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Catalytic growth of single- and double-walled carbon nanotubes from Fe–Mo nanoparticles supported on MgO

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Abstract

Single-wall carbon nanotubes (SWNTs) and double-wall carbon nanotubes (DWNTs) are simultaneously synthesized at range of 800–1000 °C by catalytic decomposition of methane over Fe–Mo/MgO catalyst. Carbon nanotubes (CNTs) obtained in this work consisted of SWNTs bundle, isolated SWNT, and isolated DWNTs, having diameter of around 0.8–2.4 nm, 2.4 nm, and 2.4–2.8 nm, respectively. The proportion of DWNTs increases with increasing reaction temperature. The nanotubes synthesized at 800 °C and 900 °C composed of about 95%SWNTs/5%DWNTs and 80%SWNTs/20%DWNTs, respectively. Raman analysis indicates that the quality of CNTs decreased with increasing reaction temperature.

Keywords: Carbon nanotubes; CVD; Diameter; Number of walls; SWNTs; DWNTs

1. Introduction

After the discovery of carbon nanotubes (CNTs) [1], the extraordinary properties of CNTs, such as chemical, physical, electrical, thermal, and magnetism properties, have attracted much interest in the search for low-cost synthetic production, large-scale production, control of diameter and walls, and their chiralities [2–4]. The properties of CNTs depend strongly on their chiralities. Especially, single-wall carbon nanotubes (SWNTs) and double-wall carbon nanotubes (DWNTs) have created an active area of current research because they show unique chirality-dependent electronic structures, conspicuous mechanical strength, and high electrical and thermal conductivities.

Since their discovery in 1991 [1], CNTs have been synthesized by many processes, such as laser ablation [5], arc discharge [1], and supported or unsupported catalytic chemical vapor deposition (CVD), etc. [6,7]. Among them, the CVD process has been recognized as an effective means to synthesize SWNTs and DWNTs. In the CVD, transition metal particles act as seeds of nanotubes so that they strongly influence the structure and quality of the nanotubes. For example, the diameter and chirality of nanotubes can be controlled by size of catalyst, such as Fe, Ni, Co, Mo, and their alloy [5,8,9,10–12]. Also, it is well known that carbon sources, such as acetylene, benzene, methane, ethylene, and xylene, etc., play an important role in structural properties of CNTs [13–16]. Mukul Kumar and Yoshinori Ando [17] reported that single-wall and multi-wall carbon nanotubes of controlled diameter distribution were selectively grown by thermal decomposition of a botanical hydrocarbon on a high-silica zeolite support impregnated with Fe–Co catalyst. Smalley and co-workers [9] reported that SWNT, in some cases including DWNT was synthesized by catalytic decomposition of C_2H_4 over a supported Fe–Mo catalyst. Also Resasco and co-workers [8] confirmed that the ratio of Co and Mo was critical to synthesize SWNTs. Porous inorganic materials, such as Al_2O_3, SiO_2, MgO, and zeolite [18–21], have been widely studied as catalyst support materials for the CVD growth of SWNTs and/or DWNTs because of the simplicity of catalyst preparation and high-scale production. Among the above mentioned support materials much attention has been focused on MgO because it can be easily removed by acidic a treatment. The methane is a carbon source for production of SWNTs and/or DWNTs because of high stability at elevated temperature. As above mentioned, many researchers have focused their attention on the production of SWNTs and DWNTs. However, few results for synthesis of

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SWNTs and DWNTs as function of reaction temperature were reported. In this paper, we have grown SWNTs and DWNTs by catalytic decomposition of methane over Fe–Mo/MgO catalyst at temperature of 800–1000 °C. The synthesized SWNT and DWNT is characterized by FESEM, HRTEM and Raman analysis.

2. Experimental

We prepared Fe–Mo/MgO catalysts by impregnation method. The loading ratio of Fe:Mo was 9:1 molar ratio and their total weight in the supported catalysts were 4 wt.%. For the preparation of catalysts, $Fe(NO_3)_3{\cdot}6H_2O$ (98%, Junsei) and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (99%, Junsei) salts were used. Stoichiometric amount of MgO powder (Aldrich) was mixed with the solution of salts and was stirred at room temperature to obtain homogeneous impregnation of salts in support. After 1 h, the impregnate slurry was obtained and it was dried at 100 °C for 24 h in an oven and the material was ground in mortar to break the chunks into powder. The powders were then calcined at 400 °C for 4 h in 50 sccm m^{-1} O_2 gas flow to achieve oxide forms of metals. Then, the powders were reduced at 500 °C for 10 h in 40 sccm m^{-1} H_2 gas flow in the reactor. These catalysts were then used for the growth of CNTs. The experimental were carried out in a CVD apparatus of a conventional horizontal tube furnace with a quartz tube (of diameter 50 mm, length 850 mm) as the reaction chamber. Approximately 20 mg catalyst powder was uniformly dispersed in the base area of a alumina boat and in the central region of a horizontal quartz tube reactor of length 850 mm. The carbon source was methane with hydrogen as carrier gas. The reaction temperature was raised to 800 °C, 850 °C, 900 °C, 950 °C and 1000 °C in Ar atmosphere at a flow rate of 100 sccm min^{-1} before CH_4 was introduced into the reactor. Then, the growth of CNTs was performed for 30 min at reaction temperature under the flows of 50/100 sccm min^{-1} CH_4/H_2 mixture. After growth for 30 min, the furnace was cooled to room temperature in an Ar flow. The structure and morphology of the synthesized CNTs were characterized using field-emission scanning electron microscopy (Philips XL30S, operated at 15 kV) and transmission electron microscopy (JEOL JEM2010, operated at 200 kV). Selected CNTs specimens were studied by high-resolution TEM (HRTEM, JEOL JEM2100F, operated at 200 kV). Raman spectra were recorded using a FT-Raman spectrometer (FRS-100S, Bruker) with Nd:YAG laser excitation.

