Synthesis And Characterization Of Bamboo-like Multi-walled Carbon Nanotubes By Alcohothermal Process

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Abstract. Bamboo-like multi-walled carbon nanotubes have been synthesized by an alcohothermal approach between cobaltocene and absolute ethanol at 500 °C. The as-obtained product is characterized by FESEM, TEM, HRTEM and Raman spectroscopy. The results show that the sample consists of a large number of nanotubes with a range of outer diameters from 50 to 100 nm, inner diameter of about 25〜50 nm and several micrometers in length. These nanotubes consist of a linear chain of hollow compartments that are spaced at nearly equal separation of 20 nm for an about 50 nm diameter nanotube. A possible growth mechanism of the bamboo-like carbon nanotubes has been proposed based on the observation of Co particles embedded at the nanotubes’ tips.

1. Introduction

Since the discovery of carbon nanotubes (CNTs) in 1991 by Iijima [1], there has been great interest in developing new methods for the synthesis of CNTs due to their potential applications in various technologies [2]. By using the unique electronic properties [3], the semiconductor junction with the smallest size would be achieved for further development of nanoscale electronic devices. Moreover, carbon nanotubes are the best candidate for developing the new generation of ultra-thin and high-clarity flat displays because of its excellent field emission property [4]. Therefore, it is an important project to fabricate carbon nanotubes with the needed special structure such as bamboo-like [5], octopus [6], fish-bone [7], and so on.

Different from the normal carbon nanotubes, the structure of bamboo-like carbon nanotubes is made up of separated hollow compartments and bamboo knots which grow straight along the axis. Compared with standard carbon nanotubes, bamboo-like carbon nanotubes possess peculiar properties, such as high specific surface and high density of defects, and in the most recent years have drawn increasing attention [8-16]. Although various procedures have been applied for the synthesis of carbon nanotubes, the controllable and selective synthesis of bamboo-like carbon nanotubes still remains a challenge. Several methods such as dry reforming reactions [8-9], hydrocarbon thermal decomposition [10-12], pyrolysis and gasification of plastic wastes [13] and special chemical vapor deposition [14-16] are commonly used to prepare bamboo-like carbon nanotubes. In this paper, we developed an alcohothermal approach between cobaltocene and absolute ethanol to synthesize high quality bamboo-like multi-walled carbon nanotubes.
2. Experimental Section

2.1. Synthesis
All reagents used in our experiments were of analytical pure grade and used as the starting material without further purification. For the synthesis of bamboo-like multi-walled carbon nanotubes, 0.15 g cobaltocene was added into a 12 mL stainless steel reactor, which was then filled with absolute ethanol to 90% of the total volume. The sealed reactor was heated from room temperature to 100 °C with the heating rate of 10 °C/min, and then maintained at this temperature for 1 h. Next the sealed reactor was heated to 500 °C with the heating rate of 10 °C/min sequentially, and then maintained at this temperature for 8 h. After cooling to room temperature naturally, the reaction product was collected from the reactor and washed with absolute ethanol and distilled water in sequence, and then dried in vacuum at 80 °C for 8 h.

2.2. Characterization
X-ray powder diffraction (XRD) measurements were carried out on a Philip X’ Pert PRO SUPER rA rotation anode with Ni-filtered Cu Kα radiation (λ = 1.54187 Å). Raman spectrum was recorded at room temperature with a LABRAM-HR Confocal Laser MicroRaman Spectrometer. Field emission scanning electron microscopy (FESEM) images were taken on a JEOL JSM-6700F SEM. Transmission electron microscopy (TEM) images were taken with a Hitachi H-800 TEM with an accelerating voltage of 200 kV. High-resolution TEM (HRTEM) images and selected-area electron diffraction (SAED) patterns were obtained from a JEOL-2010 TEM.

3. Results and discussions
The X-ray powder diffraction (XRD) pattern of the final product is shown in Figure 1. The main phases included in the product can be indexed as face-centred cubic cobalt (JCPDS No. 89-4307) and hexagonal graphite (JCPDS No. 41-1487), respectively. No phases of cobalt oxide and cobalt carbide were detected in the final product.

