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Carbon nanotubes produced by tungsten-based catalyst using vapor phase deposition method

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Abstract

We have demonstrated that W-based catalysts can produce carbon nanotubes (CNTs) effectively. Well-aligned, high-purity CNTs were synthesized using the catalytic reaction of C_2H_2 and $W(CO)_6$ mixtures. The CNTs had a multiwalled structure with a hollow inside. The graphite sheets of CNTs were highly crystalline but the outmost graphite sheets were defective.

1. Introduction

Since the first observation of carbon nanotubes (CNTs) [1], CNTs have been of great interests because of their novel physical and chemical properties, suggesting that they have numerous potential applications such as electron field emitter [2,3], scanning microscopy tips [4], hydrogen storage materials [5,6], and molecular electronic devices [7,8].

In preparation of CNTs using catalytic methods, the initial stage of growth involves the decomposition of carbon-containing gas on the surface of the metal catalyst and subsequent dissolution in the metal, thus the chemical nature as well as the shape and size of the catalyst also affects the CNT growth and morphology [9]. With regard to the species of metal catalyst, iron (Fe) [10,11], cobalt (Co) [12], nickel (Ni) [13,14], or their bimetallic systems [15,16] have been mostly utilized for CNT growth, and additionally molybdenum (Mo) [17], rhodium (Rh) [18], Rh–Pt [19], palladium (Pd) [20], gold (Au) [21], silver (Ag) [22] and copper (Cu) [23] have been studied as a candidate material. Although synthesis of CNTs with the mixture of cobalt and tungsten (W) catalysts using arc discharge has been reported [24], there is no report on the tungsten-catalyzed synthesis of CNTs using chemical vapor deposition or vapor phase deposition method until now.

In this work, we report the production of CNTs from tungsten-based catalyst using vapor phase

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deposition method, moreover investigate the structure and crystallinity of CNTs. For large-scale production of CNTs, several research groups have employed catalytic pyrolysis of hydrocarbons [25–31]. We have synthesized CNTs by the catalytic reaction of tungsten hexacarbonyl ($W(CO)_6$) and C_2H_2 mixtures using hot-wall type furnace.

2. Experimental

The vapor phase deposition system consists of a two-stage furnace with an inner diameter of 20 mm and a length of 300 mm. The first heating zone was maintained at a low-temperature of 180 °C for sublimation of catalyst and the second heating zone was maintained at a high-temperature of 950 °C for CNT growth. A known quantity (~50 mg) of the $W(CO)_6$ powder (99.9+%, Sigma-Aldrich) was loaded on the quartz boat located at the first heating zone and was sublimated inside the first heating zone. The $W(CO)_6$ vapor was carried by Ar gas with the flow rate of 1500 standard cubic centimeters per minute (sccm) and was introduced into the reactor. C_2H_2 gas with the flow rate of 30 sccm was used as a carbon source. To synthesize CNTs, C_2H_2 and Ar gases were supplied into the reactor when the temperature of the first heating zone and the second heating zone are arrived at 180 and 950 °C, respectively. After the reaction, the reactor was cooled down to room temperature in flowing 500 sccm of Ar gas. Large quantities of black-colored deposits were homogeneously produced inside the second heating zone.

The deposits were scraped off the wall of the quartz tube and examined by electron microscopy. A scanning electron microscopy (SEM) (Hitachi S-4700) was used to measure the length and diameter of CNTs. A transmission electron microscopy (TEM) (JEOL, JEM-3011, 300 kV) was used to analyze the structure and crystallinity of CNTs. A Raman spectrometer (Renishaw micro-Raman 2000) was used to evaluate the overall crystallinity of CNTs. The 632.8 nm line of a He–Ne laser was used for excitation. Since TEM does not provide the overall information on the crystallinity of entire specimen, we attempted to overcome this shortcoming by using a Raman spectroscopy.

3. Results and discussion

Fig. 1a shows SEM images of deposit on the inner surface of the quartz tube, revealing that well aligned carbon deposit was densely compacted and uniformly grown. The average length of deposits is about 30 μm as shown in Fig. 1b and the diameter of deposits is in the range 20–40 nm as shown in Fig. 1d. By adapting our method, the deposits are homogeneously produced along the total heating zone of the quartz tube.

We employed Raman spectroscopy analysis to investigate the elements and structure of deposits. Fig. 2 shows a Raman spectrum of the deposits, indicating the graphite structure. The G band at 1584 cm^{-1} with a small bump at 1621 cm^{-1} reveals that deposits are multiwalled CNTs. The D band at 1337 cm^{-1} indicates the existence of defects or carbonaceous particles on the surface of CNTs. Since the CNTs synthesized using W-based catalyst have a little carbonaceous particles on the surface as shown in Fig. 1, it is suggested that the D band mainly indicates the defective feature of graphite sheets. In Raman spectra, we notice that the relative intensity of G band to D band is close to unity, indicating good crystallinity of graphite sheets. Therefore, Raman analysis confirms that the CNTs have a high-crystalline multiwalled structure and some defects on the wall surface.

