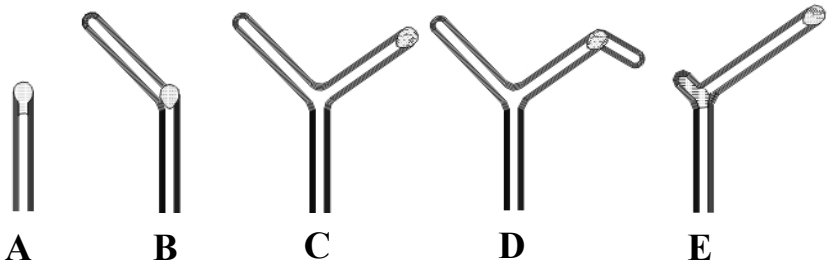

Figure 4. Schematic mechanism of YCNT synthesized by arc-discharge: (A) A CNT with catalyst particle on the top formed at the round of cathode; (B) First branch grew on the catalyst particle by end-growth model; (C) Second branch formed by top-growth model; (D) Another Y-junction formed; (E) Short branch filled with catalyst.

Up to now, most mechanisms of YCNT have been discussed, as a result of which the function of catalyst particles in the YCNT growth process has been affirmed. In this study, possible mechanism about the growth of YCNTs has been researched. In Figure 4. sketch of the catalyst inducement growth mechanism of YCNT is clearly shown. Firstly, a catalyst particle on the top of CNT induces the growth of YCNT's stem [Figure 4. (A)]. By reason of the fluctuation of growth conditions, especially that of the rate of diffusion and the saturation of carbon in the catalyst particle, a branch grows gradually from the top catalyst particle by end-growth model [Figure 4. (B)]. When the second branch grows from the same catalyst particle, the growth of the first branch will stop due to inexistence of liquid-gas interface. Therefore, the length of the first branch should be decided by burgeoning time of second branch which

leads the first branch with very short length. Most of plausible growth mechanisms of CNT suggest that the growth of second branch keeps tip-growth model, because no more carbon in the catalyst is provided for the growth of so long a CNT if it grows by end-growth model [Figure 4. (C)]. The catalyst particle on the top of the second branch will induce the growth of another Y-junction [Figure 4. (D)], so currently almost every YCNT has several junctions. Because of capillary force of CNT, part of liquid catalyst may fill the short branch sometimes [Figure 4. (E)]. In the experiment, most YCNTs grew according to this mechanism, but Figure 5. (A) and (B) show that some Y-junctions in the product were not induced by catalyst particles. This kind of branch should be induced by pentagonal and heptagonal defects in the lattice.

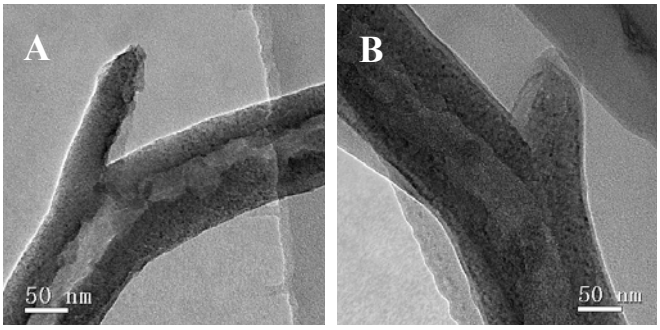

Figure 5. TEM images of Y-junction induced by structure disfigurements.

Conclusions

Y-junction carbon nanotubes with long stem and several short branches have been synthesized successfully in large scale by arc-discharge method in an atmosphere of H_2 and Ar (1:2/v:v) mixture at 300 Torr. Most YCNTs in the product grow by catalyst inducement growth mechanism, and structure disfigurement is another influence factor for YCNT growth.

Acknowledgements

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