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Bamboo-shaped carbon tubes from coal

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Abstract

Bamboo-shaped carbon tubes (BCTs) were first synthesized in high yields from iron-loaded carbon electrodes prepared from coal by arc discharge. The BCTs were characterized by scanning electron microscopy and transmission electron microscopy (TEM). The TEM characterization reveals that the tubes have bamboo-like structures consisting of hollow compartments separated with conical shaped graphite layers. The diameters of BCTs are in the range of 40–60 nm with their length being about several micrometers. For some BCTs, the hollow compartments are quite uniform with a size of 100 nm. A growth model is suggested to explain the formation of bamboo structure in tubes.

1. Introduction

Carbon nanotubes have been intensively studied theoretically and experimentally because of the scientific importance and potential applications since their discovery [1]. Recently, there has been growing interest in variety of special types of carbon nanotubes such as helix shaped, bamboo-shaped, fish-bone shaped and chain-shaped tubes, which are different from the conventional straight tubes [2–5]. In this regard the study of bamboo-shaped carbon tubes (BCTs) which covered its structure, preparation methods, as well as formation mechanism [6–11] has drawn much attention of the scientists around the world due to its particular morphologies. The BCTs were first found by Saito and Yoshikawa [2] while they were trying to fill carbon tubes with iron group metals. The typical structures in BCTs usually consist of many hollow compartments that are spaced at nearly equal separations. One end of the BCTs is usually capped with a needle-like metal particle, and the other end is empty. According to the literature [3], the typical BCTs are approximately 30 nm in diameter and the tube wall is made up of several tens graphitic layers.

Up to now, different methods including the arc-discharge evaporation of graphite rod filled with metal particles and the catalytic pyrolysis of hydrocarbons have been developed to synthesize BCTs [2,7]. In this Letter, we report the synthesis of BCTs from coal, the cheapest natural carbon

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source, by an arc-discharge method. The feasibility of preparing carbon nanomaterials from coal has been verified since the synthesis of C_{60} and C_{70} from coal was first reported by Pang et al. [12]. Over the past 6–7 years our group has been trying to develop techniques for synthesis of fullerenes and carbon tubes from Chinese coals. Previous results have shown that the plasma arcing of coal-based carbon has chemical and process advantages over high purity graphite in the formation of carbon nanomaterials due to the presence of weak links between small aryl structures in coal [13–17]. Here, we extend our work to produce BCTs from coal with Fe as catalyst. The low cost of coal with peculiar chemical structures may make it possible for producing bamboo-shaped tubes in large scale with reasonable price. This paper presents the experimental results about the synthesis of coal-based BCTs, of which a growth model is put forward to explain the formation of bamboo structure in carbon tubes.

2. Experimental

One Chinese anthracite from Sinkiang Uighur Autonomous Region of China was used in this study. The proximate and ultimate analysis of the coal sample is shown in Table 1. The coal sample without any pretreatment was crushed and sieved to 150 μm, and fully dried at 110 °C for 12 h before use. The coal powder was finely mixed with coal tar binder in a weight ratio of 20%, and subsequently pressed at about 10–20 MPa to form hollow coal rods. The coal rods were carbonized in an electric furnace under flowing N_2 to make electrodes. The furnace was ramped at 3 °C/min to 500 °C and was kept at that temperature for 1 h to obtain hollow semi-char rod which was further carbonized at 10 °C/min to 900 °C, at which the rod was further heated for 4 h, finally a hollow carbon rod with outer diameter of 9 mm, inner diameter of 5 mm and length of 100 mm was obtained. The mixture of Fe powder and carbon powder was packed into the hollow rod, and then both ends of the filled rod were sealed with graphite plugs. The carbon powder used here was obtained by re-crushing some of the hollow carbon rods which were prepared following the procedure stated above. The ratio of Fe catalyst to carbon powder in the mixture was 1:1 by weight. The hollow carbon rod filled with iron catalyst was used as the anode in the arc-discharge experiment. The cathode was made by high purity graphite rod with diameter of 16 mm and length of 30 mm. The arc-discharge experiment was carried out with direct current of 50–70 A and voltages of 30–50 V in an atmosphere of He at 0.065 MPa. The distance between two electrodes was maintained at about 1–2 mm by manually feeding the anode. The arcing experiment lasted about 20 min. After arc discharge, fiber-like materials that deposited on and surrounded the cathode along its edge at the top were collected and characterized by scanning electronic microscopy (SEM, JEOL JSM-5600LV) operated at 20 kV and transmission electronic microscopy (TEM, JEM-2000EX) operated at 100 kV. The sample for TEM observation was dispersed in ethanol with ultrasonic treatment for 5 min and several drops of the suspension were placed on a carbon coated copper grid for TEM examination.

