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Complex branching phenomena in the growth of carbon nanotubes

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Abstract

We report here the experimental observation of complex branching phenomena in the growth of carbon nanotubes produced under specific arc-discharge conditions. High-resolution transmission electron microscopy (HRTEM) images demonstrate that two or three carbon nanotubes can join together under specific angles in L, Y, and T patterns with saddle surfaces at the junction. Adding to the observation of negative curvature surface in straight-line tubes that change their diameters, we report here negative curved areas that support the topography of a branching structure.

1. Introduction

The discovery by Ebbesen and Ajayan [1] of a process for synthesizing bulk quantities of carbon nanoclusters, especially carbon nanotubes, has opened up new opportunities for producing unique carbon-based materials. Theoretical calculations and experimental results have demonstrated that the electrical and mechanical properties of the carbon nanotubes depend greatly on their structure [2,3]. The carbon nanoclusters produced from an arc-discharge between graphite electrodes in helium show a rich variety of morphologies that reflect a strict discipline of the growth. Structural analyses of the carbon nanotubes by technique such as HRTEM have revealed details of the growth, and the closing of individual carbon nanotubes [4,5].

Based on the HRTEM observations of concentric carbon nanotubes, several growth models of carbon nanotubes during carbon arc-discharge have been proposed [6–8]. The most plausible growth mechanism to account for the experimental observations is the open-ended growth in which carbon elements from the plasma concentrically add on to the reactive dangling bonds at the edge of the nanotubes [6]. To establish the morphology of the nanotubes, the distribution of areas of positive and negative curvature, which are observed in linear concentric nanotubes only, plays an important role.

Adding to the results observed on linear nanotubes, we report here the experimental observation of the growth phenomena of branching carbon nanotubes produced from carbon arc-discharge by a graphitic anode with a hollow core in the center. HRTEM images show that branching occurs at the junction in L, Y, and T patterns with saddle surfaces. The existence of this branching phenomenon reveals that the carbon nanotubes are not always constructed by concentric linear graphite walls, at least not at the junction area. In contrast to the microstructure of carbon nanotubes from previously studies [5–8], this observation of novel branching growth phenomena

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adds to the rich variety observed before that will ultimately lead to an identification of the growth mechanism.

2. Experimental procedures

The materials used in this study were produced by arc-discharge, operating under a helium atmosphere of 500 Torr at a current density of 220 A/cm^2 and 27 V potential difference between the electrodes. A hollow anode was employed with a core of 0.32 cm diameter drilled along the center of a cylindrical graphite rod of 0.64 cm diameter. The cathode consisted of a graphite rod of 0.95 cm diameter and 3 cm in length. The gap between the two electrodes was maintained at approximately 1 mm. During the carbon arc-discharge vaporization the hollow anode was consumed, and a carbonaceous deposit was built up on the surface of cathode as a slag with a black core at the center and silver color shell around. The distribution of carbon nanotubes in the slag was similar to our previous report [9]. TEM examination was performed on a sample prepared by grinding the initial slag into powder and dispersing the powder in acetone. After sonicating for approximately 5 min, the black suspension was dropped on a holey carbon copper grid and the solvent was allowed to dry. The sample was then examined in a Hitachi H-8100 TEM operated at 200 keV.

