

Dependence of carbon fiber morphology with deposition conditions

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Abstract

Carbon fibers with different morphologies including carbon nanotubes, short crossed carbon fibers, carbon nanofiber network structures, and nodular carbon fibers covered with carbon microbeads were synthesized using a floating catalyst method by changing the flow rate of xylene solution containing ferrocene, the concentration of ferrocene in xylene, and carrier gas. The general tendency is: Higher flow rate of xylene solution contributed to the formation of short crossed carbon fibers and deteriorated the graphitic crystalline of carbon fibers, which might play a critical role in their connection. Lower ferrocene concentration in xylene solution improved the graphitization of carbon nanofibers and changed the connection way of carbon nanofibers. Nodular carbon fibers covered with microbeads were obtained in N₂ ambience. Carbon nanotubes with well graphitic crystal were prepared with the concentration of ferrocene in xylene 1.5 g/100 ml, the flow rate of xylene solution 0.12 ml/min and hydrogen 150 ml/min.

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1. Introduction

Since the discovery of fullerenes and nanotubes [1,2], many different routes have been employed to prepare new forms of carbon. The chemical vapor deposition (CVD) of hydrocarbon is a traditional method to produce vapor-grown carbon fibers (VGCFs). However, this method is also powerful for the preparation of other forms of carbon materials with different conformations and microstructures via adjusting carbon sources, catalysts, carrier gases, and other reaction conditions [3–6]. Hou et al. [7] reported that they have observed carbon nanotubes with multiple hollow cores using a floating catalyst method. A single branched pattern of Y junction carbon nanotubes were obtained by different CVD routes [8–11]. Recently, several research groups [12–17] reported that the fabrication of tree-like carbon architectures using floating catalyst method technique. Shi et al. [18] synthesized branched carbon nanofibers using an improved floating catalytic method through the addition of TEOS into the reaction tube. These

studies make it feasible to obtain more complex carbon architectures through control of CVD conditions for specific requirements. These carbon materials have attracted much attention due to their special atomic configurations and important applications in engineering, such as hydrogen storage, field emission devices, reinforcement materials, et al. The variety of CVD products indicates that the microscopic processes occurring therein are rather complicated and various carbon architectures follow different formation mechanisms [19].

Here we report the preparation of carbon fibers with various morphologies including carbon nanotubes, short crossed carbon fibers, carbon nanofiber network structures, and nodular carbon fibers covered with microbeads using the traditional floating catalyst method by adjusting the reaction conditions.

2. Experimental details

The experiments were conducted in a horizontal tubular reactor. An evaporator was equipped to vaporize xylene solution containing ferrocene and thiophene at the inlet of the reactor. The ferrocene and thiophene concentrations in xylene were 0.5–3 g/100 ml and 3.4 ml/100 ml, respectively. The

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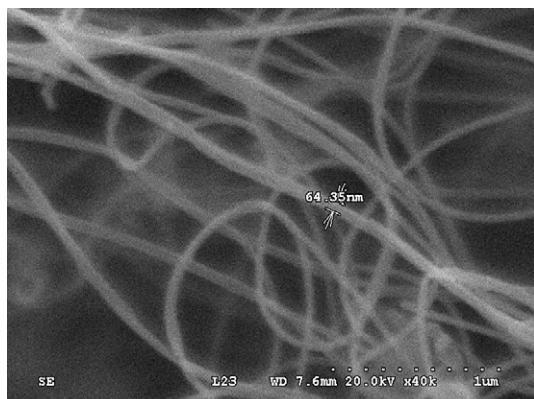


Fig. 1. SEM images of carbon nanotubes synthesized with the ferrocene concentration in xylene 1.5 g/100 ml, the xylene solution flow rate 0.12 ml/min, and hydrogen as carrier.

horizontal quartz tube furnace was heated to 700 °C in nitrogen. Nitrogen was then substituted by hydrogen at a flow rate of 150 ml/min. Xylene solution containing ferrocene and thiophene was introduced at the flow rate of 0.1–0.4 ml/min into the evaporator, and then flowed into the reactor by the carrier gas H₂ at 1100 °C. After 30 min, the products were cooled to room temperature in nitrogen and collected at the outlet of the reactor for observation using scanning electron microscope (SEM) and high-resolution transmission microscope (HRTEM). The concentration of ferrocene in xylene and the flow rate of xylene