Table 1
Analysis data of coal sample

Proximate analysis (%)			Ultimate analysis (daf%)				
Mad	Ad	Vdaf	C	H	N	S	O[a]
2.78	3.92	15.18	87.86	3.66	0.73	0.36	7.39

[a] By difference.

3. Results and discussion

Fig. 1 shows the SEM images of the carbon tubes obtained from arcing coal-derived hollow carbon rods filled with Fe catalyst powder, showing that the carbon tubes have web-like morphology at low magnification (Fig. 1a) and noodle-like tube structure at high magnification (Fig. 1b). The TEM characterization was conducted to examine the structure in detail. Fig. 2 shows the TEM images of the as-synthesized carbon tubes from coal. The TEM image at low magnification in Fig. 2a shows that the carbon tubes have a narrow size

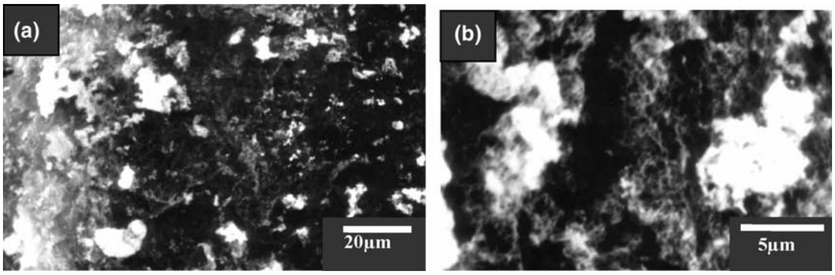

Fig. 1. SEM images of carbon tubes obtained from arcing coal-derived carbon electrode: (a) a low magnification SEM image, (b) a high magnification SEM image.

distribution in diameters. Most of the tubes have an outer diameter of about 50 nm and some tubes have diameters in the range of 40–60 nm. It is interesting to note that the tube consists of a lot of hollow compartments with quite uniform size and looks like bamboo, the inner part of which is hollowed without any catalytic particles. It can be clearly seen from Fig. 2a that the purity of these BCTs is quite high and only a little amount of carbon encapsulated metal particles exist as impurity. We have found that the length of the tubes with bamboo structure is on the order of micrometer. A perfect bamboo-shaped carbon tube with a length of about 5 μm is shown in Fig. 2b. The hollow compartments in the bamboo-like tubes are separated at a distance of ca. 100–200 nm by conical shaped graphite layers whose curvatures could be traced back to the root of carbon tubes. Fig. 2c shows a typical TEM image of the well-developed bamboo structure in one carbon tube with an outer diameter of about 50 nm and an inner diameter of 40 nm. The tube consists of several linear chains of hollow compartments that are spaced at nearly equal distance of 100 nm. Similar structures have been reported in literature [4] but they are obtained from graphite rather than from coal. The compartments in this type of bamboo-shaped tubes are present in a V-shape, which somewhat looks like a water droplet. The angle between the tube walls forming the conical compartment is about 19°. Fig. 2d shows another type of BCTs which are different from the tube shown in Fig. 2c. For these carbon tubes, their size distribution in diameter and the distance between compartments are not uniform and varies in an irregular way. In this case, the compartments is separated with conical shaped graphite layers, and the curvature angle is larger than 60°, which can be termed as undeveloped BCTs. Fig. 2e shows a plug-like catalyst particle located at the tip of a bamboo-shaped carbon tube, and the vertex angle of the particle is similar to the angle of the compartment, this leads one to speculate that the formation of compartments in carbon tubes and its growth angle are determined by the shape of catalyst particles.

