Formation of Carbon Nanotubes and Cubic and Spherical Nanocages

Jianwei Liu, Liqiang Xu, Wu Zhang, Wan Juan Lin, Xiangying Chen, Zhenghua Wang, and Yitai Qian*

The Structure Research Laboratory, Department of Chemistry and Department of Materials Science & Engineering, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

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Three types of carbon nanomaterials, including bamboo-shaped carbon nanotubes and cubic and spherical carbon nanocages, have been prepared by an ethanol thermal reduction process. Scanning electron microscopy studies showed that carbon nanotubes predominated. Transmission electron microscopy investigations indicated that as-synthesized sample contained mostly bamboo-shaped carbon nanotubes, with some carbon cubic and spherical nanocages. Detailed examination of high-resolution transmission electron micrography showed that the walls of bamboo-shaped carbon nanotubes consisted of oblique graphene planes with respect to the tube axis, whose interlayer spacing was about 0.335 nm. The experimental results suggest that the growth mechanism of the bamboo-shaped carbon nanotubes follows the base growth model and the appearance of cubic and spherical carbon nanocages arises from the graphitic sheets bending in an attempt to eliminate the highly energetic dangling bonds present at the edge of the growing structure. At the same time, we report that the correlative reaction factors influence the morphology of carbon nanomaterials and elucidate the formation mechanism of different carbon structures.

Introduction

The discoveries of buckminsterfullerenes[1] and carbon nanotubes[2] have stimulated a great deal of research on different carbon morphologies due to their promising applications in the fields such as electrochemical devices,[3] hydrogen storage,[4] field emission devices,[5] and nanotweezers.[6] In the following years, various special types of carbon nanotubes, including helix shaped,[7] bamboo-shaped,[8] and fish-bone,[9] which are different from the conventional straight tubes, have drawn much attention from scientists around the world. Saito and Yoshikawa[10] first found the bamboo-shaped carbon nanotubes, which usually consist of many hollow compartments that are spaced at nearly equal separations. Later, Lee et al.[11] proposed a base growth model for the bamboo-shaped carbon nanotubes, which illustrates whereby the wall grows vertically and connects periodically with the compartment layers. Due to the flexible carbon structure, considerable efforts have also been made to study other carbon morphologies. A new form of carbon cubic nanocages was produced by arc evaporation of carbon with the alkaline-earth metals calcium or strontium.[12] The authors claimed that the carbon cubic shape was probably produced by folding graphitic sheets into a rectangular form, a process catalyzed by alkaline-earth metals.

In general, the fabrication of carbon nanomaterials usually calls for high temprature or expensive apparatus. In many examples, carbon materials are prepared by metal-catalyzed chemical vapor deposition (CVD),[13] arc evaporation,[14] laser ablation of carbon,[15] or catalytic decomposition.[16] Chemical routes have also been attempted. More recently, Korgel's group[17] synthesized multiwall carbon nanotubes and nanofibers in supercritical toluene using ferrocene, Fe, or FePt nanocrystals as growth catalysts. The technology is similar to the solvothermal route, which was used for the synthesis of solid functional materials, such as diamond[18] and carbon nanotubes.[19]

Previously, we synthesized carbon nanotubes by using the reaction of ethanol with magnesium in a stainless steel autoclave.[20] We have since prepared various carbon nanostructures by this technique over a wider range of reaction conditions than those previously reported and have found that some carbon nanocages with cubic and spherical shape coexist with bamboo-shaped mutiwalled carbon nanotubes. The appearance of cubic and spherical carbon nanocages arises from the graphitic sheets bending in an attempt to eliminate the highly energetic dangling bonds present at the edge of the growing structure. In this paper, we report that the correlative reaction factors influence the morphology of carbon nanomaterials and elucidate the formation mechanism of different carbon structures.

Experimental Section

Synthesis of Carbon Material. In a typical experiment, ethanol (or methanol) and the metallic magnesium powders were mixed in a stainless steel autoclave of 20 mL capacity. The autoclave was sealed and maintained at 500−700 °C for 10 h and then it was allowed to cool to room temperature naturally. A dark precipitate was collected and washed with absolute ethanol, dilute HCl aqueous solution, and distilled water in that order. The obtained sample was then dried in a vacuum at 65 °C for 6 h.

Characterization Techniques. The morphologies of the samples were observed through scanning electron microscopy (SEM) and transmission electron microscopy (TEM) measurements, which were made on a JEOL JSM-6700F field emission and a Hitachi Model H-800 transmission electron microscope using an accelerating voltage of 200 kV with a tungsten filament, respectively.