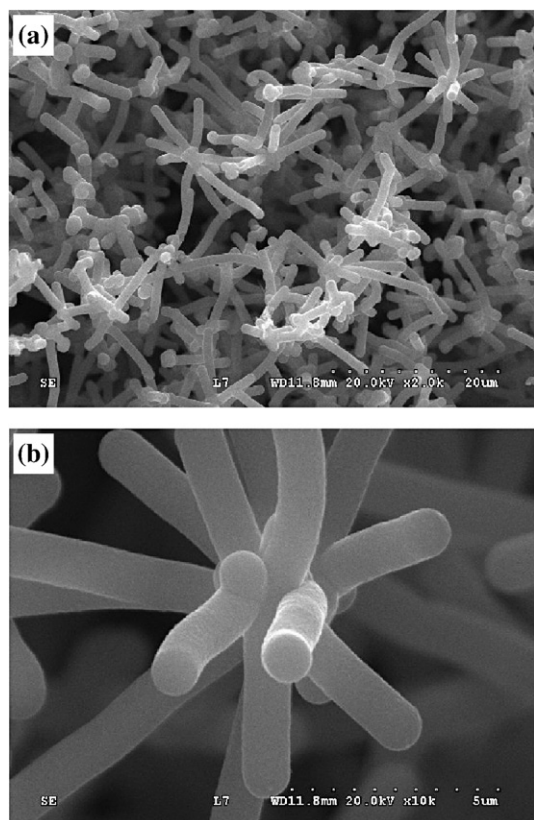


Fig. 2. SEM micrographs of crossed carbon fibers prepared with the concentration of ferrocene in xylene solution 1.5 g/100 ml and the xylene solution flow rate 0.36 ml/min.

solution were changed to study their effect on the morphologies and microstructures of carbon product.

3. Results and discussion

In the experiment, the catalyst ferrocene, along with hydrocarbon solution, was carried into the reactor by the carrier gas and decomposed into iron atoms. The iron atoms would collide with one another and congregate into appropriate particles to grow carbon nanotubes/fibers. During the initial growth, the grown carbon nanotubes/fibers tangled with one another to form a thin film blocking up the reaction tube. After that, large quantities of carbon fibers/nanotubes were stopped by the thin film and formed foam-like black blocks in the reaction tube. Fig. 1 shows the morphologies of carbon nanotubes prepared with the concentration of ferrocene in xylene 1.5 g/100 ml and the xylene solution flow rate 0.12 ml/min. From Fig. 1, it is clearly seen that the carbon nanotubes were very pure but curved with the diameters from 40 nm to 70 nm and length up to several tens of micrometers. And these carbon nanotubes tangled together.

However, the morphologies of carbon products have been greatly changed as the xylene solution flow rate was increased to 0.36 ml/min (Fig. 2), assuming that the other factors were fixed. From Fig. 2, it is seen that short carbon fibers were obtained with the diameters about 1 μm and the length in the

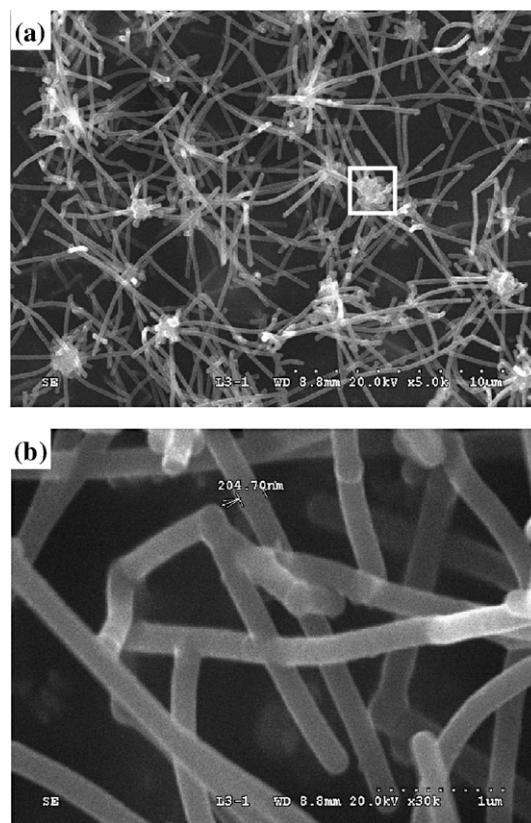


Fig. 3. SEM micrographs of carbon nano-fibers synthesized with ferrocene concentration in xylene solution 0.5 g/100 ml and the xylene solution flow rate 0.36 ml/min. (a) low magnification, (b) high magnification for the center part in (a).

range of 0–25 μm . These short carbon fibers were relatively straight and pure. The most prominent features of these short fibers are that they were crossed and simply connected with one another, just like flowers.