The results presented here make it clear that a large amount of BCTs can be obtained from coal by arc method with Fe as catalyst. Up to now, different mechanisms for the formation of this special type of tubes have been proposed [7–11], these include a model showing the movement of catalyst particles under the action of shell stress [3] and a model based on the surface diffusion with two-particles corporation [18]. These models have shaded some lights on the growth or formation of the BCTs, but the detailed mechanism involved in the growth process of BCTs is not yet well understood. In our work coal was used as the starting carbon material for preparing BCTs. In this case, the formation mechanism of BCTs might be different from that with graphite as the starting precursor. Above all, the models currently available cannot explain our results completely and satisfactorily. Therefore, a new model needs to be explored to explain the growth of coal-derived BCTs, and the peculiar chemical structure and properties of coal should be taken into account, specifically speaking, this new model should help us to understand how these BCTs found in our experiments are formed.

It is well known that coal is a molecular solid, rather than graphite that is an expensive lattice

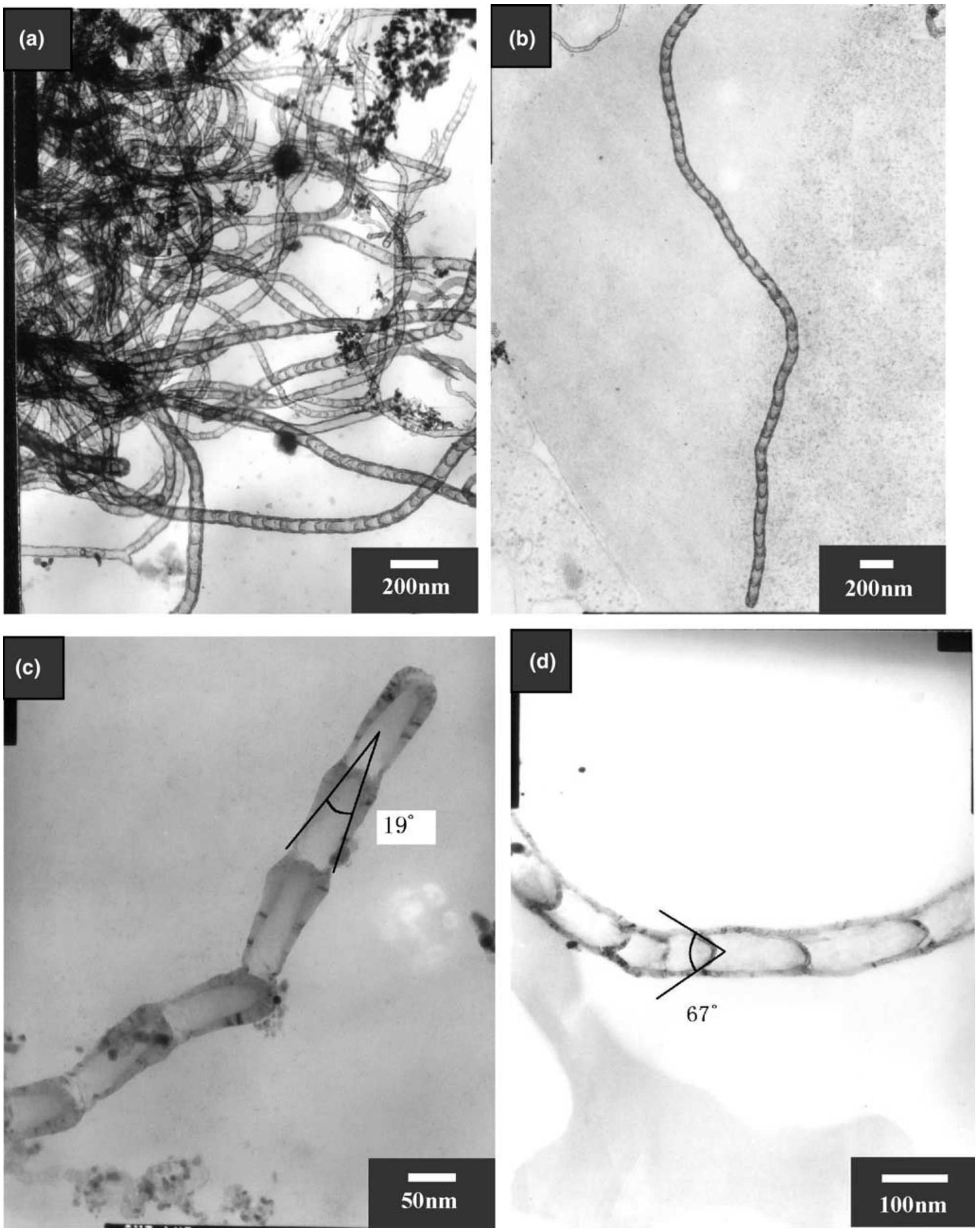

Fig. 2. TEM micrographs of carbon tubes with bamboo-shaped structure: (a) a low magnification TEM image of BCTs, (b) TEM image of a long tube with perfect bamboo-shaped structure, (c) TEM image of a well developed BCTs with an outer diameter of 50 nm and an inner diameter of 40 nm, (d) TEM image of a bamboo-shaped tube with irregularly distributed compartments, (e) TEM image of a catalyst particle, looking like a plug, located at the tip of a tube.

solid. In the case of graphite, the formation process of carbon tubes has to start from or proceed through single atoms (C_1 carbon units) in the plasma. However, for coal-derived carbon rods which have chemical structures resembling graphite crystalline in the domain of 1–10 nm, the basic

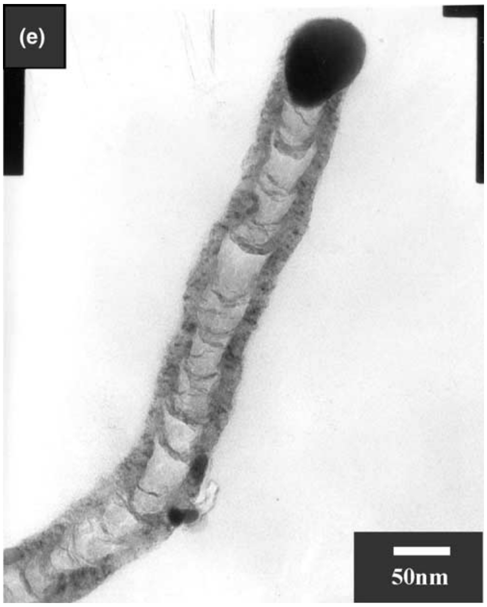

Fig. 2 (*continued*)

