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Low temperature synthesis of multiwall carbon nanotubes from carbonaceous solid prepared by sol–gel autocombustion

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ABSTRACT

Multiwall carbon nanotubes (CNTs) were synthesized by the annealing of carbonaceous solid at a low-temperature (450 °C). The average diameter of the CNTs is about 50 nm. The length of the CNTs ranges from 200 nm to nearly 1 μm. The as-synthesized CNTs are crystallized. Cobalt nanoparticle is capped at the tip of the CNT. The carbonaceous solid, which contains cobalt nanoparticles, was obtained by the sol–gel autocombustion method. The growth of CNTs occurred in the annealing process, while the combustion process only produced carbonaceous solid and cobalt nanoparticles. The cobalt nanoparticles catalyze the decomposition of carbonaceous solid into carbonaceous gas species, and also catalyze the growth of CNTs during the annealing process.

1. Introduction

Carbon nanotubes (CNTs) have attracted considerable attention due to their unique physical and chemical properties [1,2]. Various methods have been developed for the synthesis of CNTs, such as arc discharge [3], laser vaporization of a graphite electrode in the presence of metal catalysts [4], catalytic decomposition of hydrocarbon vapor over a transition metal incorporated silica or zeolite support [5,6], pyrolysis of metallocene [7], detonation-assisted synthesis [8], etc. Recently, it was reported that CNTs can also be synthesized by solid-phase transformation of carbonaceous materials containing metal particles [9–11]. Various kinds of materials, such as carbon black, amorphous carbon, fullerene soot and kinds of polymers can be used as raw materials in the solid-phase transformation synthesis. The transformation can be achieved by annealing the raw materials at a very high temperature (higher than 1000 °C) in inert atmosphere. Besides the use of high temperature, the preparation of the carbonaceous materials needs complicated metal organic materials [9,11], vacuum heating [10] or long time mixing [10].

In this work, we report the synthesis of multiwall CNTs from low temperature annealing of carbonaceous solid containing cobalt nanoparticles. The carbonaceous solid, containing cobalt nanoparticles, is obtained by the sol–gel autocombustion method. The cobalt nanoparticles formed in the combustion have two functions during the growth of CNTs: to catalyze the decomposition of carbonaceous solid, forming carbonaceous gas species, and to catalyze the growth of CNTs from the gas species.

2. Experimental

$Co(NO_3)_2 \cdot 6H_2O$ (1.456 g, 5 mmol) and EDTA (1.948 g, 6.6 mmol) were dissolved in 200 mL boiling distilled water in a breaker heated by a heating stage. The solution became transparent after a few minutes. Then the breaker was transferred into an electric oven. The temperature of the electric oven was increased to 90 °C within 20 min and maintained at this temperature for 30 h. After that transparent deep purple gel can be found at the bottom of the beaker. The dried gel was transferred into a quartz tube, which was inserted into a horizontal tube furnace. The gel was far from the heating zone when the quartz tube was mounted. Nitrogen gas was introduced to wash the quartz tube. After the furnace was raised to 300 °C, the nitrogen stream was turned off. Then the gel was move into the heating zone by moving the quartz tube. White gas was slowly released after a while. When the release of gas stopped, the furnace temperature was raised to 450 °C and kept for 1 h. After that, the furnace was cooled to room temperature with nitrogen stream. Then the product was took out and ground into powder in an agate mortar for further characterizations.

X-ray diffraction (XRD) patterns of the product were collected

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at Philips X'Pert diffractormeter using Cu Kα radiation ($\lambda = 1.54$ Å). Raman spectra of the product were measured on HORIBA LabRAM HR800 spectrometer with excitation using a 532 nm laser. Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectrum (EDS) were obtained in a Hitachi-S-4800 instrument attached with EDS spectroscopy. Transmission electron microscopy (TEM) images and high resolution TEM (HRTEM) images were obtained in a JEM-2100 instrument. The specimens for SEM measurements were prepared by pasting the powder sample on the aluminum specimen stage with conductive adhesive tape. TEM samples were prepared by dispersing the powder in alcohol by ultrasonic treatment, dropping onto a porous carbon film supported on a copper grid, and then dried in air.

3. Result and discussion

The XRD pattern of the as-synthesized product is shown in Fig. 1a. Peaks corresponding to cobalt with face-centered cubic (FCC) structure (JCPDS 15-0806) are found. Because the peaks from cobalt are too strong covering the peaks from carbon nanotubes, the product was washed with nitric acid solution to remove cobalt. A prominent peak is observed at around 26° from the XRD pattern of the washed product (Fig. 1b), which corresponds to the (002) planes of graphite, indicating the graphitization of carbon in the product. Raman spectrum of the product was also measured. Two peaks are observed at 1350 and 1595 cm^{-1}, corresponding to graphite D- and G-bands, respectively (see Fig. 1c). We cannot determine the crystalline of CNTs from XRD and Raman spectra since the two spectra cannot differentiate CNT from carbonaceous solid base. The crystalline of CNT can be determined by HRTEM images in the following part.