The microstructure of carbon nanotubes and nanobelts was analyzed by high-resolution transmission electron microscopy

* To whom correspondence should be addressed. Tel: +86-551-3603204. E-mail: ljw@mail.ustc.edu.cn.

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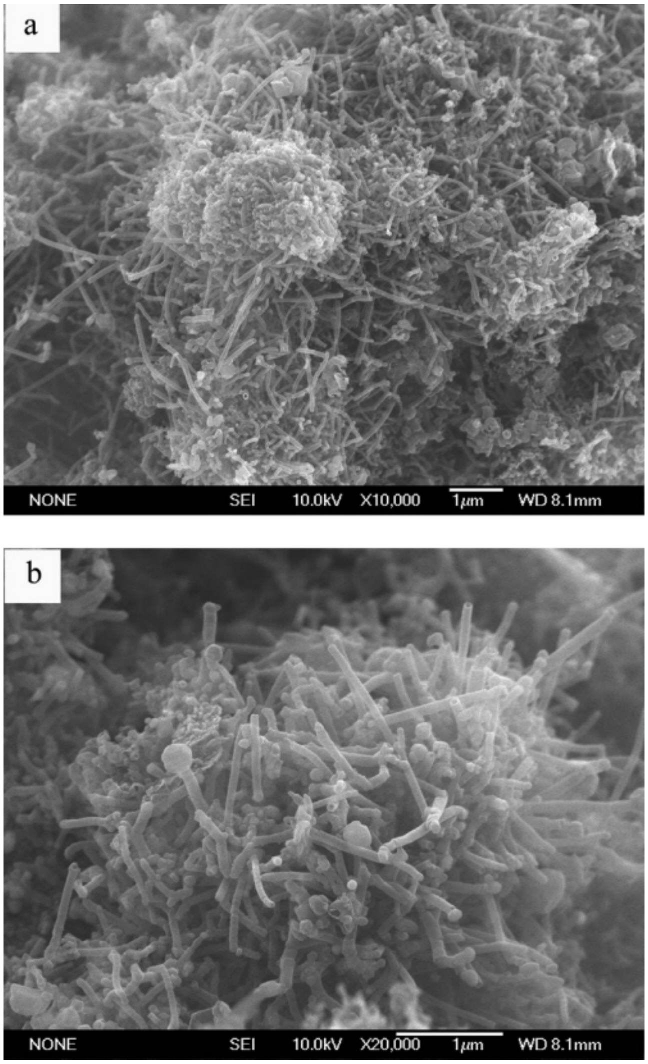

Figure 1. Field-emission SEM images displaying a large quantity of carbon nanotubes with diameters of 20−200 nm.

(HRTEM) observation, which was performed with JEOL-2010 transmission electron microscope using an accelerating voltage of 200 kV. Samples for the electron microscope were prepared by ultrasonic dispersion for 1 h of 0.1 g of the as-prepared power with 10 mL of ethanol in a 30 mL conical flask. Then, the suspension was dropped on a carbon-coated copper microgrid and dried in air before performance.

The purity and phase structure of products were obtained by X-ray powder diffraction (XRD) analysis, which was performed with a Philips X′ Pert PRO SUPER diffractmeter using the monochrochromatic high-intenstity Cu Kα radiation (λ = 0.1541874 nm).

Results and Discussion

The morphology of the product obtained by reducing ethanol with metallic magnesium at 650 °C has been investigated by scanning electron microscopy (SEM). The field-emission SEM images (Figure 1a,b) display that a large quantity of carbon nanotubes with diameters of 20−200 nm is formed and some nanotubes have open ends. From Figure 1b, we can see that a great deal of carbon nanotubes accumulate together. In addition, some particles can be found in Figure 1a.

