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A structure model and growth mechanism for novel carbon nanotubes

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The growth of carbon nanotubes from catalytic thermal decomposition of acetylene on fine iron particles has been studied. Electron microscopic images of the carbon nanotubes "as formed" and after annealing treatment are presented. Besides the ordinary carbon nanotubes which have been reported (S. Iijima, Nature, 354 (1991) 56), we have found, at first time, two other new kinds of carbon nanotubes: one is straight or curved nanotube with many irregular multi-layered diaphragms in the hollow core, in particular, the fringes of the wall of the tubes are not parallel to the axis of the tube; another one has many regular diaphragms (bamboo-like) which keep almost constant distance with each other. A model that postulates two steps growth of nanotubes from catalyst particles is proposed to explain the microstructure of the novel carbon nanotubes.

1. Introduction

Recently, the discovery of carbon nanotubes has attracted great interests of scientists. The carbon nanotubes which were prepared in d.c. arc discharge using graphite electrodes (at about 3000 °C) under He atmosphere were first reported by Iijima [1]. The new method developed by Ebbesen and Ajayan [2] can supply gram quantities of carbon nanotubes under certain conditions. Large scale synthesis of single-shell carbon nanotubes has been performed by using suitable transition metals as catalysts [3–5]. Besides the production of carbon nanotubes by d.c. arc discharge, it can also be prepared by thermal decomposition of hydrocarbon vapour (for example, benzene or acetylene) over some metal particles (such as iron, cobalt, nickel and platinum or their alloys) [6–10] or by electron beam evaporation of graphite [11]. Moreover, helical-shaped tubes have only been observed in the catalytic pyrolysis growth procedure [8].

The yield of the carbon nanotubes from the catalytic growth is higher than from arc discharge method. But the catalytically fabricated tubules are usually thicker and covered by amorphous carbon. In the present work, we report two new kinds of nanotubes (bamboo-like) which have different structures compared with those reported before. Undoubtedly, various forms and structures of the tubes will affect their chemical and physical properties. In addition, studies on the various morphology and structures of the tubes will be helpful in understanding the growth mechanism. A model concerning these new type nanotubes is proposed to explain the morphology and structure of these kinds of nanotubes.

2. Experimental

The catalytic decomposition of acetylene was carried out in a stainless steel reaction chamber. A quartz boat containing graphite sheet coated with iron particles was located in the central part of a horizontal reaction tube (45×1100 mm i.d. length) which was heated from the outside by nichrome element. The reaction mixture of 10 vol % C_2H_2/N_2 was passed over the catalyst bed at flow rate 110 cc/min over several hours at temperature 973 K.

The Fe/graphite samples used in the synthesis of the carbon nanotubes were prepared by impregnating high pure graphite sheets with saturated aqueous solution of iron(III) oxalate for several hours or several days. The resulting samples were dried at 550 K for 2 hours in flowing nitrogen (100 cc/min) and reduced at 650 K in a flow of 10 vol % H_2/N_2 for 5 hours. During the whole reacting, the pressure in the reaction chamber was maintained at 110 Torr.

The "as-formed" carbon tubes were annealed at 873 K for several hours in a flow of 10 vol % H_2/N_2 (110 cc/min) to remove amorphous carbon stacked on the surface of the carbon nanotubes. The samples were examined before and after annealing by SEM (Hitachi S-4200). The samples for TEM (JEM 200-cx) were dispersed in acetone by ultrasound, and then dropped on the copper grinds.