Fig. 3 shows the SEM images of carbon nano-fibers synthesized with ferrocene 0.5 g/100 ml xylene solution and the xylene solution flow rate still fixed at 0.36 ml/min. From Fig. 3a, the carbon nanofibers seem to have the similar morphologies of carbon fibers in Fig. 2 at a first glance except a decrease in the diameters to about 200 nm and a clear increase in the lengths. However, higher magnification indicates that the carbon nanofibers are connected through multiple junctions (Fig. 3b), instead of simple connection. These carbon nanofiber junctions formed complicated network structures.

The SEM results indicate that the flow rate of xylene solution and the concentration of ferrocene in xylene have a great influence on the morphologies of carbon fibers. Higher flow rate of xylene solution resulted in a clear increase in the diameter and a great decrease in the length of carbon fibers. And short carbon fibers were obtained. The most prominent feature is that the carbon fibers were connected with one another. However, the connection ways were changed as the ferrocene concentration decreased. Moreover, the diameters were decreased greatly and the length increased clearly.

In order to investigate the formation of different carbon fiber morphologies, TEM analysis has been conducted to observe their microstructures. Typical HRTEM and electron diffraction images of carbon fibers synthesized under different conditions are shown in Fig. 4. As can be seen, carbon nanotubes are well graphitized with an interwall distance (d_{002}) of ≈ 3.4 Å.

Graphitic layers are almost parallel to the axis of carbon nanotubes (Fig. 4a). However, the crystalline of the graphite sheets was deteriorated with the xylene solution flow rate increased from 0.12 ml/min to 0.36 ml/min (Fig. 4b). There is a large angle between graphitic sheets and the axis of carbon fibers. The crystalline of the graphite sheets was improved and the angles between graphite layers and carbon nanofiber axis were also decreased with ferrocene concentration in xylene decreased to 0.5 g/100 ml (Fig. 4c), but the graphitic crystal structures are still worse than carbon nanotubes (Fig. 4a). Fig. 4d shows the microstructures of carbon nanofiber junction in Fig. 3. It is clearly seen that the graphitic sheets of two carbon nanofibers were overlapped at the connection.

The TEM analysis shows that the flow rate of xylene solution and the ferrocene concentration also affect greatly the nanostructures of carbon products. The graphitic structures of carbon products were deteriorated as the flow rate of xylene solution was increased. With decreasing ferrocene concentration in xylene solution to 0.5 g/100 ml, the graphitic crystal structures of carbon nanofibers are improved greatly.

The concentration of carbon source and Fe catalyst particle size in the reaction tube control the diameter and length of carbon fibers/nanofibers, and also influence their graphitic structures. Ting et al. [20] argued that the stem diameter of carbon fiber is proportional to carbon source concentration. After a carbon fiber stem ceases to grow, thickening may take place by the deposition of pyrolytic carbon from carbon source on the surface of carbon fiber, depending on the hydrocarbon concentration [21,22]. Therefore, thickening will deteriorate the graphitization degree of carbon fibers. At the same time, the