A more detailed investigation of as-prepared products by TEM reveals that there are three kinds of carbon nanomaterials. From Figure 2a, we can observe that carbon nanotubes have

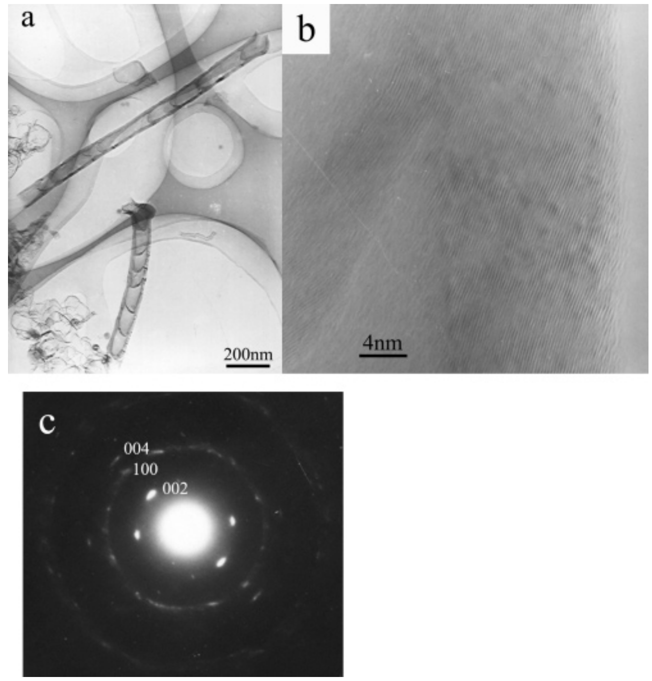

Figure 2. (a) TEM image of two bamboo-shape carbon nanotubes. (b) HRTEM image showing that the bamboo-shaped carbon nanotubes consist of slanted graphene layers with respect to the tube axis. (c) SAED image of the nanotube indicating the existence of two sets of hexagonal diffraction spots symmetrical about the nanotube axis

bamboo-shaped structure with a diameter of about 60−80 nm, which implied that the growth mechanism of carbon nanotubes pursued a gradual growth process like bamboo, thus appearing as bamboo-shaped sticks or with a growth ring like trees.[21] Furthermore, we may find that every bamboo-shaped carbon nanotube is made up of many compartments with mostly uniform size.

A further analysis by high-resolution transmission electron microscopy (HRTEM) (Figure 3b) reveals that the interlayer distance of carbon nanotube is about 0.335 nm, consistent with the (002) plane lattice parameter of graphited carbon. The compartment joins with the wall without any defect. It is worth mentioning that the walls of bamboo-shaped carbon nanotube consist of oblique graphene planes with respect to the tube axis. The observed apex angle is 38° on the image, which is fairly close to the theoretical value of 38.9° for the apex angle of a 240° disclination.[22]

To give more weight to the above claim, the selected area electron diffraction were taken for the bamboo-shaped carbon nanotubes. Figure 2c shows the SAED image of the nanotube, which was obtained by using the electron beam focused onto the tube axis. The existence of two sets of hexagonal diffraction spots symmetrical about the nanotube axis can be a strong indication that the bamboo-shaped carbon nanotubes possess 2-fold symmetry and therefore 240° disclination, which further confirms that the bamboo-shaped carbon nanotubes consist of slanted graphene layers with respect to the tube axis.

In the processing of TEM and HRTEM examinations of as-prepared carbon nanomaterials some carbon nanocages with spherical and cubic shape were detected. Figure 3 shows the TEM and HRTEM images of carbon spherical nanocages. From Figure 3a, we can find that two Y-shaped carbon nanotubes coexist with some carbon spherical nanocages, as indicated by the arrow. High-resolution transmission electron microscopy (HRTEM) images (Figure 3c) indicate that the spherical carbon