3. Results and discussion

Fig. 1 is a SEM image of "as-formed" carbon nanotubes, the size of the carbon tubes is in the range of

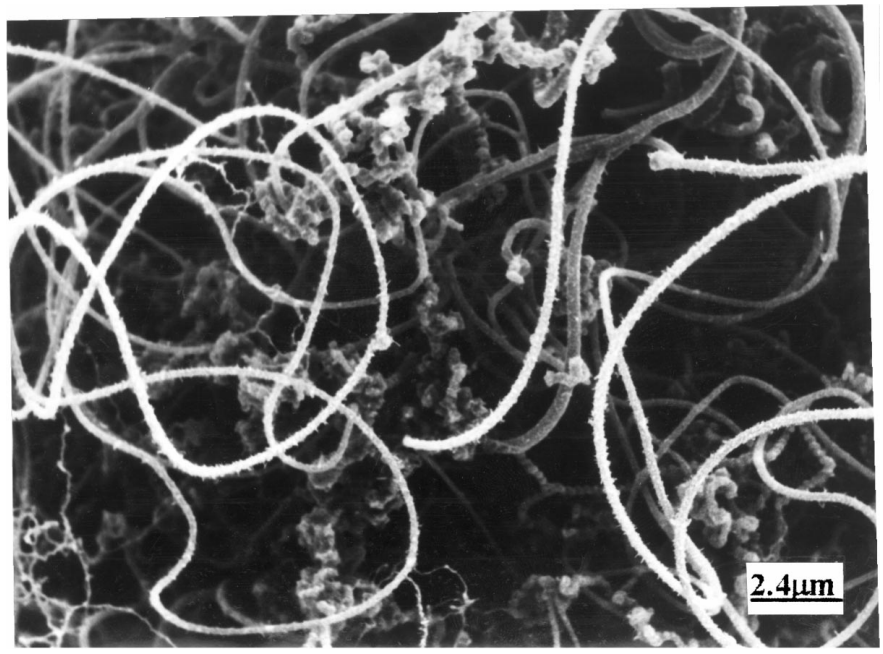

Figure 1 SEM image of "as formed" carbon nanotubes.

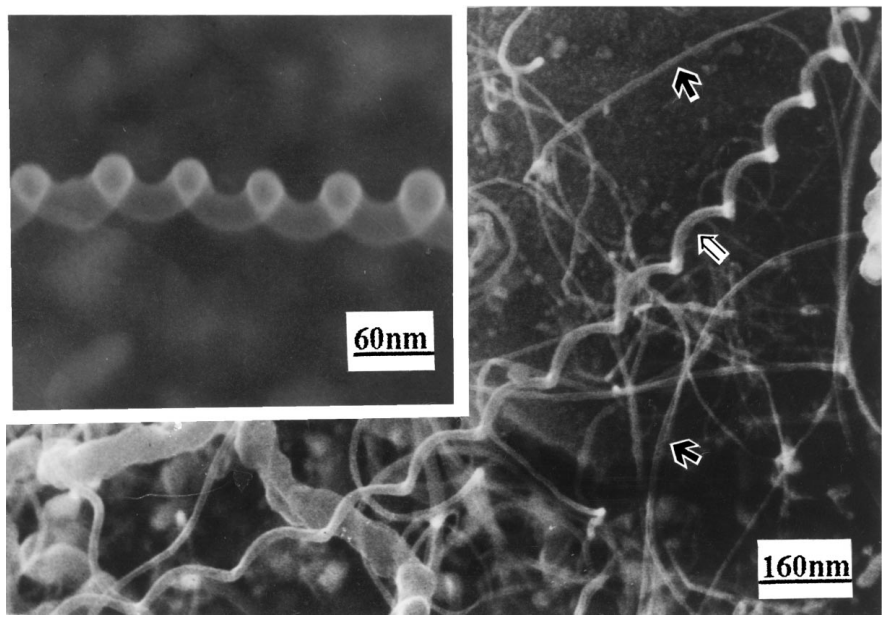

Figure 2 SEM image of carbon nanotubes after annealing treatment. Inset shows a regularly coiled carbon nanotube.

200–500 nm in diameter and up to a few micrometers in length. It is very interesting to note that there are many vertical needles on the surfaces of these tubes, these needles may be amorphous carbon or "secondary nanotubes".