![Figure 1. XRD pattern of as-obtained bamboo-like CNTs.](image)

Raman spectroscopy is a frequently used technique to characterize the carbon nanomaterials. It is a non-destructive tool applied to the identification and characterization of a wide variety of carbon nanomaterials, and the technique has been shown to be an excellent tool to investigate the crystallinity
The Raman spectrum of the as-obtained product is clearly a sharp doublet at 1604 cm$^{-1}$ (G band) and 1348 cm$^{-1}$ (D band) with a ratio of about 0.73, which is characteristic for a disordered sp$^2$-bonded carbon and similar to the case of multiwall carbon nanotubes [17].

Figure 2. Raman spectroscopy of as-obtained bamboo-like CNTs.

Figure 3. FESEM images (a) and (b) of as-obtained bamboo-like CNTs; TEM images (c) and (d) of as-obtained bamboo-like CNTs; the inset of (c) is the SAED; HRTEM image (e) of as-obtained bamboo-like CNTs.
The morphology of the as-obtained product was investigated by FESEM, TEM and HRTEM observations. The results indicate that the samples are mainly composed of nanotubes. The yield of CNTs, based on the statistical analyses of the FESEM and TEM micrographs, is over 95%. Figure 3a and b show the low- and high-magnification FESEM images of as-obtained product. The sample consists of a large number of nanotubes with a range of diameters from 50 to 100 nm and length of several micrometers. Some open-ended tips of the nanotubes are also observed, which indicates the hollow structure of the CNTs.

The morphology and structure were further characterized by low- and high-resolution TEM examinations, which reveals that all nanotubes exhibit a bamboo-like (compartmentalized) structure. Figure 3c and d show the low-resolution TEM images of as-obtained product. In general, the nanotubes have an outer diameter around 50 nm and a length of several micrometers. These nanotubes consist of a linear chain of hollow compartments that are spaced at nearly equal separation of 20 nm for an about 50 nm diameter nanotube. Each bamboo knot appears periodically along the tubule axis. Metal cobalt particles embedded at the nanotubes’ tips are also observed, which indicates that the particles promote CNTs formation in the reactor. The inset of Figure 3c shows the corresponding SAED pattern of as-obtained bamboo-like CNTs, which confirms the nature of multi-walled CNTs. The bright rings could be indexed to the (002), (110) and (112) reflections of hexagonal graphite. HRTEM image (figure 3e) shows the detail structure of bamboo-like CNT’s wall. The inter-space between two adjacent layers from the sheath is around 0.35 nm, which coincides with the (002) spacing of graphitic carbon. The included angle between the (002) fringes and growth direction of CNTs is around 40 degree.

It is worth noting that Co particles can be found at the ends of bamboo-like CNTs in the TEM images, which indicates the growth mechanism is “root growth mode” [10, 18]. When the reaction temperature rise to 500 °C, carbon formation occurs over the surface of the Co particle derived from the thermolysis of cobaltocene during the ethanol thermal decomposition process. After that, a diffusion step over the droplet shaped metal particles takes place. Stress force generated during the formation process of the carbon shells pushes the Co particles toward the growing direction, which results in a jump of the Co particle followed by the formation of conical holes. The bamboo-like structure of the carbon nanotubes was produced when the above process occurred repeatedly.

4. Conclusions
Bamboo-like multi-walled carbon nanotubes have been synthesized by an alcohothermal approach between cobaltocene and absolute ethanol at 500 °C. The as-obtained product is characterized by FESEM, TEM, HRTEM and Raman spectroscopy. The results show that the sample consists of a large number of nanotubes with a range of outer diameters from 50 to 100 nm, inner diameter of about 25 ~ 50 nm and several micrometers in length. These nanotubes consist of a linear chain of hollow compartments that are spaced at nearly equal separation of 20 nm for an about 50 nm diameter nanotube. A possible growth mechanism of the bamboo-like carbon nanotubes has been proposed based on the observation of Co particles embedded at the nanotubes’ tips.

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