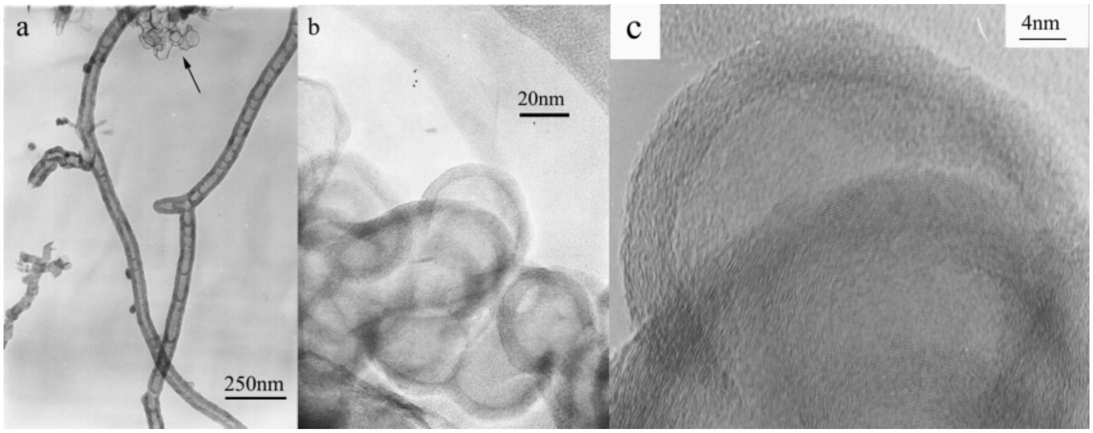

Figure 3. (a) TEM image showing two Y-shaped carbon nanotubes coexist with some carbon spherical nanocages, as indicated by the arrow. (b) TEM image for carbon spherical nanocages. (c) HRTEM image for carbon spherical nanocages indicating that the spherical carbon nanocages are composed of graphite layers with a spacing of up to 0.34 nm.

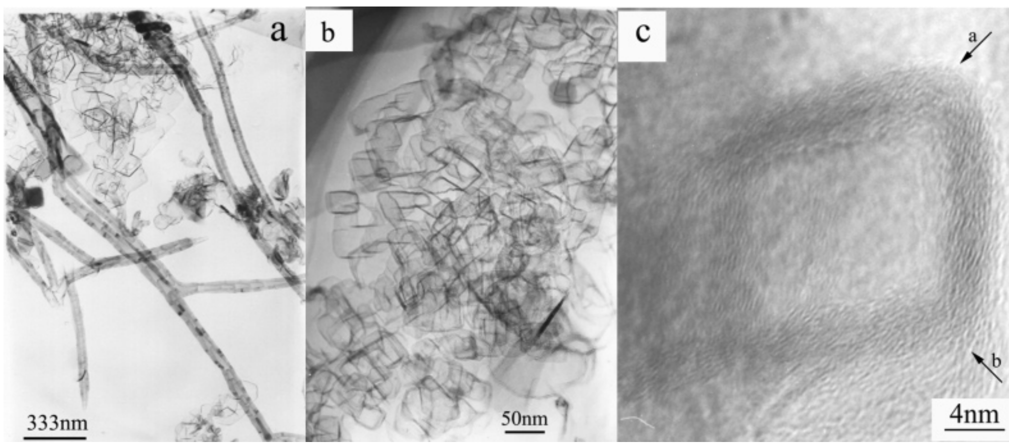

Figure 4. (a) TEM image for bamboo-shaped carbon nanotubes and Y-shaped carbon nanotubes together with many carbon cubic nanocages. (b) A typical TEM image of abundant of cubic cages. (c) HRTEM image showing that cubic nanocage consists of multiwalled graphitic carbon with a spacing of 0.34 nm.

nanocages are composed of graphite layers with a spacing of up to 0.34 nm.

It is very interesting to find a lot of carbon cubic nanocages in as-synthesized carbon nanomaterials, as shown in Figure 4. From Figure 4a, we can observe bamboo-shaped carbon nanotubes and Y-shaped carbon nanotubes together with many carbon cubic nanocages. Figure 4b displays a typical TEM image of abundant of cubic cages, which range in size from 10 to 100 nm. The nature of the cubic cages is clearly demonstrated in the HRTEM images (Figure 4c). A representative cubic nanocage consists of multiwalled graphitic carbon with a spacing of 0.34 nm. At some of the cubes' corners, smooth folding can be observed (as indicated by arrows a and b), while extrusion of graphitic layers or breakages occur at other corners. The cubic shape is probably produced by folding graphitic sheets into a rectangular form, a process catalyzed by alkaline-earth metals. Saito and Matsumoto[12] also prepared the carbon nanocages with cubic shape by arc evaporation of carbon with the alkaline-earth metals calcium or strontium. Our observation supports the suggestion that the alkaline-earth metals play an important role in the formation of carbon cubic nanocages.

In our experiment, alcohol reacts with metallic Mg powder to produce carbon, magnesia, and hydrogen. The reaction process can be represented as follows:

$$CH_3CH_2OH + Mg = 2C + MgO + 3H_2 \qquad (1)$$

X-ray diffraction powder patterns were taken to follow the reaction. Figure 5a shows the XRD pattern of the products that