The "as-formed" nanotubes exhibit rather poor crystallinity. To improve the crystallinity and remove the extra amorphous carbon, they are treated in the furnace at 873 K under a flow of mixture of nitrogen and hydrogen. After annealing, the very thin hollow structure is retained. Fig. 2 shows SEM photos of nanotubes after proposed annealing process, revealing that most of the amorphous carbon has been removed from the samples. The surfaces of the nanotubes are very smooth, and the size is about 10 nm in diameter and several micrometers in length. Solid arrow in Fig. 2 indicates a bundle of nanotubes consisting of two nanotubes which combined each other by Van der Waals interactions. The thickness of the bundle is smaller than the sum of the two individual nanotubes due to the flattening resulted from the Van der Waals forces between the two tubes along the contact region [12]. Hollow arrow in Fig. 2 indicates a long helical nanotube which is 20 nm in diameter. One can see that, from right to left along the helical nanotube, the pitches become smaller and smaller. Regularly coiled carbon nanotubes were often observed in our experiments, as indicated in the inset of Fig. 2, the thickness of the tube is 30 nm, the helix angle α is about 45° and the pitch is about 67 nm. It was suggested that the formation of coiled nanotubes is due to the mismatch between the extrusion velocity by the catalyst particle and the rate of carbon deposition