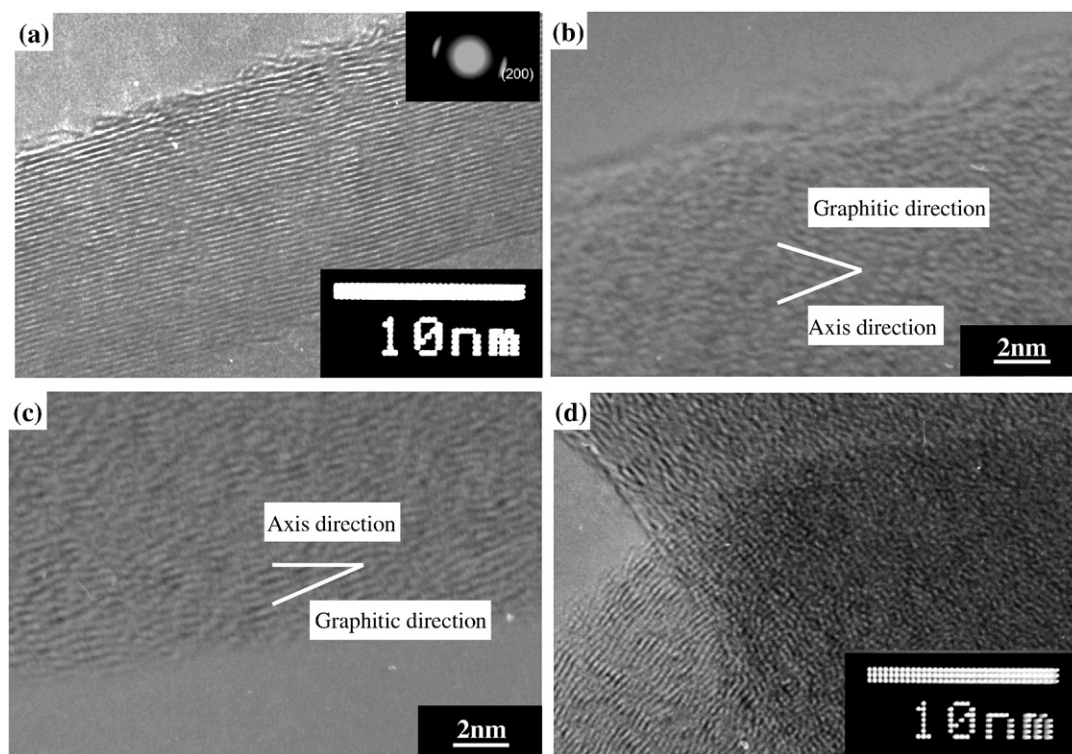


Fig. 4. HRTEM images of different carbon products. (a) Carbon nanotubes in Fig. 1; (b) Carbon fibers in Fig. 2; (c) Carbon nanofibers and (d) their junction in Fig. 3. The Inset shows the electron diffraction pattern of the corresponding carbon nanotubes.

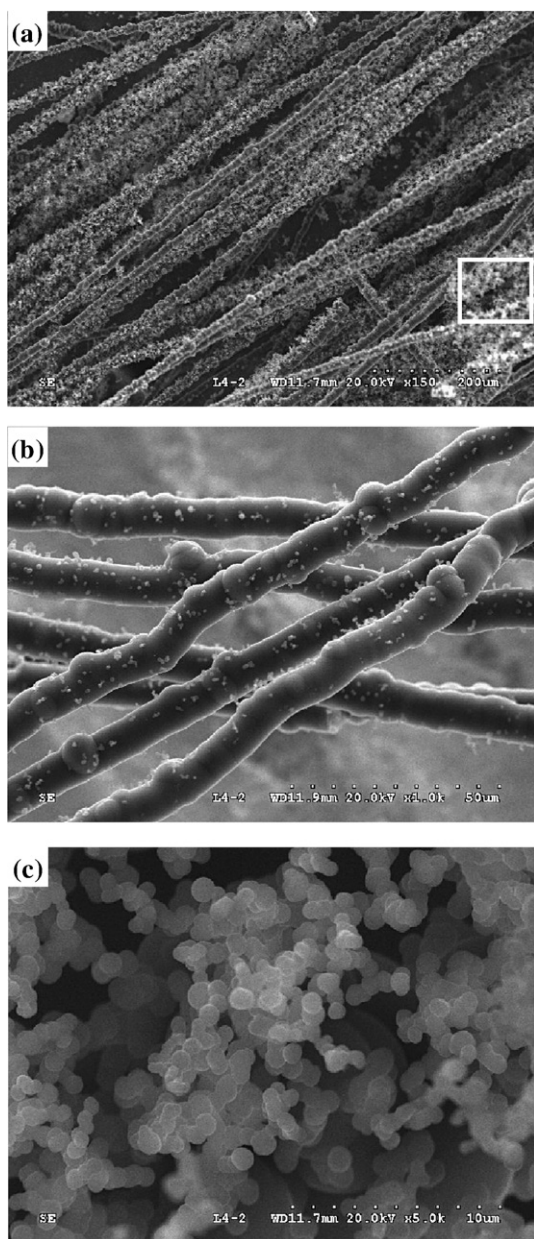


Fig. 5. SEM images of carbon products synthesized at the concentration of ferrocene in xylene 0.5 g/100 ml and nitrogen as carrier gas. (a) Macroscopic view; (b) Close view; (c) Carbon microbeads in the white frame in (a).

metal particle size is also one of the important criteria for the fiber diameter and growth rate. Catalyst particle size determines the diameter of carbon fibers. Baker et al. [23] has reported that the growth rate of carbon fiber has an inverse square root dependence on the radius of metal particle. In our experiment, xylene and ferrocene concentrations in the reaction tube were increased with increasing the flow rate of xylene solution to 0.36 ml/min, inevitably resulting in the higher carbon atom concentration from xylene and an increase in Fe particle size due to the higher collision chance of iron atoms decomposed from ferrocene. Higher carbon atom concentration and larger catalyst particle size contributed to the formation of shorter and thicker carbon fibers, and also deteriorated the graphitic crystalline. With decreasing ferrocene concentration in xylene solution to 0.5 g/100 ml,

smaller catalyst particle size determined the smaller diameters of carbon nanofibers and increased their lengths. Interestingly, the graphitic crystal structures were also improved. This might be related to the hexagonal radicals serving as building blocks of carbon fiber growth, which reduced the catalyst role [24]. However, their graphitic crystal structures were still worse than that of carbon nanotubes, because of thickening at higher xylene concentration.