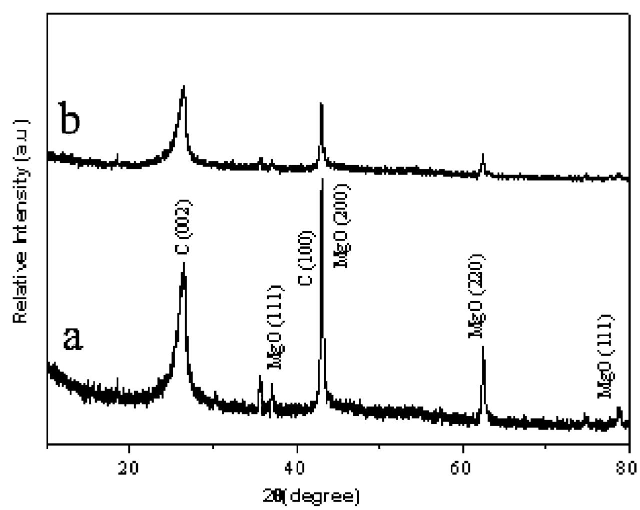

Figure 5. XRD patterns of the products with various treatments: (a) not washed and (b) washed with dilute HCl aqueous solution and distilled water.

were not washed. Reflections in the figure can be indexed to be cubic MgO (JCPDS Card File, No. 77−2364) and hexagonal graphite. Figure 5b is a typical XRD pattern of the as-prepared products washed with dilute HCl aqueous solution and distilled water. From the pattern, we can see that reflection intensities for cubic MgO decrease but not disappear, which implies that

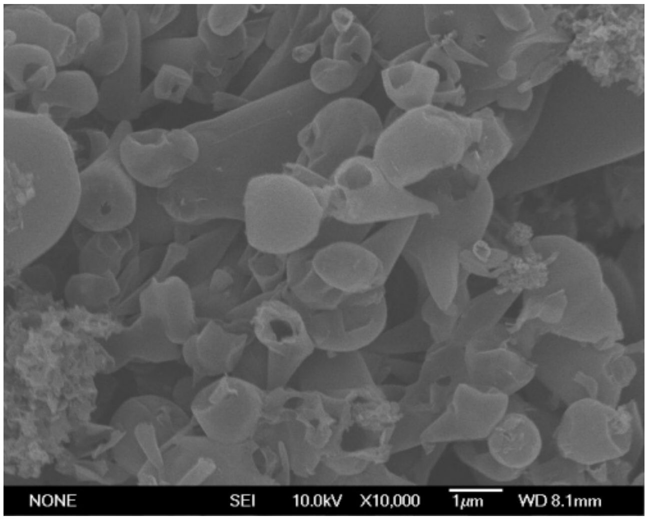

Figure 6. Field-emission SEM image of the product prepared by using methanol as carbon source.

some magnesia particles may be encapsulated inside carbon materials. The thorough TEM investigations are in favor of the deduction.

A series of relevant experiments was carried out through similar processes to investigate the effect of reaction conditions on the formation of carbon nanomaterials. It is obvious that the reaction temperature played a critical role in the formation of carbon nanotubes. Lower temperatures than 400 °C could not initiate the reactions. When the reaction temperature was at 500 °C, the carbon spheres prevailed in the sample. At 600 °C for 10 h, many carbon nanotubes could be observed in as-synthesized sample (re. previous communication).[20] Raising reaction temperature to 650 °C, we could find abundant carbon nanotubes, as shown in Figure 1. In addition, the influence of the carbon sources on the carbon materials has also been studied. When substituting ethanol with methanol, we could see a lot of carbon hollow cones and carbon spheres in the final product (see Figure 6).

The experimental results suggest that the growth mechanism of the bamboo-shaped carbon nanotubes follows the base growth model, which demonstrates that carbons first adsorb on metal particle and then form graphitic sheets as a cap. As the cap lifts off the particle, a closed tip with inside the hollow is produced. While the wall grows upward, the next compartment layer is produced. In this experiment, we observe that all of carbon nanotubes have bamboo-shaped structure in which the curvature of the compartment layer is directed toward the closed tip. In addition, there is no encapsulated solid particle at the closed tip in most carbon nanotubes. According to experimental investigations, a possible growth process for the bamboo-shaped nanotubes has been proposed. First, carbon produced from the reaction 1 adsorbs on magnesia particles. Then the carbon diffuses via the surface of magnesia particles to form graphitic layers as a cap on the magnesia particles. Due to the stress accumulated in the graphitic sheath, the magnesia particles probably jumped out of the cap to produce a compartment of bamboo-shaped tubes.[8] Once sufficient stress has been released, the next wave of graphite layers can start to form the next compartment. If the carbons are supplied under constant conditions, the compartment layers can appear periodically. The proposed model could be testified by experiential results. As shown in Figure 7, we can observe different bamboo-shaped carbon nanotubes. Some nanotubes consist of several compartments (indicated by arrow in Figure 7a,b), which may indicate