3. Results and discussion

Fig. 1 shows the FESEM images of as-prepared nanotube material at temperature of 800–1000 °C. Observation by FESEM shows entangled carbon nanotubes and the aboundance is very high in most all observed samples, as shown in Fig. 1. However, for sample prepared at the 1000 °C, amorphous carbon was observed, as shown in Fig. 1(e). The diameters of the fibers are in the range of 10–15 nm. The SEM images shown here is of as-prepared nanotubes. The FESEM images hence demonstrates that high-purity carbon nanotubes are synthesized by catalytic decomposition of methane over Fe–Mo/MgO, and the yield nanotubes after synthesis was over 100%. Fig. 2 shows the HRTEM images of the as-synthesized carbon materials at temperature 800 °C, 850 °C, and 900 °C. HRTEM images of the sample show that each nanotube consists of not only bundles of SWNTs but confirms also the presence of isolated SWNTs sometimes. On the other hand, some isolated DWNTs were observed with increasing synthesis temperature. The diameter of the SWNT can be measured by high resolution transmission electron microscopy. The SWNTs aligned in the bundle have the diameter of range 0.8–1.6 nm, and the diameter of isolated SWNTs is about 1.6–2.4 nm. And those of isolated DWNTs are around 2.4–2.8 nm. SWNTs and DWNTs with a thick diameter as a function of increasing synthesis temperature were frequently observed. Fig. 3 shows three Raman spectra of SWNT and/or DWNTs. In this work, Nd-YAG laser with wavelength of 1064 nm was used. Fig. 3 typically shows Raman spectra of the SWNTs and/or DWNTs. In the Raman spectra shown in the figure, strong G-bands at 1587 cm^{-1} and weak D-band at 1272 cm^{-1} indicate high quality of our SWNTs and DWNTs. As shown in Fig. 4, the relatively intensity of the G-band to the D-band was found to decrease with increas-

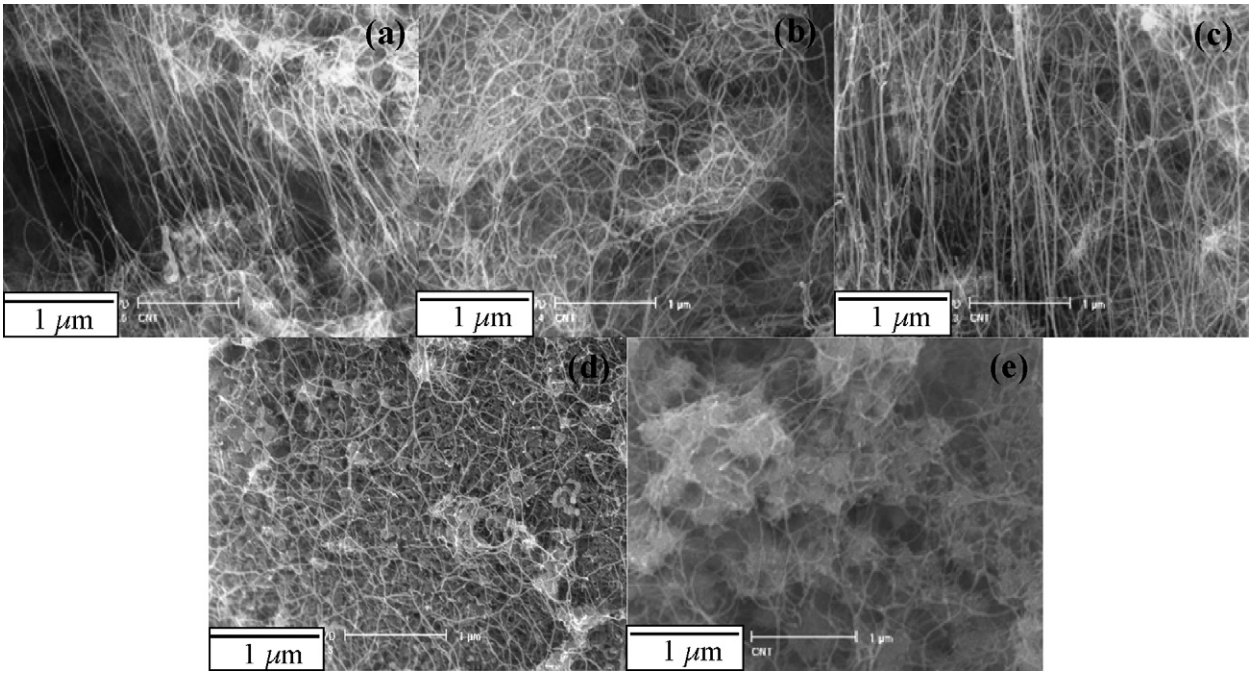

Fig. 1. SEM images of the CNTs grown over Fe–Mo/MgO catalysts for 30 min at (a) 800 °C, (b) 850 °C, (c) 900 °C, (d) 950 °C and (e) 1000 °C.