The TEM results together with the SEM analysis indicate poor graphitic structures might play an important role in the connection of carbon fibers and the formation of nanofiber network structures. Poor graphitic structures induce the presence of a large number of dangling bonds in carbon product and on their surfaces. At high reaction temperature (1100 °C), the dangling bonds at the contact area between carbon fibers/nanofibers may form new carbon–carbon bonds, resulting in their connection and the formation of carbon nanofiber network structures, which may be driven by the force of the decreasing free energy. In contrast, the carbon nanotubes with perfect graphitic crystal structure didn't connect together even if they tangled together due to the lack of dangling bonds. Possibly, the iron catalyst and volatile compounds also play important roles in the connection of carbon fibers and the formation of carbon nanofiber network structures [25]. However, the difference in the connection ways for carbon fibers is not understood yet. Further investigation need to be done for elucidating their formation mechanism.

Additionally, we also changed the carrier gas hydrogen into nitrogen to investigate the influence of carrier gas on the morphologies of carbon products. The experimental results show that the situation was completely different when nitrogen was used as the carrier gas (Fig. 5). After reaction, we only collected a little amount of fiber-like carbon products on the inner walls of the reaction tube. From Fig. 5, it is obvious that the morphologies of carbon product are different from the VGCFs obtained under similar conditions. The carbon product consists of two kinds of carbon morphologies: nodule carbon fibers with diameters about 15 μm and carbon microbeads with diameters about 2 μm (Fig. 5c). The carbon fibers are aligned in certain direction and covered by carbon microbeads, and formed into aligned slurry carbon fibers (Fig. 5a). From Fig. 5b analysis, the surfaces of carbon fibers are not smooth, and spherulitic nodules can be observed clearly on the surfaces of the fibers (Fig. 5b). Most of the carbon microbeads are adhered on the surfaces of carbon fibers but not distributed uniformly. According to the nodular structures of carbon fibers, these carbon fibers should be formed through the aggregation of carbon micro-spheres and subsequent restructuring [15,16]. The aggregation process may be similar to the diffusion-limited aggregation (DLA), in which a large fractal object is constructed by adding small building blocks [26].

In our CVD process, it is difficult for Fe particles resulted from ferrocene to catalyze the growth of carbon nanofibers/nanotubes due to their deactivation in N_2 ambience. The catalytic pyrolysis of xylene on Fe particles generated a great deal of iron-encapsulated carbon microbeads, which float in the vapor phase. Due to the relatively high density of carbon microbeads in the vapor phase, they aggregate into larger carbon micro-spheres with diameter in

the range of 2–15 μm through mutual collision. These micro-sized spheres serve as building blocks for the fibers. However, most of them have been carried out of the reaction tube by vapor flux because of no films blocking up the tube. In the reaction tube, the remaining carbon spheres diffuse and deposit on the inner wall and then some of them become nuclei for the further evolution of carbon fibers. Once the nuclei have been formed, other microspheres continuously were added to the nuclei to form aligned nodular fibers under suitable flux field of N_2 . After a period of time, the nodular carbon fibers become relatively smooth due to the restructuring of carbon surface. At the same time, carbon microbeads continuously were generated and adhered on the surface of as-formed carbon fibers as the reaction proceeded. Therefore, the aligned slurry nodular carbon fibers were obtained. Possibly, the iron catalyst and volatile compounds play important roles in the formation and adhesion of building blocks-carbon spheres [25]. The above experiment results well demonstrate that carrier gases have a great influence on the morphologies of carbon products.

4. Conclusions

In our present work, we obtained carbon fibers with different morphologies by changing the reaction conditions. This work shows the evidence to construct complex carbon architectures by controlling CVD conditions. Although the crystallization degree of the crossed carbon fiber and carbon nanofiber network structures are poor, it is possible that their complete graphitization can be achieved by heat treatment at high temperature [27]. Therefore, these carbon fibers are promising in incorporation with resin and applied in the areas such as electrostatically painting for automobile parts, preventing the electronic devices from electrostatic discharge and shielding electromagnetic wave. At the same time, they also have a potential application as reinforcements in composite materials.

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