units in the chemical structure are small graphitic crystallites containing a few layer planes which are joined together by crosslinks. These crosslinks are strong enough at the carbonization temperature of 900 °C but cannot stand up the extreme heat treatments under the arc plasma conditions, in other words, the links between adjacent units are relatively weak in comparison to the bonds in the structural units, and will be broken up easily when the coal-derived carbon rods are vaporized in arc-discharge process, as such, a large amount of larger fragments would be released. With the assistance of the Fe catalyst in the reaction system, these larger fragments would be easily incorporated into the carbon tubes structures. That is to say, all bonds in the coal-derived carbons need not be necessarily broken for the carbon tubes formation, which has been confirmed by related experiments [19]. With these in mind, here we put forward a possible growth model that is schematically shown in Fig. 3, in which the adsorption and decomposition of carbon layers or large carbon fragments released from coal-based carbon rod upon heat treatment under plasma conditions and the driving force between carbon layers and metal particles have been taken into account. In this model, the reaction that continuously releases carbon fragments during the arcing process of coal-derived carbon rod is the rate-determining step. Fig. 3a shows the growth process of the first compartment of the BCTs. In this step, carbon fragments dissolve on the surface of Fe particles and following that, several carbon layers start to grow gradually. The constant supply of carbon atoms or aromatic larger fragments due to the arcing of coal-based carbon rod will further lead to the propagation of carbon layers. As Saito suggested [3], the growth region on the tip of the compartment results from the absorbed carbons on Fe particles, and this also is the reason why Fe particles are frequently found at the cap of the final integrate conic shape, as can be seen in Fig. 2e and as schematically shown in Fig. 3b. For the model shown in Fig. 3, the relative movement