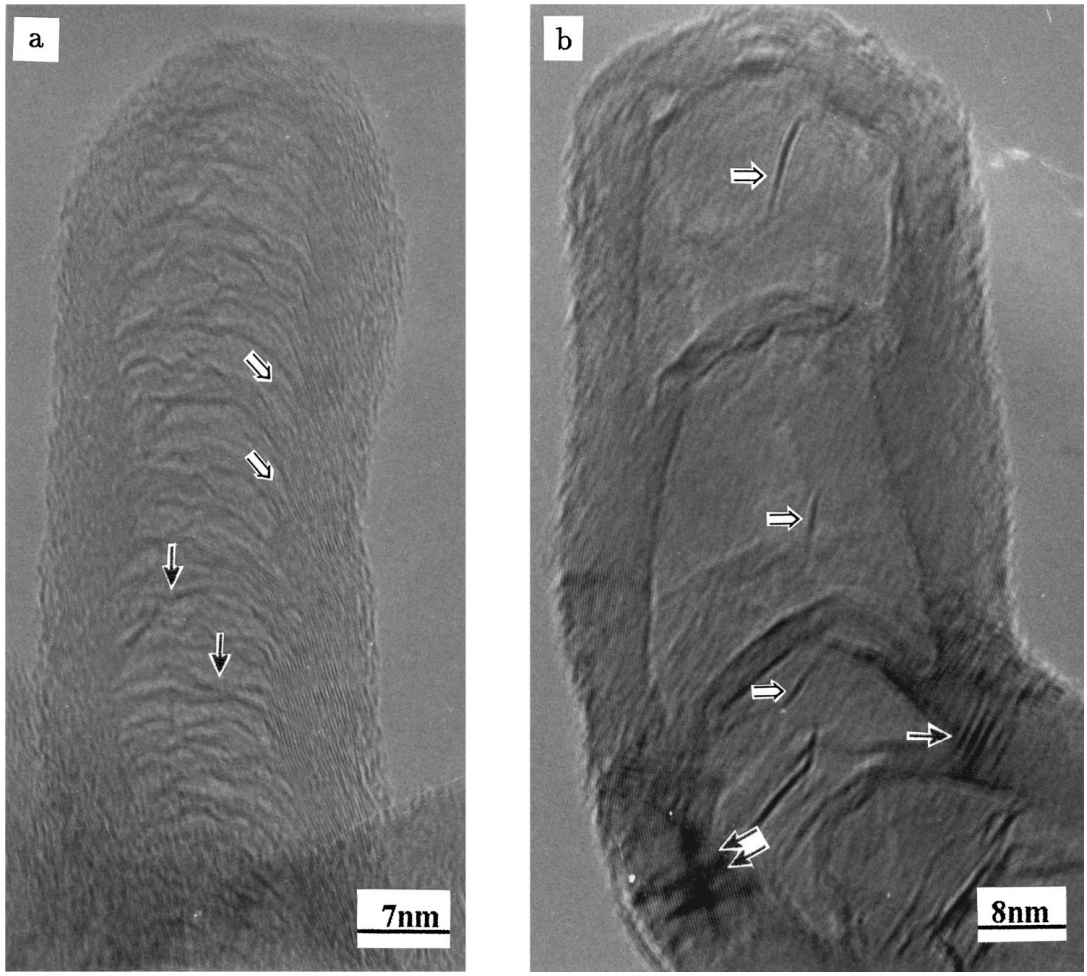

Figure 3 TEM images of one new kind of carbon nanotubes with many irregular diaphragms in their hollow cores. (a) a straight carbon nanotube, (b) a curved carbon nanotube.

[8]. Motojima *et al*. [13] have studied the morphology and extension characteristic of regularly coiled carbon filaments which are very thick, about several hundreds nanometers in diameter. They have found that the coiled filaments could be elastically extended up to about three times versus the original coiled length.

Many nanotubes have been observed, some nanotubes are end capped. We haven't found any catalyst particles encapsulated in the tip of the nanotubes, this is different with some results reported before. Besides the closed nanotubes, a few end-opened nanotubes were also observed, these nanotubes may be opened during the annealing process.

In our experiment, we have observed two new kinds of interesting structures. One is shown in Fig. 3. From HRTEM image of the straight nanotube (Fig. 3a), one can see that the fringes of the right side of the nanotube are almost parallel to each other, the distance between two adjacent fringes is 3.4 Å in accordance with that in the graphite. These fringes terminate on the surface of the nanotube, namely, the fringes are short and forms acute angle with the axis of the tube. In addition, another distinguishing feature of this kind of nanotubes is that they consist of many diaphragms in the core region. Most of these diaphragms are complete, some are discrete (solid arrows) or has not been formed (hollow arrows). These diaphragms are often wrinkled, and from the fringes number connected with the diaphragms we can infer that every diaphragm consists of 2 or 3 graphite layers. The surface of the tube is coated with a turbostatic stacks of carbon layers which may be removed by further annealing. The structure of the curved tube (Fig. 3b) is similar to that of straight tube (Fig. 3a), but the diaphragms consist of many graphite layers and the distance between two adjacent diaphragms is relatively large.

Fig. 4 shows another new type carbon nanotube (bamboo-like). The tube is several micrometers in length, and the outer and inner diameters of the special tube are 22 and 13 nm, respectively. Although the growth direction has changed, its structure is almost the same in the whole tube. Inset of Fig. 4 is a schematic representation of this kind of carbon nanotubes, indicating the inner layer connects with a number of regular hemi-sphere-like diaphragms.

Several models were postulated to explain forming mechanism of carbon nanotubes. Iijima [1] thought that the tube were formed by curling and rolling of graphite sheets, and the carbon atom hexagons are arranged in a helical fashion about the needle axis, this helical structure may aid the growth process. A model that postulated a mixture of scroll-shaped and concentric, cylindrical graphene sheets was proposed by Amelinckx *et al.* [14] to explain the microstructure of multishell carbon nanotubes and the formation of multishell closure domes, nucleation is attributed to the

