Synthesis of coiled carbon nanofibers and Y-shaped carbon fibers

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Abstract. In this paper, the synthesis of carbon fibers (CFs) with different morphology, that is, coiled carbon nanofibers with symmetrical structure and Y-shaped carbon fibers was presented by using copper tartrate as catalyst precursor at low temperature, 279 ºC. Hydrogen and commercial acetylene or commercial acetylene only was introduced into the reaction tube, respectively, during the synthesis reaction, the introduction of hydrogen will be the key factor to the formation of Y-shaped carbon fibers. According to the analysis, the growth model for carbon fibers has been established. X-ray diffraction, field emission scanning electron microscopy, transmission electron microscopy were used to carry out the product characterization.

1. Introduction
Similar to carbon nanotubes [1-4], carbon fibers with different morphologies have been extensively investigated by researchers [5-12], which have a wide potential application in thermal, mechanical, electric areas, due to their superior properties. At the same time, the growth mechanism of carbon fibers and carbon tubes has particularly attracted the attention of many scientists, and lots of growth models for carbon fibers have been established. These one-dimension carbon nanostructures are usually prepared by chemical vapor deposition (CVD) method, in which hydrocarbon (C\textsubscript{2}H\textsubscript{2}, C\textsubscript{2}H\textsubscript{4}, CH\textsubscript{4}) and small metal particles (Fe, Co, Ni, Cu or their alloys) were used as carbon sources and catalyst, respectively.

In this paper, coiled carbon nanofibers and Y-shaped carbon fibers with high purity were successfully prepared by CVD using copper tartrate as catalyst precursor at 279 ºC and the effect of hydrogen on the morphology of carbon fibers were also examined.

2. Experimental
In this paper, copper tartrate was used as catalyst precursor for the preparation of carbon fibers. The preparation method of copper tartrate is as follows: potassium sodium tartrate aqueous solution (0.0586 mol/l) was slowly added to 0.0586 mol/l copper dichloride aqueous solution under vigorous stirring, copper tartrate (light blue precipitate) was formed quickly. At last, copper tartrate was filtered and washed with distilled water, anhydrous ethanol, respectively, and then dried for 1 h at 100 ºC.

In the present work, a horizontal quartz tube (9 cm in diameter and 90 cm in length) was used as the reaction tube. The preparation method of carbon fibers is as follows:
2.1. Coiled carbon nanofibers
A ceramic plate containing copper tartrate was placed in the reaction tube. After the tube was heated to 279 ºC in a vacuum (5 Pa) and the catalyst precursor was pushed into reaction area (holding at 279 ºC for 30 min in order that all the precursor particles decomposed to form metallic copper particles), acetylene was introduced into the reactor for a selected reaction time. The pressure within the reaction tube was atmospheric. After the reaction, the quartz tube was cooled in a vacuum (5 Pa) to room temperature.

2.2. Y-shaped carbon fibers
A ceramic plate containing copper catalyst was placed in the reaction area of the reaction tube in a hydrogen atmosphere. After the tube was heated to 279 ºC, hydrogen was immediately replaced by acetylene and the reaction started subsequently. After the reaction, the quartz tube was cooled in a vacuum (5 Pa) to room temperature.

FE-SEM micrographs were obtained with a cold field emission scanning electron microscope (FE-SEM, JEOL, JSM-6700F); transmission electron microscopy (TEM) was carried out on a JEOL JEM-2000EX; X-ray powder diffraction (XRD) patterns were recorded on a Philips X’Pert MPD diffractometer with Cu Kα radiation (λ = 1.5418 Å).

3. Results and discussion
The FE-SEM image (Fig.1a) shows Y-shaped carbon fibers with high purity, in which the bright parts (indicated by arrows) in the junction of Y-shaped carbon fibers represent copper catalyst particles. The TEM image of Y-shaped carbon fibers was shown in Fig.1b, in which the inset is selected area electron diffraction (SAED) pattern of the copper particle in the junction of carbon fibers, which indicates that

Figure 1. FE-SEM and TEM images of coiled carbon nanofibers and Y-shaped carbon fibers
these copper particles are polycrystalline structure. On the other hand, the FE-SEM image of coiled carbon nanofibers was shown in Fig.1c and copper catalyst particles included in carbon nanofiber are clearly observed in Fig.1d (indicated by arrow). Through TEM analysis, we know that these two pieces of carbon nanofibers, grown from a single copper nanocrystal, have identical fiber diameter, coil diameter, coil number, coil pitch, and different helical sense.

It is well known that the diameter of carbon fibers is decided by the size of copper catalyst particles. The size of copper catalyst particle is in accord with the diameter of carbon fibers, whether Y-shaped carbon fibers (0.8~1 μm) or coiled carbon nanofibers (~100 nm).

In this study, we proposed that the growth model of carbon fibers is decided by the existing structure of copper catalyst particles, that is, monocrystalline or multicrystalline. In the synthesis reaction of Y-shaped carbon fibers, many small copper particles, decomposed from catalyst precursor with reaction temperature increasing, slowly aggregated together to form larger copper particles through Van der Waals force in a hydrogen atmosphere. Then each of these larger copper particles as a whole possesses three carbon fibers growth faces after a period of surface reconstruction [13-15], and can synthesize catalytically three pieces of carbon fibers simultaneously, and then Y-shaped carbon fibers have been obtained. In a word, it is the reconstruction of crystal face of bigger copper catalyst particles due to the effect of hydrogen that lead to the formation of Y-shaped carbon fibers.

![Figure 2. The growth model for Y-shaped carbon fibers](image)

The growth model for Y-shaped carbon fibers was shown in Fig.2. Fig.2a represents a bigger copper catalyst particle in Y-shaped carbon fibers, which consist of several monocrystalline copper particles. These grey faces in Fig.2a represent carbon fibers growth face of catalyst particle. The model of Y-shaped carbon fibers was displayed in Fig.2b, in which there are three pieces of carbon fibers grown from the same copper catalyst particle, and then Y-shaped carbon fibers have been obtained.

In the synthesis reaction of coiled carbon fibers, the catalyst precursor was located in the reaction area when the reaction temperature arrived. Therefore, lots of small copper catalyst particles were formed quickly in an acetylene atmosphere and acted as catalyst to synthesis coiled carbon nanofibers. Due to the anisotropy of copper monocrystalline for carbon fibers growth, there is carbon fiber growth rate difference between different crystal faces, and the considerable dispersion of growth rate over the surface of catalyst particle induced the formation of coiled carbon nanofibers [16]. The SAED pattern gives evidence of the presence of well-developed monocrystalline structure in small copper particle located in coiled carbon fibers.

Through XRD analysis (see Fig.3), we know that both of Y-shaped carbon fibers and coiled carbon nanofibers have the same components. The sharp peaks and the disperse peak correspond to the metal copper and amorphous carbon. In addition, copper oxide (78-0428) was also found due to their weak signals. No copper carbide solution peaks were detected in these two kinds of carbon fibers.
4. Conclusions

Coiled carbon nanofibers and Y-shaped carbon fibers with high purity have been successfully obtained, respectively. The formation of Y-shaped carbon fibers is related to the introduction of hydrogen before the start of the reaction. It is the participation of hydrogen that leads to the formation of the growth faces of catalyst particles for carbon fiber and Y-shaped carbon fibers subsequently. The copper catalyst particles included in Y-shaped carbon fibers exist as polycrystalline structure. The anisotropy of monocrystalline copper particles included in carbon nanofibers lead to the formation of coiled morphology, that is, the growth rates of nanofibers on different crystal faces are different.

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