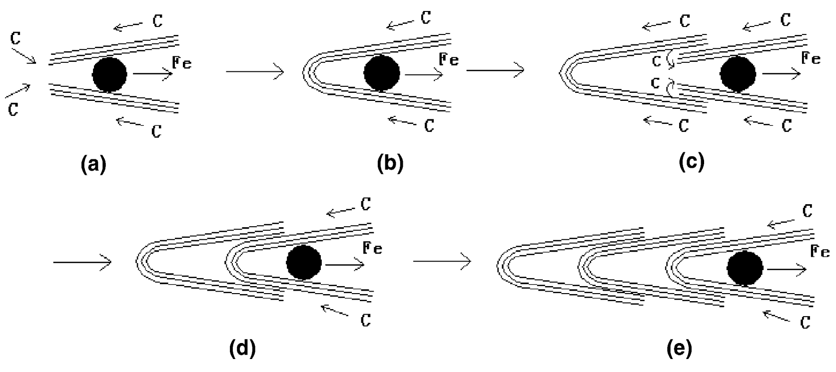

Fig. 3. Schematic growth model of bamboo-shaped carbon tubes.

between the carbon layers and catalyst surface is the basic driving force for the continuous formation of new compartments in carbon tubes. In addition, we cannot rule out the possibility that the fluctuations in temperature in the arcing zone might also play a role in the formation of compartments in a repeated way. Above all, the continuous insertion of new carbon layers should be considered as the main driving force pushing the Fe particle forward. If the forward movement speed of Fe particle is faster than the growth of carbon layers, the next compartment will start to grow (Fig. 3c). Slower movement speed would result in bigger distance or gap between the compartments. The process of periodical formation of compartments in carbon tubes is repeated if the movement between carbon layers and metal particles occurs at moderate rate, as shown in Figs. 3d and e. Finally, the bamboo-like carbon tubes are formed.

It is well known that the size, shape and surface nature of catalyst may greatly affect the morphology of carbon tubes products. In our work presented here, there is a temperature gradient in the arc region, which determinates the shape and state of Fe metal because the liquid–solid transition of metal is temperature dependent. Considering possible existence of wide range of temperature gradient in arcing process, the Fe metal particles might be in liquid, quasi-liquid or solid state under the reaction conditions. The melting point temperature of Fe is 1537 °C, which means that Fe metal would melt at high temperature (ca. 3000 °C) and subsequently transforms into the droplets, of which the size is quite uniform due to the high surface tension. The metal droplets would act as catalyst for the growth of BCTs with well-developed structures, as shown in Fig. 2c. In other words, high temperature will contribute to the growth of prefect BCTs. In this case, if the temperature in the reaction zone were equal or lower than the iron melting point, the catalyst particles would exist in quasi-liquid or solid state. Consequently, a variety of shapes for the catalyst particles such as nearly elliptic and pear-like shape can be formed. As such, the size of particles is in random distribution, resulting in irregular bamboo structure as shown in Figs. 2d and e.

4. Conclusions

The well-defined BCTs have been synthesized by arc evaporation of carbon electrodes from coal with Fe as catalyst. The outer diameter of BCTs is 40–60 nm with a length of several microns. The bamboo-shaped tubes consist of many hollowed compartments that are separated by carbon layers. Some BCTs have uniform compartments along the tube axis. The possible growth mechanism of the BCTs is put forward and has been discussed in terms of the chemical structure of coal-based carbons and the temperature gradient in arc region as well as the properties of iron catalyst used in the experiment.

Acknowledgements

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