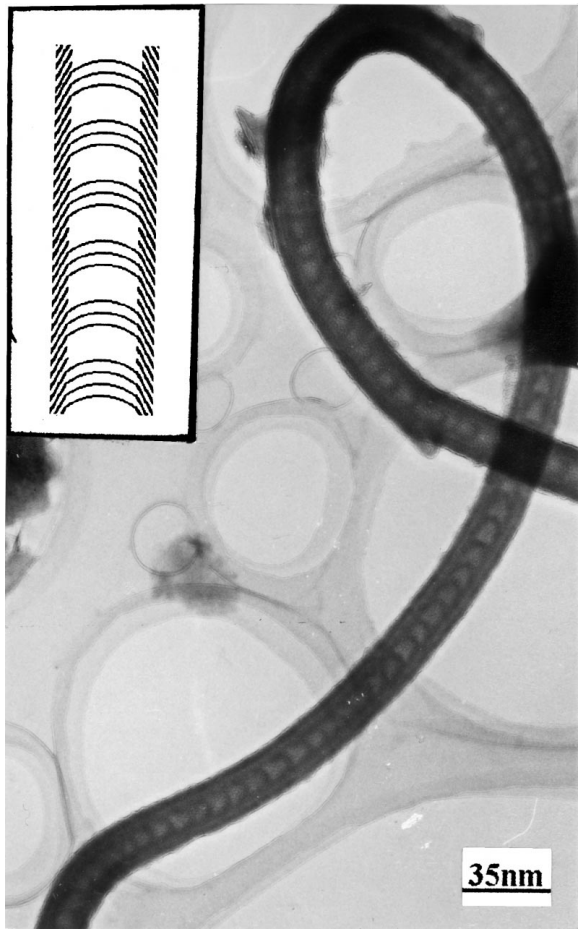

Figure 4 A TEM image of another novel carbon nanotube. Inset is a schematic representation of the carbon nanotube.

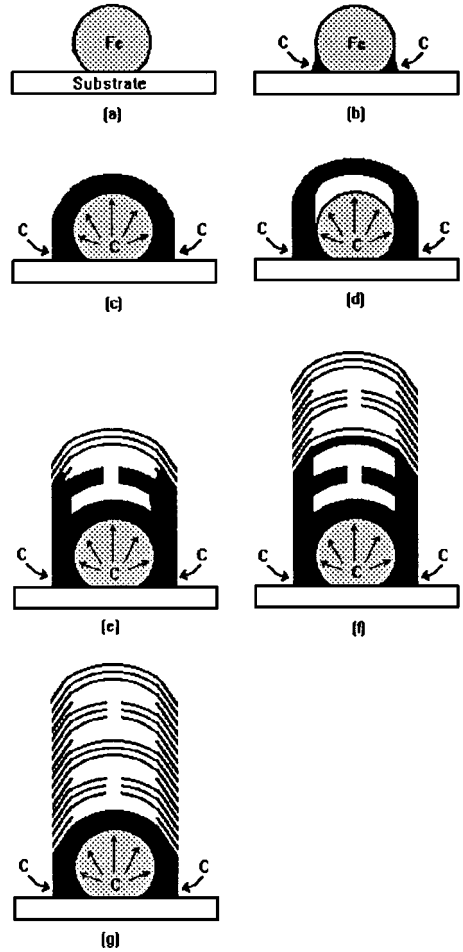

Figure 5 Successive stages of the forming process of the novel carbon nanotubes depicted in Fig. 3. (a) an iron particle was located on graphite substrate, (b) carbon atoms resulted from decomposition of acetylene deposited first at the contact region between the iron particle and the substrate, (c) a complete hemi-sphere-like carbon coat has formed, (d) a hemi-sphere-like carbon coat has been raised up by extrution mode (see the text), (e) an incomplete hemi-sphere-like carbon coat with has formed, (f) a carbon nanotube with many hemi-sphere-like carbon diaphragms has formed. As the forming of the tube, graphitizing of the carbon nanotube was gradually undergoing (g).

initial formation of a fullerene "dome". A structural model of a conical shaped carbon nanotube based on a rolled-up hexagonal network was proposed by Endo *et al.* [6], the helical graphene-walled nanotube was produced by insertion of carbon atoms dimers and clusters into a closed fullerene end-cap, the cap effectively rotated by a wholesale reorganization movement.