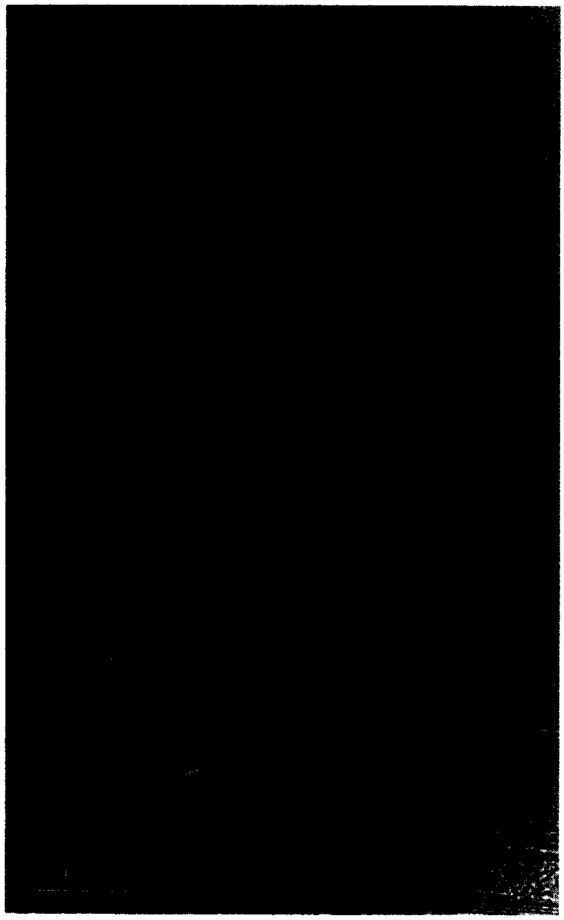

Fig. 1. A HRTEM image of carbon nanotubes shows that two carbon nanotubes (labeled by 'A' and 'B') can be joined together in an 'L' pattern. Labels 'c' and 'd' indicate the negative curvatures between the tubes 'A' and 'B'. In contrast, the labels 'e', 'f', 'g', and 'h' point to positive curvatures.

3. Results and discussion

The HRTEM image, shown in Fig. 1, demonstrates that two carbon nanotubes can be joined together in an 'L' pattern. The outer and inner diameters of the tube 'A' are 13.4 and 5.2 nm, respectively, while the tube 'B' is 10.5 nm in the outer diameter, and 3.9 nm in the inner diameter. The tube 'A' and the tube 'B' are joined together by curved graphitic networks. Steric models for the topography of graphitic surfaces suggest that deviations from the planarity of hexagonal networks can be introduced by pentagonal or heptagonal defects in the lattice, resulting in positive and negative curvatures, respectively [10]. Notice that the positive curvature is defined as the inward bending with respect to the tube axis, but the negative curvature is the outer bending [4]. Therefore, based on the HRTEM image, the labels 'c' and 'd' indicate that the graphitic walls are negatively bent at angles of 50° and 55°, respectively, and label 'e' points to a positive curvature at a 15° angle. On the other hand, the positive curvatures are all 30° at the positions of 'f', 'g', and 'h'. This three-step bending (or connecting) makes tubes 'A' and 'B' almost perpendicular to each other. The specific angles repeatedly observed will ultimately find an interpretation in the steric requirement of the pentagonal and heptagonal defect structure [11,12]. The island formation inside the tube is routinely observed in linear tubes, and is apparently

Fig. 2. A HRTEM image indicates that three carbon nanotubes are joined together in a 'Y' pattern. The labels 'a', 'b', 'c', and 'd' point to the negative curvatures in the graphitic layers.

not connected to the peripheral topography discussed here.

The Y-type carbon nanotube configuration, shown in Fig. 2, is also observed in the same carbonaceous deposit. This HRTEM image indicates that three carbon nanotubes are joined together in a 'Y' pat-

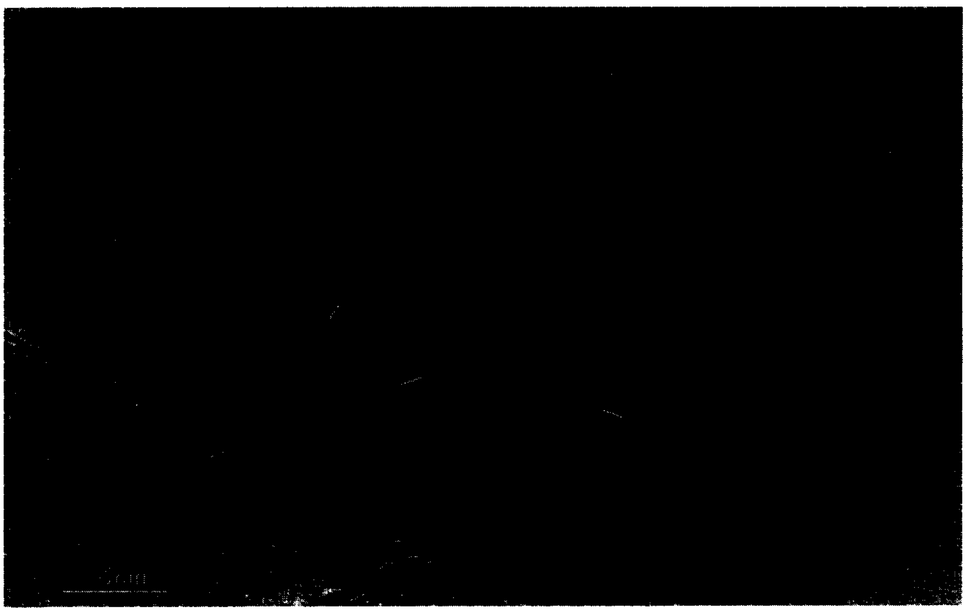

Fig. 3. A HRTEM image of carbon nanotubes show that a T-type configuration of carbon nanotubes can be achieved by negatively bending the graphitic layers. The negative bends are pointed out by labels 'a', 'b', 'c', and 'd'. Notice that the graphitic layers take a two-step curvature to make a T-type configuration.