A representative TEM image of the synthesized CNTs is shown in Fig. 3a. The CNTs have a multiwalled structure with a hollow inside. In our experiment, W catalyst particles are largely existed on the one side of CNTs, but sometimes they are appeared in CNTs inside hollow. There were many reports for the synthesis of CNTs using various catalysts instead of Fe, Ni, and Co catalysts [17–23]. It reveals that many metal particles can contribute to CNT growth as an effective catalyst. In our previous results, we suggested that a nanometer-sized catalyst particle is inevitably necessary to synthesize CNT using the CVD method [32]. We could find that there was no CNT growth if the size of catalyst particle (Fe, Co, Ni) is larger than about 300 hundreds nanometer. Our result shows that W particles can also perform catalytic role for the CNT growth

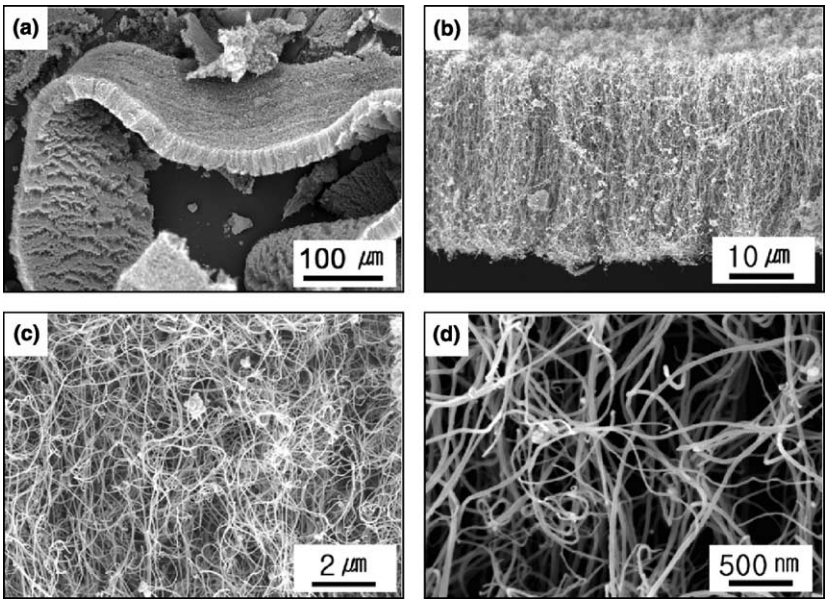

Fig. 1. SEM micrographs of deposits produced by W-based catalyst at 950 °C. (a) Large quantities of carpet-like deposits were scraped off the inner wall of the quartz tube. (b) Magnified view of (a), revealing that the deposits have a length about 30 μm. (c) Magnified view of (b). (d) High-resolution SEM image of deposits, showing the average diameter of about 20–40 nm.

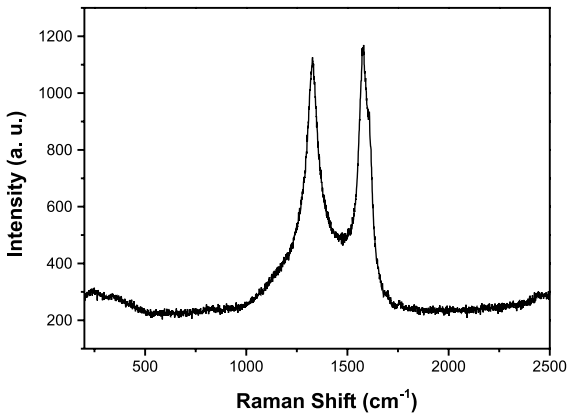

Fig. 2. Raman spectra of CNTs, showing multiwalled structure of CNTs.

effectively when their size is limited to several tens nanometer.

Fig. 3b shows a high-resolution TEM (HRTEM) image, showing the wall structure of a CNT. The fringes on each side of the tube represent an individual cylindrical graphite sheet. Most graphite sheets have straight fringes, indicating a good crystallinity but the outmost graphite sheets have a defective crystalline structure. HRTEM images demonstrate that highly crystalline graphite sheets are generated by the introduction of the W-based catalyst.

In summary, we have demonstrated that W-based catalysts can be used to synthesize CNTs using the vapor phase deposition method effectively. Well-aligned, high-purity CNTs are synthesized by the catalytic reaction of C_2H_2 and $W(CO)_6$ mixtures at 950 °C. The CNTs are homogeneously produced along the total heating zone of the quartz tube. The Raman spectra and TEM images indicate that the CNTs have multiwalled structure and most graphite sheets of CNTs have a good crystallinity but the outmost graphite sheets show a defective structure.

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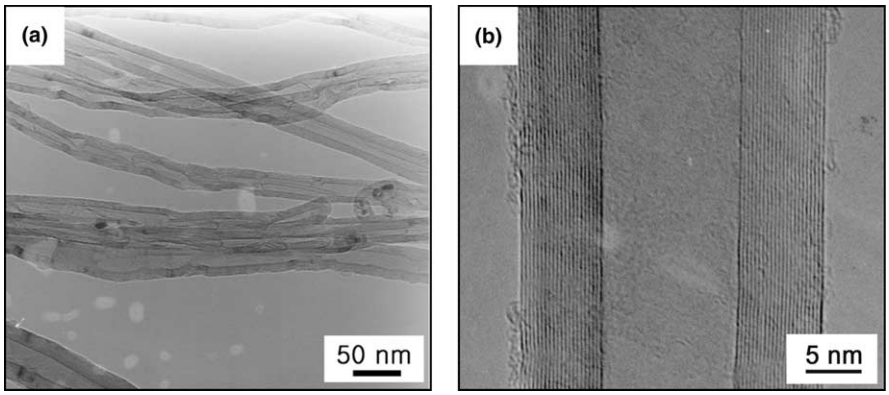

Fig. 3. (a) TEM image of CNTs, showing a multiwalled structure with a hollow inside. (b) HRTEM image of a CNT, showing high-crystallinity of graphite sheets.

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