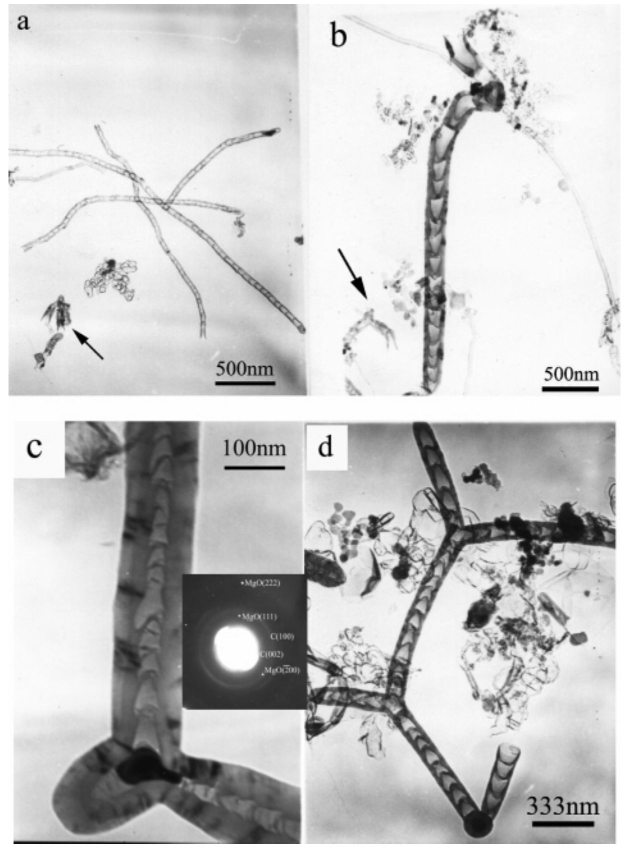

Figure 7. (a) TEM image showing that the majority of tips are free of magnesia particles, but some of the tips are encapsulated with particles. (b) TEM image for a bamboo-shape carbon nanotube with some nanotubes consisting of several compartments. (c) TEM image showing a piece of magnesia particle left in a compartment located in the corner of a Y-shaped carbon nanotube. (d) TEM image of a multijunction carbon nanotube.

an insufficient carbon supply at the end of the reaction. In the above HRTEM image (Figure 2c), we found that the bamboo-shaped carbon nanotubes consist of slanted graphene layers with respect to the tube axis, which provided more proof for the base growth model.

In TEM examinations, the majority of tips are free of magnesia particles, but some of the tips are encapsulated with particles (shown in Figure 7a), which may be due to the capillary action of carbon nanotube of small diameter. A piece of magnesia particle was left in a compartment located in the corner of Y-shaped carbon nanotubes, as shown in Figure 7c. The diffraction spots in SAED image (inset Figure 7c) can be indexed to be face-centered cubic MgO. And a pair of arcs in the pattern corresponds to the (002) planes of hexagonal carbon. The result supports the XRD analysis, which indicates that some magnesia particles may be encapsulated inside carbon materials. At the same time, we can find a multijunction carbon nanotube, as shown in Figure 7d. At the below junction, we can see a magnesia particle, which may be the base for growth of bamboo-shaped carbon nanotube. The TEM image clearly shows the whole growth process of bamboo-shaped carbon nanotube, which further confirms the base growth mechanism.

Conclusions

Three types of carbon nanomaterials, including bamboo-shaped carbon nanotubes and cubic and spherical carbon nanocages, have been prepared via an ethanol thermal reduction route using ethanol as carbon sources and powdered magnesium metal as reductant. The bamboo-shaped carbon nanotubes are made up of many compartments with mostly uniform size, and the curvature of the compartment layers is directed toward the closed tip. The HRTEM image reveals that the bamboo-shaped carbon nanotubes consist of slanted graphene layers with respect to the tube axis. On the experimental results, a base growth mechanism for the bamboo-shaped carbon nanotubes is proposed. In addition, the appearance of cubic and spherical carbon nanocages arises from the graphitic sheets bending in an attempt to eliminate the highly energetic dangling bonds present at the edge of the growing structure. Our investigation provides some support for growth processing of carbon nanotubes and carbon nanocages with cubic and spherical shape.

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