The morphologies of the product were measured by SEM. High density multiwall CNTs are observed lying on carbonaceous solid base as shown in Fig. 2a. Most of the CNTs have outer diameters around 50 nm and lengths ranging from 200 nm to 1 μm (see Fig. 2b). Furthermore, most of the CNTs are capped with metal particles at the tip. A typical one is labeled by a square in Fig. 2b. In addition, both the signals from carbon and cobalt are observed from the EDS spectrum of the product shown in the inset of Fig. 2b.

The typical TEM image of the as-synthesized multiwall CNTs is shown in Fig. 3a. The CNTs normally show cylindrical morphologies with hollow channel along the full length. The diameters of the CNTs are from 20 nm to 80 nm. The lengths of the CNTs are from 200 nm to 1 μm and the ratios of the length to the diameter are kept in the range of 20–30. The CNT is usually capped with a cobalt metal particle at the tip with the size closing to the diameter of the tube. The shape of the cobalt metal particle is cone as shown in Fig. 3b. The results are consistent with SEM characterization. In addition, most of the other end of the CNTs are found broken and have irregular shapes shown in TEM image (Fig.3a), which may be ascribed to the separation of CNTs from the base in the ultrasonic bath during sample preparing. While some of the unbroken ones show close ends with a cobalt particle inside as also shown in Fig.3b. The HRTEM image of a CNT is shown in Fig. 3c, clear lattice fringes at the wall of the CNT can be seen. The distance between the fringes is 0.34 nm, corresponding to the

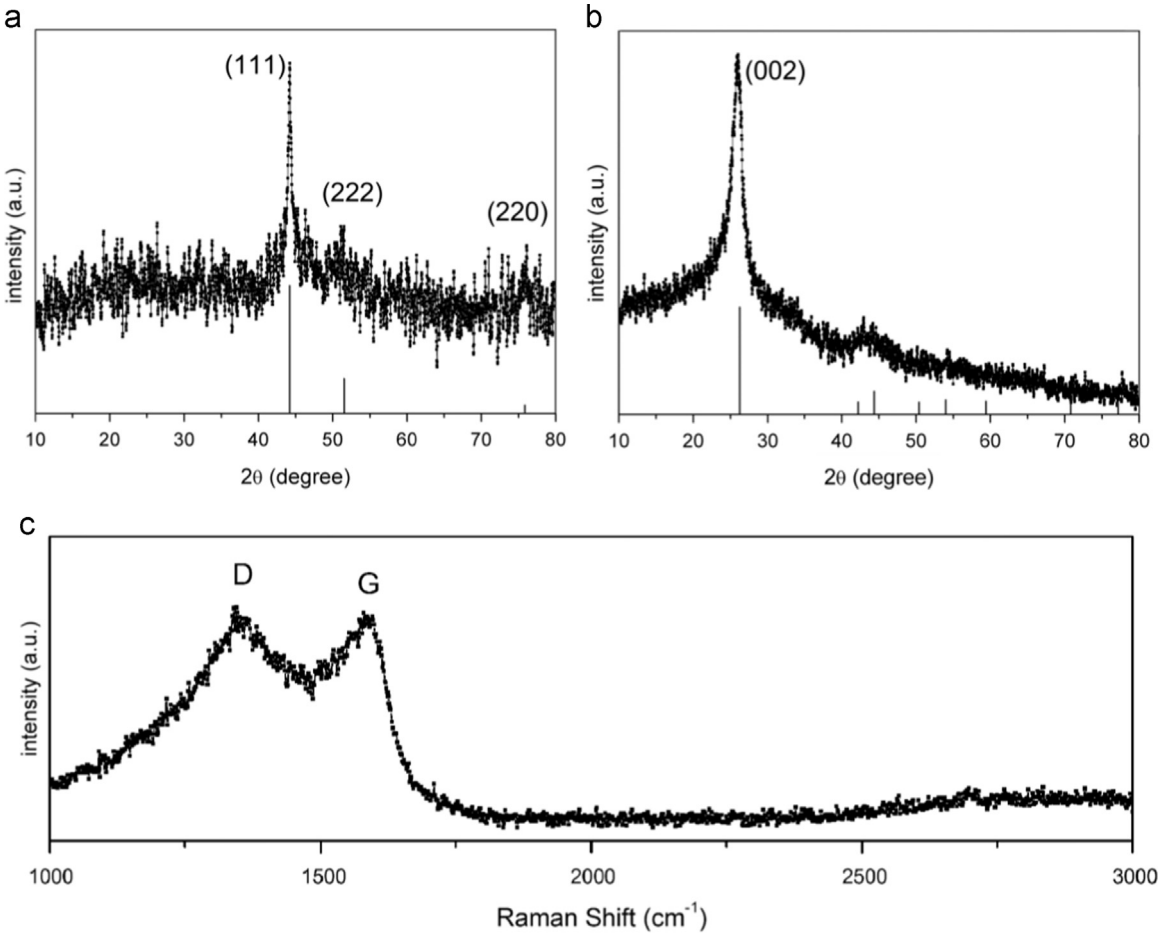

Fig. 1. (a) The XRD pattern of the as-synthesized product, reference face-center cubic cobalt (JCPDS 15-0806, bottom). (b) The XRD pattern of the product washed with nitric acid solution, reference graphite (JCPDS 75-1621, bottom). (c) Raman spectrum of the product.