Preparation of bamboo-like carbon nanotubes by the reaction of cobaltocene and methanol

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Abstract. Carbon nanotubes have been prepared by the reaction of cobaltocene and methanol at 500 °C. FESEM, TEM and HRTEM observations show the carbon nanotubes with bamboo-like structure. These nanotubes are made up of separated hollow compartments and bamboo knots which grow straight along the axis. The bamboo knots are spaced at nearly equal separation of 25 nm for an about 60 nm diameter nanotube. The possible growth mechanism for CNTs is proposed.

1. Introduction
Since their discovery in 1990s by Iijima, Carbon nanotubes (CNTs) are continuously of great interest in both fundamental research and practical applications [1]. Owing to their excellent electrical conductivity, large surface area and high charge mobility, CNTs have shown better potential in the application of energy storage applications [2]. Recently, CNTs with special structures, such as bamboo-shaped, octopus and fish-bone [3-5], which are different from their straight counterparts, have attracted immense attention.

As a prominent representative of carbon nanomaterials, bamboo-shaped carbon nanotubes have been explored extensively due to their unique properties resulting from their hollow compartments inside nanotubes [6-7]. Several methods have been developed to prepare bamboo-like carbon nanotubes, such as special chemical vapor deposition [8-9], pyrolysis and dry reforming reactions [10-11], hydrocarbon thermal decomposition [12-13] and gasification of plastic wastes [14]. Nevertheless, the controllable and selective synthesis of the bamboo-shaped carbon nanotubes still remains a huge challenge. To address this problem, we herein propose a simple alcohothermal approach to prepare bamboo-like carbon nanotubes.

2. Experimental Section

2.1. Synthesis
Cobaltocene and methanol were purchased from Aldrich Chemical Co. In a typical synthesis, 0.15 g cobaltocene was added into a 12 mL stainless steel autoclave, which was then filled with methanol to 90% of the total volume. The autoclave was sealed and placed in the muffle furnace. Then it was heated from room temperature to 100 °C in 10 minutes, and maintained at this temperature for 1 h. Next the autoclave was heated to 500 °C in 40 minutes sequentially, and then maintained at this temperature for 8 h. When the autoclave was cooled to room temperature, the black product was...
collected and washed with absolute ethanol and distilled water in sequence, and treated by vacuum drying at 80 °C for 4 h in the end.

2.2. Characterization

X-ray powder diffraction (XRD) measurement was carried out on an 18 KW advanced X-ray diffractometer with Cu Kα radiation (λ = 1.54187 Å) in the scanning range of 10°-70°. Raman spectrum was taken out with a LABRAM-HR Confocal Laser MicroRaman Spectrometer at room temperature. Field emission scanning electron microscopy (FESEM) images were performed 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 were measured on a JEOL-2010 TEM.

3. Results and discussions

Figure 1 shows the X-ray powder diffraction (XRD) patterns of the final product. The two broad peaks at 2θ=26.3 and 43.8 correspond to the (002) and (101) planes of graphitic carbon. The sharp peaks appearing at 44.3 and 51.6 are indexed to the (111) and (200) reflections, respectively, of face-centred cubic cobalt nanoparticles. No other impurities, such as cobalt oxide and cobalt carbide were observed in the XRD patterns.

![XRD patterns of as-obtained bamboo-like CNTs.](image)

To further identify and characterize the crystallinity and graphitic nature of carbon nanomaterials, Raman spectrum of the sample was performed. As shown in Figure 2, the sample exhibited D and G bands centered at 1336 and 1601 cm⁻¹, respectively, owing to the sp³-bonded carbon structures or defects (D band) and the vibration mode of sp²-bonded carbon in a single graphitic sheet (G band). The G band is a characteristic feature of graphitic layers, while the D band is due to out-of-plane vibrations attributed to structural defects. The ratio between the intensities of the D band and G band is 0.67, which is characteristic for a disordered sp²-bonded carbon and similar to the case of multiwall carbon nanotubes [15].
Figure 2. Raman spectroscopy of as-obtained bamboo-like CNTs.

Figure 3. FESEM images (a) and (b) of as-obtained bamboo-like CNTs; TEM image (c) of as-obtained bamboo-like CNTs; HRTEM images (d) ~ (g) of as-obtained bamboo-like CNTs.
Figure 3a-b show FESEM images of the product. The results reveal that the samples are mainly composed of CNTs with a content exceeding 85%. The CNTs synthesized through the reaction of cobaltocene and methanol consists of fibers with the length of several micrometers. They have an average diameter of 50-150 nm. Some tips of open-ended nanotubes are also observed, which mean that CNTs have a hollow structure.

The typical SEM image shown in Figure 3c reveals the one dimensional (1D) twisted nanostructures of CNTs, which are up to several tens of micrometers in length. They have an average outer diameter of 50-150 nm and inner diameter of 25-50 nm. The bamboo knots are spaced at nearly equal separation of 25 nm for an about 60 nm diameter nanotube. High-resolution TEM images in Figure 3d-g reveal the lattice fringes with the space of 0.34 nm, which corresponds with the (002) plane lattice parameter of graphitic carbon. Co particles embedded at the nanotubes’ tips are clearly observed. The lattice spaces of nanoparticles are calculated to be about 0.2 nm corresponding to the (111) plane of cubic crystal cobalt.

It is noteworthy that Co particles can be found at the end of CNTs in the TEM images, which show evidence of root-growth of bamboo-like CNTs produced by alcohotermal process [11, 16]. As the temperature increases to 500 °C, carbon is formed on the surface of the Co particle which was obtained from the solid-state thermolysis of cobaltocene precursor. Subsequently, a diffusion step over the metal particles with droplet shape occurs. Stress force in the process of the carbon shells formation drives the Co particles toward the growing direction, which results in a jump of the Co particle and then the formation of the cavity. When the above process occurred repeatedly, Carbon nanotubes with the bamboo-like structure were produced.

4. Conclusions
In summary, bamboo-shaped carbon nanotubes have been prepared by the reaction of cobaltocene and methanol at 500 °C. These nanotubes consist of separated hollow compartments and bamboo knots which grow straight along the axis. The bamboo knots are spaced at nearly equal separation of 25 nm for an about 60 nm diameter nanotube. The possible growth mechanism for CNTs is proposed.

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