tern, with angles between two arms of 30° (indicated by 'a' and 'c') and 65° (labeled by 'b'). An additional bent at 'd' makes an angle of 45°. According to the theoretical models [11,12], at the positions of 'a', 'b', 'c' and 'd' the hexagonal networks are all negatively curved, requiring heptagons to be introduced into the graphitic network to make the Y-type geometry possible. Notice that in this 'Y' fork structure the steric constraint may in addition require a change of the layer spacing, such as the region between 'c' and 'd' showing irregular spacings of graphitic layers.

Other carbon nanotube configurations, such as a T-type, have also been observed in the cathodic carbonaceous deposit. Fig. 3 is a HRTEM image of such a T-type configuration of carbon nanotubes, which shows that the graphitic layers are negatively curved at angles of 30° (indicated by 'a' and 'd'), 50° (labeled by 'b'), and 60° (labeled by 'c'). Notice that as in the L-type configuration of carbon nanotube, the graphitic layers take a two-step bent to make a T-type carbon nanotube configuration, in variation of the smooth transition predicted by theory [11].

Topographical speculations on the possible configurations of carbonaceous surfaces have actually proceeded the synthesis of such materials by as much as 20 years [13,14], including fullerenes and nanotubes. Only gradually will the experiment catch up with the large catalog of these predicted structures, as reported here in our study. The observation of the novel branching phenomenon proves that carbon nanoclusters cannot only be constructed by concentrically adding carbon elements along one direction. The growth process of carbon nanotubes is apparently more complicated than open-ended models suggest, and our results reported here will guide their necessary expansion.

4. Conclusion

A novel growth phenomenon of carbon nanotubes produced by carbon arc-discharge has been demonstrated by HRTEM analysis. The branching structures of L-, Y- and T-shapes are difficult to explain by straight-line growth models that continue a linear seed in one direction since negative curvature elements are required. Such elements have been postulated before [15] and even observed in the regions of diameter change of linear tubes [4], but never in junction regions as observed here. The technology is still far from a systematic control of the morphology through variations of the system parameters, not only for the branched growth reported here, but for any type of tubes. However, results such as reported here will ultimately outline the requirements one must impose on existing growth models that require straight-line continuation through an open-ended dangling bonds.

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References

[1] T.W. Ebbesen and P.M. Ajayan, Nature 358 (1992) 220.
[2] N. Hamada, S. Sawada and S. Oshiyama, Phys. Rev. Letters 68 (1992) 1579.
[3] C.H. Olk and J.P. Heremans, J. Mater. Res. 9 (1994) 259.
[4] S. Iijima, T. Ichihashi and Y. Ando, Nature 356 (1992) 776.
[5] S. Seraphin, D. Zhou and J. Jiao, Acta Microscopica 3 (1994) 45.
[6] S. Iijima, P.M. Ajayan and T. Ichihashi, Phys. Rev. Letters 69 (1992) 3100.
[7] Y. Saito, T. Yoshikawa, M. Inagaki, M. Tomita and X. Hayashi, Chem. Phys. Letters 204 (1993) 277.
[8] X.F. Zhang, X.B. Zhang, G. Van Tendeloo, S. Amelinckx, M. Op de Beeck and J. Van Landuyt, J. Crystal Growth 130 (1993) 368.
[9] S. Seraphin, D. Zhou and J. Jiao, Carbon 31 (1993) 1212.
[10] B.I. Dunlap, Phys. Rev. B 46 (1992) 1933.
[11] L.A. Chernozatonskii, Phys. Letters A 172 (1992) 173.
[12] G.E. Scuseria, Chem. Phys. Letters 195 (1992) 534.
[13] E. Osawa, Kagaku 25 (1970) 854.
[14] D.A. Bochvar and E.G. Galpern, Dokl. Akad. Nauk SSSR 209 (1973) 610.
[15] A.L. Mackay and H. Terrones, Nature 352 (1991) 762.