Bamboo-shaped carbon tubes have been reported [15, 16], but the growth mechanism of this kind of tubes is not so clear. Those models which have already been postulated before [8, 14, 17] aren't suited to the new type nanotubes reported here. We postulate a new model to explain the growth process of this sort of carbon nanotubes, the whole process includes two steps: first, many hemi-sphere-like carbon shells formed a carbon rod as a continuum; second, the carbon rod was graphitized. From the observation of the tip of the nanotubes, one can infer that tip growth probably occur [18]. A successive stages of the two steps in the formation of the carbon nanotube are shown in Fig. 5. A catalyst particle (Fe) located on the graphite support is shown in Fig. 5a. Carbon atoms resulted from decomposed acetylene deposit, at first, at the contact circle of the particle and the support (Fig. 5b), whereas some carbon atoms solved in the particle move towards the particle top by diffusion and condense gradually to form a hemi-sphere-like graphene coat (Fig. 5c). With continuously producing, solving, diffusing and condensing of carbon atoms, the coat is becoming thicker and thicker. But the condensing rates of carbon atoms around the catalyst particle are different, the condensing rate of carbon atoms on the lateral surface is higher than that on the top of the particle, so the growth in the vertical direction (with respect to the substrate surface) is fast, the carbon coat is extruded by the continuously aggregating carbon atoms. In case the iron particle combine with the graphite substrate in strong interaction, as a result, the carbon coat is raised up by extrusion mode before another carbon coat forming (Fig. 5d). If the diffusing rates (v_d), and condensing rates (v_c), of carbon atoms are the same on the surface of the top region of the particle, then a complete homogeneous hemi-sphere-like carbon shell can be formed. In fact, the diffusing rate (v_d) and condensing rate (v_c) of the carbon atoms are influenced by many conditions, such as the producing rate of carbon atoms from decomposition of acetylene, the concentration distribution of carbon atoms in the particle and the catalysis of the metal particles, etc. When some of these conditions are mismatch, an incomplete carbon shell may be form. If the diffusing rate v_d towards the top of the particle is less than the condensing rate v_c, then a

discrete carbon shell can be formed (Fig. 5e). As the reaction processing, many diaphragms with various forms may be formed, as a consequence, a carbon nanometer tube with many complete or incomplete diaphragms has been formed (Fig. 5f). During this process, on the other hand, the carbon nanotube is graphitizing, and the graphitizing extent depends on the temperature and the reaction time. During the graphitizing of the carbon nanotubes, the directions of the parallel fringes of the wall depend on the directions of outer crystal planes of the catalyst particle. Finally, a carbon nanotube has been formed (Fig. 5g) as observed in Fig. 3a.

The catalytic effect of the particles is determined by its outer crystal planes and its morphology. If the catalyst is isotropic, then a straight carbon nanotubes may be formed. But the catalyst is often anisotropic, the growth rate of the wall of the tube around the catalyst particle may not be the same, thus the curved carbon nanotubes can be formed, as indicated in Fig. 3b. In this tube the curvature is more severe. One can see that on the right side of curved area of the tube (single solid arrow) the fringes are crumpled seriously. The stress on the concave side of the tube results in crumpling during the forming of the tube. The crumple direction is perpendicular to the bending radius of the tube, which is different with those have been reported before [19–21]. We think that the diaphragms in the tube has a strong impact on the crumpling direction of the layers on the concave side of the tube. This diaphragms prevent the layers on the concave area from being bent in the plane of the paper, in order to minimize the strain energy the layers on the concave side have to be crumpled in the way (perpendicular to the plane of the paper) as depicted in Fig. 3b. But the opposite side of the tube (double solid arrows) is stretched and the fringes are flat. From the picture, we can see that there are many dangled rods in the hollow region of the tube, these may be carbon fragments formed during the preparation of the carbon nanotube.

During the reacting process, stable equilibrium may be established in some areas in the reaction chamber, thus many similar hemi-sphere-like carbon coats can be formed continuously, at last a regular bamboo-like carbon nanotube can be formed as shown in Fig. 4.

4. Conclusions

The present studies show that the catalytic growth may be one viable way of preparation of carbon nanotubes in large quantity. In this way, purification of "as-formed" carbon nanotubes can be easily controlled. Our results show that, under certain conditions, nanotubes with many diaphragms grow on the tips of catalyst particles. Structure study of this new type nanotubes reveals that carbon tubes were formed, at first, as a continuum, and then the tubes were graphitizing. This new type nanotubes with many diaphragms may have special implications for electric and mechanical properties. The diaphragms may can keep the tubes from collapsing and enhance their mechanical stability.

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